



Digitized by the Internet Archive
in 2010 with funding from
University of Toronto



(The Journal of) Industrial and Engineering Chemistry

PUBLISHED BY

The American Chemical Society

VOLUME IX, 1917

Board of Editors

Editor: CHARLES H. HERTY

Assistant Editor: LEOLA E. MARRS

Advertising Manager: G. W. NOTT

Advisory Board

H. E. Barnard

H. K. Benson

F. K. Cameron

B. C. Hesse

A. D. Little

A. V. H. Mory

M. C. Whitaker

145573
1913/18

EASTON, PA.
ESCHENBACH PRINTING COMPANY
1917

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

AT EASTON, PA.

Volume IX

JANUARY 1, 1917

No. 1

Editor: CHARLES H. HERTY

Assistant Editor: LEOLA E. MARRS

Advertising Manager: M. A. WILLIAMSON

ADVISORY BOARD

H. E. BARNARD, H. K. BENSON, F. K. CAMERON, B. C. HESSE, A. D. LITTLE, A. V. H. MORY, M. C. WHITAKER

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly

Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879

All communications should be sent to The Journal of Industrial and Engineering Chemistry.

Telephone: Vanderbilt 1930

35 East 41st Street, New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

By Way of Introduction.....	2
Chemistry and the Tariff Commission.....	3
The New Press and Publicity Committee.....	4
An Open Letter.....	4

ORIGINAL PAPERS:

The Manufacture of Linoleum and its Valuation. Armand de Waele.....	6
The Removal of Barium from Brines Used in the Manufacture of Salt. W. W. Skinner and W. F. Baughman.....	18
The Use of the Cottrell Precipitator in Recovering the Phosphoric Acid Evolved in the Volatilization Method of Treating Phosphate Rock. W. H. Ross, J. N. Carothers and A. R. Merz.....	26
Emulsions and Suspensions with Molten Metals. H. W. Gillett.....	31
Similarity of Vitreous and Aqueous Solutions. Alexander Silverman.....	33
Chemical Composition vs. Electrical Conductivity. Colin G. Fink.....	34
Varnish Analysis and Varnish Control. II—Viscosity of Varnishes. Max Y. Seaton, E. J. Probeck and G. B. Sawyer.....	35
The Cracking of an Aromatic Base Oil. The Temperature Factor at Constant Rate under Pressure. Gustav Egloff and Robert J. Moore.....	40
The Analysis of Antimonial Lead. C. R. McCabe.....	42
The Detection of Added Water in Milk. Halsey Durand.....	44
The Utilization of Olive Pomace. W. V. Cruess and A. W. Christie.....	45
Manganese as a Cause of the Depression of the Assimilation of Iron by Pineapple Plants. Maxwell O. Johnson.....	47
The Fertilizer Value of City Waste. I. The Composition of Garbage. W. J. O'Brien and John R. Lindemuth.....	49
Valuation of Water-soluble vs. Citrate-soluble Phosphoric Acid. E. J. Franke.....	54

LABORATORY AND PLANT:

Artificial Alkalinity in Water for Filtration. A. Wayne Clark.....	56
Some Laboratory Conveniences. A. E. Perkins.....	57
Handling a Standard Solution of Barium Hydrate. W. G. Haynes.....	58
Carbon Dioxide Absorption Apparatus. L. G. Wesson.....	59

ADDRESSES:

The German Alarm Clock. H. E. Howe.....	59
---	----

PUBLIC SERVICE SYMPOSIUM:

Public Service in the United States. Charles A. Beard.....	63
The Status and Compensation of the Chemist in Public Service. Frederick E. Breithut.....	64
The Chemist in the Service of the City of New York. Otto H. Klein.....	79
The Chemist in the Public Service. H. W. Wiley.....	81

DEDICATION OF THE NEW CERAMIC ENGINEERING BUILDING, UNIVERSITY OF ILLINOIS.....

Science as an Agency in the Development of the Portland Cement Industries. J. P. Beck.....	84
The Manufacturers' Dependence on Ceramic Research. W. D. Gates.....	86
Discussion. L. E. Barringer.....	91
Discussion. C. H. Kerr.....	94

CURRENT INDUSTRIAL NEWS:

French Dyestuffs Syndicate; South African Mineral Production; Nickel Production in Canada; Smokeless Combustion and By-product Recovery; Dehydration of Tar; Fire Protection on Ships; Synthetic Rubber; Machine Tools in Japan; Position of Tin; Natural Dye from Porto Rico; Siberian Metallurgy; Cement Industry in Japan; Minerals in Panama; Effect of Acid on Aluminum; A "Compound Gas;" Board of Trade; Acetic Acid from Acetylene; Metal-Working Gas Furnaces; Wolfram Ores for High-Speed Steel; Melting Scrap Aluminum; Tanning Materials in Russia.....	97
---	----

SCIENTIFIC SOCIETIES:

Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society; American Institute of Chemical Engineers, Ninth Annual Meeting, New York City, January 10-13, 1917; Adjourned Meeting American Chemical Society with the American Association for the Advancement of Science; The Perkin Medal Award; Nichols Medal Not Awarded this Year.....	100
--	-----

NOTES AND CORRESPONDENCE:

On Analyzed Chemicals; A Highly Unsaturated Hydrocarbon in Shark Liver Oil—Correction; Note on the Recovery of Molybdenic Acid.....	109
---	-----

PERSONAL NOTES.....

GOVERNMENT PUBLICATIONS.....	110
------------------------------	-----

NEW PUBLICATIONS.....	111
-----------------------	-----

MARKET REPORT.....	115
--------------------	-----

EDITORIALS

BY WAY OF INTRODUCTION

The first early morning plunge into a Maine lake is accompanied by an awful shiver. With the exercise of continued swimming this sensation fortunately changes, the body adapts itself to the new environment, a glow succeeds the shiver and all is well. At this writing the editorial shiver is in full sway. It is to be hoped that the aquatic analogy will be complete.

AN ACKNOWLEDGMENT

To every honest-thinking human being there come times when a sense of utter unworthiness results from unmistakable evidences of kindly thought and generous support. Such a time is the present. It is difficult to put into words the deep feeling of appreciation which arises at the thought of all the good that has fallen to our lot within the past few months. The sympathetic response of former associates to the request for early release from the old to the new responsibilities; the cordial coöperation of the Council and the Directors in planning the new work; the personal interest and wise decision of the Advertising Committee in the selection of the new offices; the easy induction into the new position by the former Editor, and his all too generous words in the last issue of *THIS JOURNAL*; the effective work of the staff who, in the midst of the turmoil and topsy-turveydom of removal to new quarters, have accomplished the arduous task of issuing this number on the first day of the month, five days earlier than usual; the many tenders of active support in the new work from members of the Society in all sections of the country—for all of these we would express an overwhelming sense of gratitude, which must manifest itself, however, not so much by words as by devotion to the interests of *THIS JOURNAL* and through this medium to the welfare of *The American Chemical Society*.

OUR HOME AND HOUSEHOLD

The new home of *THIS JOURNAL* is the eleventh floor of No. 35 East 41st Street, New York City, an address indicative of proximity to the Chemists' Club and its library and to the city public library. Here are provided offices for the Editor, the Assistant Editor, the Advertising Manager, the Treasurer, and the clerical force, these offices being reasonably fitted out for efficient work on the part of the staff. Further description will not be attempted. Drop in and see for yourselves and let us welcome you.

Fortunately opportunity was afforded to view the work in the old quarters before removal to the new, and that sight of four people at work in the smaller half (without any violation of arithmetic) of a very small office was sufficient to justify amply the statement that the *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY* as formerly produced was a wonder of modern journalism and a triumph of engineering skill in office manipulation.

Of the immediate staff, Miss Marrs, Miss Reynolds, Mrs. Price and Mr. Marrs continue their faithful

and efficient work. A new member of the household is Mr. M. A. Williamson, who to-day assumes the office of Advertising Manager of the Society.

If the same fine spirit which permeated the former microscopic quarters transfuses itself throughout the present commodious offices, all will be well.

THE MOTTO OVER OUR FIREPLACE

COÖPERATION

THE OUTSIDE KIN

Under this title is embraced the *Board of Associate Editors*. The Council at its last meeting authorized the new editor to select the associate editors, delegating its approval of such selections to the Board of Directors. The Council further authorized the curtailment of the number of Associate Editors if it were deemed advisable.

In view of the almost infinite variety of subjects in industrial and in engineering chemistry calling for critical review of papers submitted for publication, and in view of the authorization above noted, we have construed this broadly as meaning permission to change the existing order of things. With characteristic Irish perversity, but with the utmost confidence in the sincerity of the many offers of assistance in the work of the Journal, we have decided, with the approval of the Directors, upon a change in a direction opposite to that contemplated in the authorization of the Council. Briefly, the *Board of Associate Editors* has now been expanded to include the entire membership of the Society. There are, however, pitfalls ahead for the Editor. To guide his steps, as far as possible, around such unfortunate certainties and to aid further by friendly counsel as to the future policies and development of *THIS JOURNAL*, an *Advisory Board* has been added. It consists of H. E. Barnard, H. K. Benson, F. K. Cameron, B. C. Hesse, A. D. Little, A. V. H. Mory and M. C. Whitaker.

THE ADVERTISING MANAGER

Even in the face of the steady increase in pages of advertising matter secured for the Society's publications by the admirable work of Messrs. Gibling and Nellis, the Advertising Committee felt that the time had now arrived for the Society to take over in its entirety this feature. After a careful survey the Committee selected for this important work Mr. M. A. Williamson, formerly of the Norton Company of Worcester, Massachusetts. Possessing a strong personality in which is blended a pleasing manner and an aggressive disposition, confident through past successful experience in publicity work, Mr. Williamson enters upon his new duties filled with a boundless enthusiasm for the upbuilding of his department and with the determination that the advertising pages of the Society shall be the true reflection of the increased activity in the chemical industries of America.

AN INVITATION

This publication is the property of the members of the American Chemical Society. That it has the good-will of the membership is unquestionable. Abundant testimony to this effect exists in the office files and in the memory of the Editor. The responsibility for future growth and usefulness, however, has been placed upon one person, and that person without editorial experience. Two saving features make up, in part at least, for this lack of experience: no cerebral crusts have yet formed, and the heart is always appreciative of friendly suggestion and constructive criticism.

It is hoped, therefore, that all who may be interested will not hesitate to communicate their ideas of the future development of this publication and their frank criticism of anything connected with its make-



M. A. WILLIAMSON
Advertising Manager, American Chemical Society

up and operation. Assurance is hereby given that such suggestion or criticism will receive sincere and careful consideration. Some have already been made which can be counted on to make their influence for betterment felt as the months go by.

A HINT

May we speak just a bit confidentially? We might here it is. One of the chief motives which led to the recent re-organization of the Society was the earnest hope that as some as yet undefined and still hazy way we might gradually serve more and more as a coordinating influence or agency in these better, better, every-day, on-the-jump, vibrant days of individualistic effort in the rapid expansion of American chemical industries, especially among such as utilize coal-tar distillates

as raw material. That there is need of coördination no one questions; that any exists no one avers. We all know nevertheless that the halcyon days of high prices, pressing demand and almost absolute freedom from foreign competition must pass. Will we be ready to meet the grim conditions which then must be faced? Are we not already beginning to suffer from lack of coördinated effort? What will it profit us if we gain a whole world's supply of *beta*-naphthol or *para*-nitraniline and lose a market which will pay at least as much as the cost of production? These are merely imaginary illustrations and their mention is not at all based upon statistical information.

The glamour of the successful achievement of American chemists is even now hiding some of the failures which have already occurred and which are certain to increase if overproduction along certain lines is not avoided. Meanwhile there are many neglected lines, and they must be developed if manufacture is to reach that point of efficiency which will guarantee successful ability to meet world-wide competition. Now is the time for such adjustments. No illegal division of the field is intended, but a common-sense, uniform growth of the whole of the coal-tar chemical industries must be provided for, if our great mass of raw material is to be properly utilized and our country freed from outside dependence for supplies of such products.

We are rushing along blindly, each busy with his own thoughts and plans, while plainly before our eyes are the completely unified industries of each of the great nations of Europe, forced into such unity of national and even international effort by the exigencies of the great war. For such coördination of industrial effort, facts are needed—facts as to what is now being manufactured and in what quantities. From such data could be readily gleaned information as to where danger of overproduction lies and where need of expansion exists.

Can THIS JOURNAL or its Editor be of service in such a situation? An affirmative answer to this question would depend upon two things: *First*, absolute frankness on the part of manufacturers in giving information; *second*, confidence of manufacturers in the sincerity and disinterestedness of the Editor. The suggestion carries with it rather grave responsibilities and is therefore not put forward lightly, but the situation is such that it is willingly proposed in the belief that genuine service might be performed.

CHEMISTRY AND THE TARIFF COMMISSION

The author of the foregoing contribution believes in it and would like to be all-controlling now, though for the time. Another interesting phase of cooperation is that of a tariff commission.

Among the many subjects which will engage the attention and study of the Tariff Commission, there will probably come pressing closer or more imminent discussion than that of the chemical industries. The country is convinced as to the abundance and variety of the raw materials upon which such industries depend and to the danger arising to the security of their full and prompt requirements, not to mention the security from general conditions of the supply of raw

chemists as a result of the remarkable showing made at the Second National Exposition of Chemical Industries.

Chemists, however, as a class are not capitalists. Their work is the transformation of matter by reagents, in apparatus, on land and in buildings supplied by enlisted capital, and few are the cases where efficiency in manufacturing is immediately attained. In the enlistment of such capital the chief restraining influence is the question of foreign competition. No greater blessing, therefore, has come to American chemical industries than the creation of the Tariff Commission, which will report to the President or to Congress impartial studies of existing facts and conditions. With the publication of such reports invidious questions as to motive in asking compensatory protective legislation will be removed or, equally important, capital will be encouraged to invest in such industries without the imagined necessity for such legislation.

Bewildering, however, will these studies be, if no member of the Tariff Commission has intimate knowledge, along broad lines, of the inter-relations of these industries, of the technical problems involved, of relative domestic and foreign conditions of manufacture in this complicated field, and of the blending of these threads into the warp and woof of the national industrial organization.

Realizing this the Directors of our Society forwarded to President Wilson an endorsement of Mr. Ellwood Hendrick, of New York City, for nomination as a Member of the Tariff Commission, believing that in Mr. Hendrick would be found those qualities which would insure to the nation expert knowledge, balanced judgment, business experience, disinterestedness and conscientious discharge of duty.

It is a matter of all-round congratulation, as presaging future cooperation, that in this endorsement the American Chemical Society has been joined by the American Electrochemical Society, the Manufacturing Chemists' Association of the United States, the American Institute of Chemical Engineers, the Chemists' Club, the American Pharmaceutical Association, the National Wholesale Druggists' Association, the National Association of Manufacturers of Medicinal Products, and the Technical Association of the Pulp and Paper Industry.

THE NEW PRESS AND PUBLICITY COMMITTEE

Among the many noteworthy features of chemical achievement during the week of September 25, 1916, none was more striking than the admirably planned and thoroughly executed work of the Press and Publicity Committee of the New York Section of our Society. Many were amazed at the results attained, in spite of the space demands made upon the daily press by the presidential election, the European war, and the threatened strike of eight hundred thousand laborers in New York City.

At former meetings we had often witnessed the hopeless efforts of reporters to select from the mass of technical papers presented material for some kind of story interesting to the newspaper-reading public. To all the sight of this new machinery in action was

inspiring. No mystery surrounded the proceedings; men high in the ranks of chemistry sacrificed their desire to participate in the varied program, pulled off their coats and were daily "on the job" in Room D of the Chemists' Club. With keen newspaper sense, they prepared abstracts of papers in language which even the veriest layman could understand. At appointed times the reporters were met and from this prepared material they made selection *ad libitum*. To this effort of chemists the press in turn responded splendidly.

The work, however, was not to end with the close of that memorable week. The New York Section continued the Committee as a local activity and appropriated funds for its use. Regular meetings have been held and the publicity campaign has gone merrily on. During the past summer a Publicity Committee of the American Chemical Society, also a working committee, studied carefully the publicity methods of allied organizations and submitted a report to the Council which was approved by that body and referred to the Directors. It is a pleasure to record that at the annual meeting of the Directors, December 9, 1916, these two committees were consolidated as the *Press and Publicity Committee* of the Society, with Mr. Allen Rogers of the Pratt Institute, Brooklyn, New York, as *Chairman*. A modest appropriation was voted for the clerical expenses of the enlarged committee. More extensive plans can now be laid to continue the task of effectively bringing together the public and the chemist.

AN OPEN LETTER

TO THE HOUSE OF REPRESENTATIVES OF THE SIXTY-FOURTH CONGRESS:

SIRS:

On the closing day of your last session legislation was enacted, as a part of the General Revenue Bill, for the avowed and express purpose of promoting and encouraging the development of an American dyestuff industry.

This action of the Congress, controlled in both Senate and House by a political party long opposed to protective duties as a stimulus to industrial development, has been justly interpreted by the country as a patriotic answer to the nation-wide call for a domestic industry, peculiarly intricate in its character, which would free this country from the domination of a foreign monopoly; which would relieve manufacturers and laborers in many other lines from threatened distress; and which would furnish a nucleus of superintendents, foremen and workmen who would be needed for training others in the manufacture of high explosives, in case at any time our country should be involved in a great war.

The legislation was not hurriedly framed. Extensive hearings were held, and after considerable delay, a conference was held between members of both the Senate and the House, in charge of the matter, and representatives of both manufacturers and consumers of dyestuffs. This was no secret conference for it was freely mentioned on the floors of both Senate and House in the course of public debate. The result of the conference was satisfactory, though the

proposed rates were somewhat lower than had been hoped for by many. As manufacturers learned of the agreement, increased activity in development of plants was noticeable.

Then to the utter surprise of all of the manufacturers, the dyestuff section, as finally submitted to the House by the Ways and Means Committee, contained a feature which had entered into none of the previous discussions, namely, an exception from the special temporary duty of 5 cents per pound of "natural and synthetic alizarin, and dyes obtained from alizarin, anthracene, and carbazol; and natural and synthetic indigo, and all indigoids, whether or not obtained from indigo."

After a speech on this portion of the bill, a speech which marked the closing of debate, the bill as introduced by the Committee was passed by a party vote. Promptly after its transmittal to the Senate, hearings were held by and briefs were filed with the sub-committee of the Senate Finance Committee. All of the manufacturers and all, except one, of the consumers protested against the exception in the bill as passed by your body. The one exception was The Proximity Manufacturing Company, of Greensboro, North Carolina (see Senate Hearings on H. R. 16763, p. 145, and Senate Briefs on H. R. 16763, p. 253), of which Mr. Caesar Cone, of Greensboro, N. C., is President (see Senate Hearings, p. 156). Not content with the special treatment already accorded, he asked that indigo be returned to the free list. The sub-committee rejected the argument of this one consumer, removed from the bill the excepting clause and added coal-tar medicinals, thereby making the classifications of the bill thoroughly sound and logical.

In the conference committee, however, the views of your representatives prevailed and the excepting clause was finally restored to the bill and in this form passed both bodies in the closing hours of the session.

In behalf of the chemists and chemical manufacturers of the country I would respectfully call your attention to the following:

I—These substances so excepted are just as truly "coal-tar dyestuffs" as those to which you have given the full measure of protective rates.

II—The difficulties involved in their manufacture are fully as great as in that of the others.

III—Their manufacture outside of our borders is just as highly developed as that in any other line of dyestuffs.

IV—It would seem to be illogical to relieve from the special duty the indigo which is used in the manufacture of the workman's overalls, while other colored apparel which he and his family wear is left subject to the higher rate.

V—It can scarcely be argued that since these excepted dyestuffs have been used from the free list to the 30 per cent *ad valorem* duty that therefore they have received their proportionate share. That is not the question involved in this legislation. These products were on the free list at a time when tariff legislation was constructed on lines of economic duty. This present bill was intended to create a complete self-contained, American dyestuff industry. The

point of view is a new one and calls for equal development on all lines.

VI—If it be argued that the special duty of five cents on indigo would benefit only one manufacturer, it can freely be said that a direct statement from another strong chemical manufacturing firm was filed with the chairman of the Senate Finance Committee stating that experimental work was well advanced and plans were being laid for the manufacture of indigo on a large scale, provided tariff legislation was sufficiently favorable. Moreover, such an argument can scarcely hold in view of the many dyestuffs which are subject to the special duty and for whose manufacture no steps have as yet been taken, due to the impossibility of beginning all lines at once.

With such thoughts in mind, the Dyestuff Conference, held during the last annual meeting of the AMERICAN CHEMICAL SOCIETY in New York City, in a large auditorium crowded to its utmost limit, created by a unanimous rising vote a committee to draft a resolution protesting against the excepting clause of the dyestuff legislation. The resolution reported by the Committee is as follows:

"Therefore, be it Resolved that we condemn the removal of these dyestuffs from the special tariff accorded them by the Senate as detrimental to the establishment and development of the American Dyestuff Industry and subversive of the best interests of the American people."

The proof of the contention lies in the industrial situation as it exists to-day, namely, on the one hand tremendous activity in those lines which received the full benefit of the protective rates; on the other, sluggishness where the special duty was withheld. Chemists and manufacturers have courageously met the critical situation facing our industries since the practical cessation of European supplies. This has been done in the face of much foolish talk about the unsuitability of American coal for this purpose; of many unjust remarks about the inferiority of American dyestuffs; and of difficulties in the raw material situation due to the intense foreign demand for munitions. Gradually our manufacturers are gaining that experience which will eventually lead to efficient manufacture.

Must the greater part of this development be sacrificed at the cessation of the European war? Have we built a bridge across which our nation would pass to the land of industrial independence and adequate production, a bridge with solid pillars consisting of the *ad valorem* duties and with one-fourth of the superstructure the special duty, necessarily omitted?

It is realized that the present session is short, and that you have many urgent problems before you for solution. Nevertheless, it is earnestly hoped that the same patriotic spirit which led to your willingness to depart from a cherished policy in order to meet a national crisis, will again lead you, and that you will recall from the General Revenue Bill the language to the (special) duty, which the tariff commission have now recommended to be an *ad valorem* duty, the purpose and power of the otherwise indefensible legislation.

Respectfully submitted,

Two parties

ORIGINAL PAPERS

THE MANUFACTURE OF LINOLEUM AND ITS VALUATION

BY ARMAND DE WAREL
Received August 26, 1916

The literature on the subject of the valuation of floor coverings embodied under the various descriptions of floor-cloth, linoleum and cork carpet is somewhat scant and, apart from a paper on the subject by Ingle¹ in which the author submits a limited amount of chemical data, for the most part the testing of these products is limited to crude rule of thumb methods. As Ingle points out, an exception is to be found in a publication of Burchartz² who gives the tests of the German Government. Most of the English Government tests are physical, embodying determinations of specific gravity, water absorption and in rare cases a bending test, *i. e.*, the manufacturers have to tender a sample which will bend over mandrils of stated diameters without breaking. More recently certain of the governmental departments have specified compliance of goods submitted with certain chemical tests, principal among which are moisture and ash content together with two determinations, the value of which are questioned by the writer for reasons stated below, *vis*: "Acetone extract," and "Unsaponifiable matter insoluble in acetone." The latter test in the writer's opinion is an attempt to obtain an idea of the cork content of the material.

Attrition or wearing tests have from time to time been suggested, and various methods adopted with a view to obtaining a comparative measure of the wearing power of linoleums. Experience, however, has shown that none of these tests give results which are in any way trustworthy.

The determination of the ether extract as suggested by Pinette³ is very misleading, for as Ingle points out in his paper referred to above, no judgment can be made unless the constituents of the linoleum are known both qualitatively and quantitatively. With regard to the government tests of "Acetone extract" and "Unsaponifiable matter insoluble in acetone," the later remarks as to the indefinite amount of soluble matter extracted by ether from oxidized oils apply even more forcibly in the case of acetone extracting, especially as no stipulations are made as to the subdivision of the sample, and no period of exhaustion is specified. In the case of "unsaponifiable matter" it had been remarked in Ingle's paper previously referred to by S. Stewart (discussion) that this quantity was very variable and depended on the conditions under which saponification was effected. Thus saponification of cork by alcoholic potash in an open basin yielded 33 to 36 per cent unsaponifiable matter while saponification under a reflux condenser yielded about 72 per cent. In the case of a plain linoleum examined for a government tender, a great divergence

due to the cork present is seen in the following unsaponifiable organic matter insoluble in acetone:

SAPONIFICATION UNDER REFLUX	Per cent unsaponifiable
I With 8 per cent. alcoholic soda,	11.11
II With 0.25 per cent. aqueous soda	16.47

The unsaponifiable matter in each case was dried, weighed, extracted with acetone, weighed, and the organic matter therein determined by incineration. It may be mentioned that constancy is obtained by the 0.25 per cent aqueous soda saponification of cork, the unsaponifiable matter thus obtained $\times 1.43$ giving a fair approximation to the cork present.

MANUFACTURE OF LINOLEUM

The name "linoleum" defines a product of fairly characteristic composition, and represents practically the same product as that patented in 1864 by Frederick Walton, who may justly be deemed the father of the linoleum industry. The adoption of the processes employed appears to have been arrived at by a method of evolution, little chemical knowledge seeming to be possessed on the nature of the reactions involved or justification for the choice of materials; nevertheless it stands highly to the credit of the original inventor that the attention of chemists and technologists has hitherto not succeeded in effecting any change from the process as originally conceived by him half a century ago.

Floorcloth, so-called "floor oil cloth," is a material quite distinct from linoleum, consisting as it does of a strong, coarse, jute canvas to which a variable number of coats of a coarse, low-grade paint have been applied on either side, a finishing application of a printed paint design followed by a light coating of varnish being applied to the wearing surface. The manufacture of floorcloth at the present day is comparatively unimportant, as it possesses none of those qualities of resiliency and nonconductivity to heat which mark linoleum. It is, therefore, not my intention to include its discussion in the present paper.

The Taylor-Parnacott or Corticine floor coverings are, strictly speaking, not coterminous with true linoleums, as the method of manufacture of the solidified oil necessary for their production differs from the linoleum process in being mainly a polymerization process as distinct from the oxidation treatment used in true linoleum. This class of floor covering, however, differs from floorcloths and resembles linoleums in that its manufacture consists in the application of a previously prepared composition containing solidified oil to canvas, instead of allowing the oil to solidify in combination with filler actually on the canvas support as in the case of floorcloth. The main difference, however, between linoleums and "corticines" from the manufacturers' standpoint is that, considered at the particular stage of the process where the solidified oil is directly mixed with cork and pigment to make the linoleum material, the cohesive properties of "corticine" oil are too poor to allow of

¹ *J. Soc. Chem. Ind.*, **23** (1904), 1197-1201.

² *Ibid.*, **19** (1900), 255.

³ *Ibid.*, **1892**, 550.

its employment for those products which demand the use of an oil of high binding power such as is used for inlaid linoleums. Thus oil prepared by the Taylor-Parnacott or corticine process is used only for the manufacture of uni-colored or plain cloths and for "cork carpets," these latter products merely consisting of an oil-cork-pigment mixture in which the cork employed is of a coarse variety, thus ensuring the maximum of resiliency and warmth to the feet.

MANUFACTURE OF CORTICINE PRODUCTS

The manufacture of the oil-binding medium involves a partial solidification by a process of combined oxidation and polymerization at a high temperature. The object aimed at in the several processes is to obtain a product resembling an unvulcanized india rubber of maximum "covering power" or power to take up filler, this rubber-like product being capable of undergoing subsequently a further change in order to obtain a product of increased solidity resembling leather. It thus becomes at once apparent why the drying oils are universally chosen as the basis for the binder. Linseed oil possesses the property of finally yielding a dry elastic body (the main constituent of which is Mulder's "linoxyn," *vide infra*) and at the same time by special treatment can be caused to appear in an intermediate stage as a body possessing the optimum of tackiness.

In manufacturing the Taylor-Parnacott or "corticine" product a quantity representing about $2\frac{1}{2}$ tons of (preferably) tanked Baltic linseed oil is heated to a temperature in the neighborhood of 220°C . in a large open iron pan. Driers consisting of a mixture of about 2 per cent of flake litharge and 1 per cent of crystallized lead acetate are then dusted in. The latter drier has the effect of partly redissolving any metallic lead formed by reduction of the litharge by the hot oil and the water of crystallization of the salt has possibly some obscure action in distilling off volatile products¹ formed by the saponification of the oil by the basic lead drier. A certain amount of mucilage or foots will have separated out at this temperature together with some spongy lead. The hot oil is then blown for 2 or 3 hours, the fire being previously withdrawn. The object of the blowing is many fold: it ensures a thorough agitation of the oil and supplies the best conditions for the solution of the driers; it also gives an initial start to the oxidation and thus facilitates subsequent polymerization; furthermore, it is the means of reoxidizing any metallic lead in the spongy condition and it has probably also the effect of oxidizing away the separated mucilage.

This oil is allowed to cool 12 hrs. and is then transferred to pots ($1\frac{1}{2}$ -ton capacity), fixed in a brickwork setting and heated by direct fire, the coal being contained in a grate on wheels in such manner as to permit instant withdrawal of the source of heat when necessary. The contents of these small pots are then raised to a temperature in the neighborhood of

250°C . and maintained thus, receiving occasional stirring by hand. In something like 8 to 12 hours, thick skins form on the surface of the hot oil which has gradually increased in viscosity. From this point vigorous agitation of the oil is resorted to until solid rubber-like nuclei make their appearance. At a point judged by the oil boiler, stirring is stopped and the fire withdrawn. Solidification takes place gradually throughout the mass, the top surface of the oil being quite dry and leathery, and small vents form, through which acrid vapors escape. The partly entrapped gaseous products within the mass then expand the contents of the pot, the rising of the "head" necessitating the placing of short tubes or rings of the same diameter as the pan on the upper edge to prevent overflowing. The treatment of the oil is then concluded and after the rising is finished the mass contracts somewhat. The contents of the pot are then allowed to cool for 2 or 3 days, then cut into segments *in situ* and finally floated out by water.

This solidified oil presents the honeycombed appearance of a loaf of bread except that the bottom and those parts immediately adjacent to the sides are somewhat greasy. The actual treatment of the oil being concluded, the remainder of the process necessary to manufacture "Taylor cloth" or "cork carpet" consists of the mixing together of the oil with fine or coarse cork and the necessary pigment and a final rolling on to a canvas backing.

The so-obtained "raw" or "green" cloth is then hung for several weeks in bights in a "stove" or large steam-coil heated room maintained at 120 to 160°F . in order to convert it from the plastic to the leathery or finished condition. This subsequent treatment of "cloth" is the same whatever oil basis is used, so far as the manufacture in a plastic state followed by the stoving is concerned, and it is the aim of the manufacturer to obtain the maximum binding or cohesive property of his product at this intermediate stage together with the highest degree of leatheriness after stoving. It is somewhat difficult to describe the physical properties of the products which constitute what is regarded in the trade as a good yink, but the subsequent descriptions of the materials I have employed in the valuation of linoleums may give the reader the clue to this conception.

It is here necessary to mention that "cork carpets" or cloths of high resiliency made with coarse cork used by themselves as a floor covering have been entirely by the process just described. The reason for this is that the oil base and the true polymer actually contains a certain proportion of some which would not only detract from the high resiliency for which such carpet is prized but would be mechanical means present the decomposition of the large part of a cork carpet, there being a hot demand in the trade for such "hard" goods. A "cork cloth" however represents the same kind of floor covering made with this polymerization of oil merely consisting of a harder adventure with the inclusion of coarse cork. Again, from the nature of it is the larger product in the floor covering industry and in the process the cork

¹ I purposely refrain from stating that these volatile products consist of either acrolein or alloxan in spite of the general opinion of some writers that such is the case as it is obvious that the reaction involved does not bear such treatment out.

siderably more expensive "linoleum cement" plant, there exists a certain demand for it by some governmental departments. It possesses nothing but disadvantages over linoleum and is more expensive to make.

THE WALTON "CEMENT"

The other, and by far the more important process for the manufacture of a solidified oil basis, is the invention of Frederick Walton in 1864. The preparation of this oil basis which will hereinafter be referred to under its technical name of "cement" involves two distinct treatments. The raw linseed oil is first of all converted into a solid oxidized product of moderate greasiness, low elasticity and binding power; this product is then transformed by a heating process, consisting probably of an intramolecular rearrangement, into a body which has lost the greater part of its greasiness and possesses an elasticity and binding power of very high degree. Although there are no less than three distinct processes for solidifying the oil by oxidation, the second treatment referred to (the conversion of the oxidized oil into "cement") is the same in every case.

Of the three oxidation processes now in use, two are the invention of Frederick Walton. The third, or Wood-Bedford process, in spite of its being the subject of a more recent invention (being a derivation of one of the former processes and yielding a very considerably inferior product), is adaptable only to the lower qualities of plain cloths and impossible of application for inlaid linoleums which necessitate high cohesive qualities when in the intermediate or plastic stage. The Wood-Bedford process, it may be mentioned, is very little used.

The first of the Walton processes for the oxidation of linseed oil is the "scrim" process, so-called for the reason that light cotton fabrics or "scrims" are successively flooded with an oil boiled with suitable driers, each layer being allowed to dry before being followed by the next flooding. The scrims are in widths of 3 ft. and 20 ft. in length and are suspended vertically in a tall building, capable of accommodating 1000 to 2000 and maintained at a temperature of 80 to 90° F. The drainings from the scrims are returned for a further flooding, being replenished with fresh oil when necessary. According to the nature and amount of the driers used either one or two floodings are performed every 24 hrs. The skin formed will attain as a rule a thickness of about one inch in 4 mos., when its excessive weight renders it liable to fall and flooding is stopped. A final drying off is then given and the skins cut down. They are then ready for conversion into cement.

In the second Walton process, commonly known as the "shower bath" process, the raw oil is admixed in the cold with a very small percentage of insoluble drier, and subjected to a preliminary oxidation in a large "shower bath" which consists of an enclosed rectangular box about 18 ft. high, having its roof perforated with a number of holes, the upper extension forming a shallow open tank. The lower portion of the box contains steam coils to heat the oil to the

temperature necessary, usually 90° F. A large pipe fitted with a rotary pump connects the lower level to the top tank by which means the oil descends in a continual rain to the lower tank. A fan is fitted to the body of the box to replenish the air and remove acid vapors.

As a rule a 10-ton lot of oil will have attained such a viscosity in 72 hours that it will no longer flow through the openings in the roof; then the thickened oil is admixed with about 5 per cent of whiting and transferred in ton lots to short, horizontal jacketed drums fitted with a horizontal shaft with radial arms. Steam is first of all admitted to raise the oil to about 120° F. but subsequently, as oxidation proceeds rapidly, it is necessary to admit cold water to the jacket to keep the temperature under control. The object of this "smacker," as it is called, is to perform an oxidation that it is beyond the power of the shower bath to continue, while the latter apparatus is employed on account of its high efficiency and the low power required. A powerful draft of air is admitted into the smacker during its operation.

The "smacking" treatment is continued until a sample withdrawn will just barely flow, a point usually arrived at in about 48 hrs. A treacle valve is then opened in the bottom of the vessel and the nearly solid oil received onto a layer of whiting in a room immediately underneath. The oil solidifies on attaining room temperature to a mass of the consistency of liver, when it is cut into slabs, transferred to trays and kept in stoves at 100° F. for several days, when the action of the evolved acid products on the contained whiting causes the mass to rise somewhat and develop an internally honeycombed structure. An increase in body, possibly due to further oxidation facilitated by the greater surface exposed, is the result of this stoving. The oil thus prepared is then ready for conversion into cement in precisely the same way as in the case of oil prepared as previously described.

It has been observed as a general rule that slow oxidation yields a more favorable product than one that is obtained by rapid methods; hence it is advantageous from this point of view to prolong as much as possible the shower bath treatment at the expense of the smacker treatment.

The Wood-Bedford process consists merely in the performance of the oxidation throughout in the smacker, temperatures up to 140° F. being obtained. The whole oxidation can be completed in 48 hours, but as a consequence of the rapidity of reaction a vastly inferior product is obtained, suitable for thin qualities only.

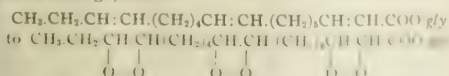
It may be mentioned at this point that thickness of "cloth" obtained and "quality" are practically synonymous terms, the several degrees of the higher qualities being usually made with similar ingredients while for the lower grades or thicknesses of cloth the high standard of ingredients employed need not be adhered to.

The next stage of the process is that of the further treatment of the oil that has been oxidized by the "scrim," "shower bath" or Wood-Bedford processes.

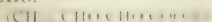
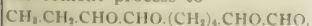
The original and yet up-to-date process as originally patented by F. Walton is as follows: 15 to 17 cwt. of oxidized oil are put into a large pan fitted with a steam jacket and agitators. The pressure of steam is such that temperatures of 130 to 150° C. are easily obtained. A quantity of molten rosin in the proportion of 1 : 8 of the oil is then poured on, followed by a similar quantity of powdered gum kauri. Agitation is continued at a slow speed until the oxidized oil runs down to a thick fluid, a considerable evolution of water, formic acid, etc., taking place. After the melting of the oil, when the mass rises up, the speed of the stirrers is increased to cause it to return. From the point at which the "turning" or diminishing of the head takes place, thickening of the mixture occurs with more or less rapidity. At the same time the oil changes from its characteristic butter-yellow to a reddish brown, this darkening being independent of the influence of the rather dark gum employed. At a point judged by the operator, the "cement," as it is termed, is tipped out of the pan either by overturning on its swivel or in other forms of plant by opening a sluice valve at the bottom. As the hot mass does not cool rapidly, means are adopted to reduce the continuation of the cooking action after leaving the cement pan. This is accomplished either by running the hot cement out onto a concrete floor mounded up to a low cone or tipping directly onto revolving water-cooled rolls. The "cement," after cooling, is then cut up into slabs, and left to "hang" or mature for a week or two to increase its body.

REACTIONS

We have thus in the linoleum process two definite reactions, the first being a simple oxidation and the second a process for which I suggest the explanation of either a molecular rearrangement of complex groupings or a condensation, or even possibly a combination of the two. At first sight the reaction occurring in the cement pan would suggest itself as a polymerization. A polymerization would include a linking together of double bonds together with an increase of molecular weight. Ingle¹ suggests that the reaction occurring is one of rupture in the chain in the middle of a peroxide group, such group being in the position of the original double linkage, thus:



This would be transformed more or less completely in the cement process to



The above equations have been shown for the sake of convenience as occurring on a monomolecular basis.

Although the above equations as indicated in Ingle for linolein do not come so far regarding the position of the double bond, to the structure previously recorded to this body, the mechanism of the decomposition of the peroxide is probably reversed exactly. We have evidence for this in the case of

volatile bodies of low molecular weight, among which I have identified bodies with aldehydic groupings, formic acid, etc. It is probable also that decomposition of the peroxides takes place in a somewhat similar manner under hydrolysis by alkali, *i. e.*, that disruption of the chain at the position originally occupied by the double bond may occur, thus yielding smaller molecules,



an oxidized linseed oil by saponification yielding considerable quantities of soluble (lower) fatty acids, together with the invariable "oxidized" acids¹ which in my opinion consist of the nine-carbon radicle terminated by an aldehydic group at one or both ends resinifying. The actual proof of such action occurring as suggested by Ingle is somewhat difficult but I offer the following as a proof negating the suggestion of polymerization.

Determinations of the content of solid fatty acids on an oil during the process to oxidation till solid and then subsequently after its treatment by heat at 150° C. in the cementing process have invariably shown the percentage of the same to remain constant. An oil polymerized till solid at 250° C. in an atmosphere of carbonic acid showed an increase in acids behaving as solid or saturated acids² of from 5.25 to 48.8 per cent. The acids isolated possessed properties different from true saturated acids in that they were viscous, gummy solids, instead of being hard and crystalline, and furthermore showed an iodine value of 86 instead of in the neighborhood of zero. The 48.8 per cent obtained would include (unless destruction of the 5.25 per cent of unsaturated acids be presumed) the original saturated acids present, and the difference of 43.55 per cent I have assumed to be true polymerized acids. I may mention that various acids have as yet been found to be the result of this test for determining polymerization, that I have constantly used it for recognizing this treatment.

Further studies of the cement pan reaction have as yet yielded no definite results. Measurement of the possible increase in the number of molecules by subdivision of the original chain, as determined by increased saponification value, solidified as I had anticipated, no data, as yet suggested none. By distilling of the cemented solid oil and condensing upon the freezing down by the double bond position.

Working on the evidence as yet known obtained in the possibility of reducing cement into volatile or soluble fractions, I have performed experiments throughout during the course of transformation from cement to the volatile "cement" and various products in order to determine the changes occurring therein.

REFERENCES

¹ The experiments performed in a gasometer have shown that any volatile products are the same.

² *J. Soc. Chem. Ind.* 1913, 340.

quent changes taking place on oxidized oils after their solidification by oxidation whether by the "scrim," "shower bath" or Wood and Bedford process are of the same order, has proved to be correct, and I need not detail the data that have led up to this assumption. For reasons of expediency, however, my work has been mostly done on the oxidized oil obtained by the "scrim" process, as the solid oils obtained thus have lower extracts as a general rule, or in other words are drier, and consequently facilitate extraction. Thus the skins obtained by the scrim process can be run into very thin sheets by passing through cold rolls and extract figures can be obtained which represent sufficiently accurate values for our purposes, by 24 hours continuous exhaustion. It will be noted that I make a reservation in the foregoing statement as to the absolute value of the figures obtained for extracts, the qualification therefor being as follows:

The "skin" obtained by the "scrim" or natural oxidation process presents an appearance and physical properties somewhat resembling a piece of bichromated glue jelly. It is somewhat harder, if anything, opaque brown to transparent yellow, according to the nature of the driers used, and in thicknesses of about an inch usually breaks when bent double thus showing its limited elasticity. When sheeted through cold rolls it is opaque light yellow. In this latter form the maximum surface can be obtained for extraction for a given weight.

A 10-gram lot of sheeted skins was transferred to an extraction thimble formed by cutting off the lower end of an ordinary 6 in. X 1 in. boiling tube and tying a piece of linen over the top lip. This was then put, linen end downwards, into an ordinary Soxhlet extractor. The apparatus, fitted up in the usual manner, was transferred to a water bath, and the skin extracted with ordinary ether of 0.720 sp. gr. At the end of 24 hrs. the ether was driven off from the extraction flask, CO₂ being used to drive off the final traces. The extract obtained amounted to 67.5 per cent. A further extraction of 24, 48 and 72 hrs. was then done in order to determine whether the exhaustion was complete. As a consequence of the results obtained, extraction was continued for a period up to 4½ mos. The figures obtained for the whole period of extraction are as follows:

PERIOD	Hours				Days					TOTAL
	24	48	72	96	9th	23rd	43rd	74th	135th	Per cent
Ether Extract	67.50	3.96	0.93	1.11	2.80	3.61	1.66	2.10	1.65	85.32

The above values when plotted in form of a curve with per cent extract as ordinates and time as abscissae give a parabolic figure. From a consideration of the enormous number of continuous extractions that the substance must have received at the end of the period quoted without an end-point having been obtained, it seems highly improbable that the simple explanation of high insolubility of any particular constituent would serve. The explanation suggested would be rather that of either the solvent having the definite effect of slowly rendering soluble a previously insoluble substance, or else the extracted portion consisting of two distinct bodies of vastly differing solubilities, the less

soluble acting as a "latent" solvent to the other. In the first suggestion it is necessary to assume that the high initial extract represents some true soluble matter whereas the succeeding small extracts consist of the transformed insoluble body. This particular phenomenon is emphasized as being of importance in showing analogy with subsequently described reactions.

Similar results were obtained with alcohol, benzene, chloroform and acetone. Petroleum ether of B. P. 35 to 50° C., however, while still showing no definite end-point of extractable matter, gave an extract which in quantity and appearance differed so far from that obtained by the other solvents as to warrant further investigation.

During the course of the routine examination of samples of skins for extractable matter, the fusibility of the skins for purposes of conversion into cement being roughly proportioned to the ether extract, it was often observed that skins of similar extract gave very different results in practice. Thus it would often happen that two apparently different skins of which one would be adjudged by the rule of thumb and fairly accurate test to be superior to the other, while yielding the same quantity, gave extracts differing in physical and chemical properties. Thus the extract would be more or less viscous, and would differ in color, while the acid value and yield of "oxidized acids" obtained on saponification would be dissimilar.

The result of a very long series of test experiments has finally shown me that the total extract can be resolved into two or even more fractions, for practical purposes being limited in utility to two: (1) the extract obtained by 24 hours extraction with low boiling point petroleum ether, and (2) the extract obtained by a further extraction of the residue with ordinary ether. Very striking is a comparison of the physical properties of these two fractions. The petroleum ether extract consists of a pale greenish yellow, fairly mobile oil, a turbidity being apparent in it due to white crystals which settle out on standing; exposure to air for very long periods shows it to possess no power to dry to a hard skin, a certain amount of thickening however taking place. The subsequent ether extract is a yellowish brown oil of such extraordinary viscosity and tackiness that it resembles melted India rubber; exposure to air resulted in its drying to a moderately hard but highly elastic skin.

A cursory examination of these two oils side by side, considered from the point of view of their bearing on the physical properties of the skin from which they originated, would at once suggest that the quality of the latter would be proportional to the quantity of the ether extract, and inversely so to the petroleum ether extract, the residual linoxyn affecting the "body" or solidity of the whole. This expectation has been fully realized, so that the valuation of various samples has been performed by me by these means for a considerable time past.

Before proceeding to the description of the uses of this test in other directions, it will be as well to append the data obtained in the hitherto unsuccessful attempts at solving the composition of the fractions.

In the following, linnoxyn (so named by the Dutch chemist Mulder) will be considered to represent the body which is insoluble after successive extraction with petroleum ether and finally ether, the petroleum-ether-insoluble but ether-soluble extract being simply named "ether extract."

The following figures have been obtained from various samples as necessity arose; it will be seen that wide variations occur in many cases. This may be due either to actual differences in the ultimate composition of various samples or to the fact that distinct fractionation cannot be obtained, owing to insolubility in a given solvent being only relative as stated above.

	LINOXYN	ETHER EXTRACT	PETROLEUM-ETHER EXTRACT
Iodine value (Wijs).....	51.5	51.8	58.0
Iodine value (Hübner).....	39.5	41.4	53.9
Iodine value (modified Waller).....	57.8	43.0	46.5
Iodine value (from Br value).....	89.3	89.0	87.1
Iodine substitution (from Br value).....	24.9	11.2	12.5
Saponification value.....	250	262	254
Acid value.....	48.6	30.7	46.9
"Oxidized acids," per cent.....	53.0	56.6	48.5
Fatty acids freed (from above per cent).....	12.9	15.8	13.5
True acetyl value.....	15.3	13.3	23.8

The distribution of the various fractions in average "skins" of oxidized oil is given in the following table:

No.	1	2	3	4	5	6	7
linnoxyn.....	49.57	47.08	43.62	48.41	49.22	57.09	42.46
ether extract.....	31.16	26.79	27.93	29.25	25.45	25.16	32.91
petroleum-ether extract.....	19.27	26.13	26.45	22.21	25.33	17.75	24.63

A wide variation also occurs in the analyses of such oxidized oils to which reference will be made later, the above figures being shown merely to give a general idea of the composition of skins as ordinarily obtained in large scale practice. It will be noted that in Nos. 1 to 6, No. 1 shows the highest proportion of ether extract, but as the advantageous significance of this is somewhat neutralized by the high linnoxyn which would reduce its fusibility to below the favorable limit, it would thus be adjudged equal only to No. 3, taking all three constituents into consideration. No. 6 would be classed as a poor sample. No. 7 is a skin made with specially chosen drier and as seen from its analysis would be adjudged as of excellent quality, and such indeed it proved in practice.

For purposes of comparison the following table gives the extraction analyses of oxidized oils prepared by the Walton "shower bath" process:

No.	1	2	3	4	5	6	7
linnoxyn.....	40.2	32.4	30.0	12.7	1.3	1.3	1.3
ether extract.....	18.1	18.1	20.3	11.1	1.1	1.1	1.1
petroleum ether extract.....	24.7	22.2	18.7	56.3	4.6	4.6	4.6

NOTE: No. 5 represents oil as turned out of the shower bath, the same oil after further treatment in the ovens.

It will be seen from these analyses that, according to the principles I have stated as governing the production of oxidized oils, the "shower bath" products are vastly superior to those obtained by the "boiler" process. The higher ether extracts in the former case need have the very definite effect in the finished cements of increasing the "covering power," as gums absorb fillers, cork, pigment, etc., but the pronounced advantageous difference is to be noted in that most of cements made with the "shower bath" product is capable of being used for the new "Walton" process.

laid." These products, owing to the exigencies of the mechanical treatment involved, necessitate a degree of tenacity and binding power in the cement that is quite unobtainable in the case of those made by the "scrim" process. A later remark will make this point clear.

The impossibility of making inlaid lineoleums with Taylor-Parnacott or Corticine oil is shown by the following extraction analysis:

LINOXYN	ETHER EXTRACT	PETROLEUM-ETHER EXTRACT
60.4	8.4	30.0

This also explains the low covering power of the oil, the proportion of oil to filler being usually 100 : 106 as against 100 : 200 in the Walton cements.

USE OF GUM KAURI

Before proceeding to the description of an investigation I have undertaken in order to determine the influence of the rosin and gum resin on the final product, a word here is necessary as to the particular reason for which gum kauri has been adopted. Walton's original patent for the preparation of cement from oxidized oil specifies the use of gum kauri in conjunction with rosin. It is to be remarked that kauri gum at the present day can be obtained only at a very high cost. The scarcity of the gum is consequent upon the huge drain on the deposits occasioned by the demand for lineoleum manufacture. The constantly increasing price since the '60's is most probably to be attributed to this cause, and at the present time, gum is actually being sold which has been obtained from the screenings or rejected portions of previously "mined" deposits. At the same time it would be unfair to the lineoleum manufacturers to say that no attempt has been made to find a substitute for this gum.

Taking into consideration this question, we have to bear in mind that the gum resin adopted for use in cement making must conform to the following requirements:

(1) The melting or softening point, although not needing to be kept to the low limit of the temperature of "oven setting," should be sufficiently low to allow a homogeneous qualification to be obtained at 100°C., when in presence of a large quantity of an oxidized oil, such as in this case rosin and oxidized oil. Such requirement eliminates the harder fossil resins, such as the Aleppo Gums, etc. At the same time the melting point must be sufficiently high to enable the body of oxidized cement to be cement. This is done the cement was made above in hot water. The latter requirement eliminates the softer gums, such as styracine, myrror, appearing below in the case of the latter.

(2) For the manufacture of lineoleum, or when the ground system is to be "scrim" and "inlaid," the gum must be supplied almost pure, the heat required for working being possible. Asphaltum and the various pitches are thus eliminated.

(3) The stability of resins, in connection with compatibility and stability, is a factor of great importance. Some resins, such as the Aleppo Gums, are unstable, and when used in the cement, they are liable to cause the cement to become brittle.

ATTEMPT TO SUBSTITUTE CHINA WOOD OIL FOR GUM
KAURI

In view of the above considerations, however, a substitute has been patented, the claim to efficacy of which appears somewhat remarkable. I refer to the use of china wood or tung oil. If this oil be held at a temperature of from 180 to 250° C., a sudden polymerization or gelatinization occurs, the center of the solidified mass being very hard and elastic, while the outside portions (which do not so persistently retain their heat during cooling) are possessed of an extraordinary tackiness. Under carefully chosen conditions a balance may be struck as regards the proportion of inner solid portion and outside tacky portion, so that the whole, when mixed through rolls, at first sight would give the impression of being an ideal material for use as a basis of binder for linoleum.

This phenomenon has long been known among oil technologists, but the difficulties of controlling the solidification have more than neutralized the advantages which this oil seemed to offer in the short time necessary for its solidification (on the laboratory scale 100 g. can be solidified at 250° C. in 5 to 8 minutes). Certain other workers, rather more successful in the control of the polymerization process, have made serious attempts to use it as a linoleum material; but the promising tackiness seemed to disappear entirely as soon as amalgamation with filler was made. It occurred to me to investigate this failure to bind, by the extraction method described, and as a result I found my previous postulation of the necessity of high ether extract fully borne out. While I could regulate the amount of "linoxyn" or solvent insoluble portion within the very wide limits of 30 per cent to 92 per cent quite easily when certain principles were borne in mind, the ether extract in no case was higher than 1.1 per cent. A recent German writer has suggested that the tacky portion probably consists of a gel of the insoluble "linoxyn" in unpolymerized oil. While having insufficient evidence to agree entirely with this statement I may mention that the extractable portion possesses no tackiness such as was observed in the case of oxidized linseed oil extracts, being merely a thin greasy oil.

The result of this disqualification of wood oil as the principal basis for linoleum, has, however, not been the means of causing its entire dismissal from the industry and it appears in the patent literature as a substitute for kauri gum. By this I mean to infer that the patentees quote formulas for linoleum in which polymerized wood oil is used in conjunction with ordinary oxidized oil and rosin in the absence of gum.

In view of the wholesale condemnation of such substitute by a German writer I have thought it of interest to investigate this point, using the method of valuation described as my basis of judgment.

It might be imagined at first sight that the additions of rosin and gum kauri to the oxidized linseed oil in the cement pan might be made in order to induce an economy in the final product. Without entering too deeply into a discussion as to how far economies in the materials are borne out in the final product, the

whole question can be easily and finally decided by the statement that a linoleum cement to be cheap must be capable of taking up the maximum amount of filler, as cork or wood fiber, and pigment. Now for a reason which will become apparent when the experiments to be described are discussed, apart from the binding effect of the resins *per se*, they have a very definite influence in advantageously modifying the covering power of the oil with which they are admixed. For effecting such change, in common with all chemical reactions, it must be presumed that a certain amount of solution of the resins in the oil, or *vice versa*, must occur.

Coming now to the consideration of the employment of solidified wood oil in place of the gum kauri, two methods of employment of the same have been suggested. In the first, mere admixture of "cement" with solid wood oil and the usual fillers is made on the rolls. The judgment as to the utility of this is not difficult to arrive at. If the solid wood oil be prepared in the tacky condition, no increase in covering power will result, as I have already pointed out, and in fact the greasy softness of the product will be detrimental to the finished article. A certain amount of diminution of extract of the actual wood oil will naturally take place during the subsequent maturing process, but it is nevertheless considered as a *sine qua non* by experienced manufacturers that to obtain a satisfactory finished cloth the linoleum at the intermediate stage of manufacture must be good, otherwise the cohesion of the individual components will be unsatisfactory. In the second suggested process which forms the subject of a patent specification, the ground solidified wood oil is mixed in along with rosin and oxidized oil in the cement pan and the mixture converted into cement in the ordinary way. It is further claimed that the solid wood oil when admixed with oxidized oil will then run down at the temperature of the cement pan (130 to 150° C.). Now, unless the latter claim is substantiated and some transformation to a soluble or miscible form of the wood oil takes place as suggested, this process differs in no way from the previous. We need not enter into a discussion as to whether an oil polymerized at a minimum temperature of 180° C. can be caused to melt alone at 130 to 150° C.; it merely remains to consider whether the oxidized oil or rosin can have any influence.

The experiments which I shall describe were undertaken among other things to investigate this particular point, but it may be stated that in a series of many other experiments unpublished in this communication, no melting of the solidified wood oil could in any case be observed. In every case the finished cement was examined under a microscope and the individual sharp cornered pieces of the ground wood oil were seen without any difficulty. However, my conclusions were not based entirely on such method of investigation, but as follows:

COMPARISON OF LINOXYN AND "CYCLOLIN"

In the course of some investigations on the nature of the comparatively ether-insoluble body linoxyn and on comparisons between it and the insoluble body

obtained by polymerizing a linseed oil by heat (a body I have provisionally named cyclolin in reference to its supposed ring structure) I found a very definite distinction between the two bodies. The following table gives a preliminary comparison of certain of their more important properties, the one under discussion being left till the last:

	LINOXYN	CYCLOLIN
Appearance, etc.....	Leathery yellow to yellowish brown, solid	Not increased over raw oil
Saponification value...	High (see above)	Difficult to saponify even by alcoholic potash
Saponifiable.....	By 1 per cent aqueous NaOH in the acid	Very stable indeed. Samples kept for 18 mos. not appearing to change
Stability.....	Spontaneously slowly evolves acid volatile products and ultimately liquefies	Nil
Oxidized acids.....	About 50 per cent (see above)	Nil

Pursuing the clue afforded by the continuous solubility of linoxyn in ether, it occurred to me to employ a solvent of higher boiling point in order to accelerate solution. The use of amyl alcohol in this respect was very remarkable. In the case of linoxyn, the substance swelled when heated in this solvent at 120° C. and in 6 to 12 hrs. went entirely into solution. The substance left by evaporation of the amyl alcohol was a viscous tacky oil possessing all the properties of ether extract from oxidized linseed oil. Further investigation is proceeding at present but it may be remarked that neither the saponification nor iodine values were altered by the process of solution.

The cyclolin on the other hand swelled to a certain extent and some slight solution occurred as seen by the yellow coloration in the amyl alcohol. It was heated for 72 hrs. at 120° C., cooled, and the solution decanted off. The residue was washed, again heated up for 24 hrs., decanted off, washed, and in further treatment, even up to another 72 hrs., no further solution occurred even in traces. Thus it was possible to obtain a distinctly insoluble portion from the cyclolin, the amount being roughly 80 per cent of the total. Similar experiments on oxidized oil from other sources and polymerized wood oil showed a general rule to hold that oxidized oils are completely soluble while polymerized (solid) oils contain an insoluble portion.

Such was the method adopted for recognizing and isolating the unchanged polymerized wood oil in cements. In every case in which ground polymerized wood oil was used, its presence could be recognized by the above described treatment on the cement. It remained yet to determine if, in spite of the insolubility of the major part of it, it had an advantageous or other influence on the oxidized oil. Should the conclusion be reached that it was without beneficial influence on the oxidized oil, it would still indirectly affect the cement in that, it being no better than so much filler, the actual covering or binding power of the cement would be decreased by an amount proportional to the solid wood oil present.

The investigation undertaken was as follows:

Comparisons of analyses of cement before and after conversion into cement.

Comparisons of analyses of cement and setting in lime mud before and after maturing, in different compositions consisting of:

	No. 1	2	3	4	5	6	7	8
Extracted oil	85.0	85.0	75.0	85.0	85.0	85.0	85.0	85.0
Linseed oil	15.0	15.0	25.0	15.0	15.0	15.0	15.0	15.0
Solid Wood Oil.....	..	9.5	7	10	..

The particular compositions chosen were those which would be actually practicable from conditions of not only limitations of cost but considerations of working practice.

METHODS OF EXAMINATION

A quantity of the middle portions of a batch of "skins" was chosen having a sufficiently high extract to enable them to melt without the addition of any added resinous flux. A very careful sampling was performed, the sample chosen being then ground to a meal in the manner described and then extracted with petroleum ether for 24 hours in a Soxhlet extractor. The extract was evaporated, the last traces of solvent being driven off in a current of CO₂. The insoluble residue was then freed as far as possible from petroleum ether, and further extracted with ordinary 0.720 methylated ether for 24 hours. The extract was then evaporated and weighed as before. A check determination by extracting with ether in the first instance showed the total extract obtained in the two steps described above to agree with this within very narrow limits. Such analyses appear in the accompanying figures as the "theoretical" or "calculated" values in the case of those compositions containing no added wood oil. In the case of other compositions containing wood oil, i. e., in Nos. 2, 3 and 7, the "theoretical" or "calculated" values represent the analyses of the resin-free mixtures of oxidized linseed oil with polymerized wood oil, as obtained both from separate analyses of these two constituents and by analysis of the mixture.

The "observed" value in the case of compositions containing resins are obtained by deducting the amount of resin mixture added originally, from the petroleum-ether extract and calculating this residue to 100 parts. Thus the treatment of the appended hypothetical composition would be as follows:

	Resin	Oil	Calculated	Observed
Extraction	10.0	90.0	90.0	90.0
Residue	10.0	90.0	90.0	90.0

A long series of experiments had led me to the conclusion that the cement filler, after removal of the surface skin, cannot be to be found cyclolin in the polymerized extract. The combination of two "petroleum-ether" extracts of the oil, using in one portions with the petroleum ether would be set as a further check on both good and bad cases.

The H. concerning the order of gravity of any cement from the method of setting is concerned by the setting method of setting portions of wood to the immediate cement composition from the parts of Fig. 1 and showing the corrected set figure of "theoretical" value. The other cement had been taken for the 100 per cent of Fig. 19.

The H. was compared by method for different figures of cement, and composition, being, however, necessary to show the set and set of wood in the H. from cement.

Fig. V needs little explanation. The testing was performed on unit width on a dynamometer and in any case the values obtained are strictly comparative.

FIGURE I

LINOXYN—It will be observed that in all cases a loss of linoxyn has occurred. The importance of the proportion of this constituent is not great provided that the percentage remains within certain limits. Thus No. 4 cement we should pronounce as being somewhat too soft for very successful working as the effect of such softness would be a disadvantage for

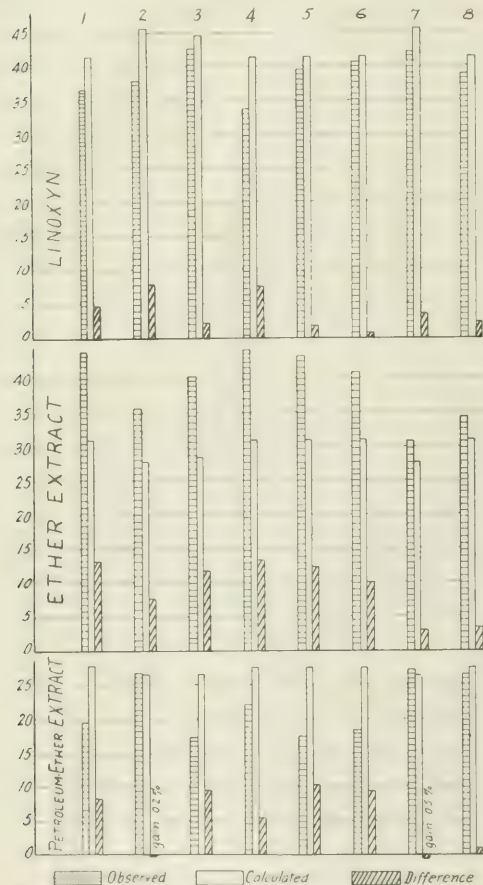


FIG. I.—COMPARISON OF PERCENTAGE COMPOSITION OF OILS EXISTING IN CEMENTS WITH THAT CALCULATED FROM THEORETICAL

manufacture of inlaid linoleum, the rigidity of the inlaid "unit" being affected by the softness.

The disappearance of linoxyn during cementation is an interesting point. The fact that the proportion of linoxyn present influences the "body" of the product shows that some softening occurs during the transformation and again indicates the probability of the reaction not being due to polymerization. The amount of linoxyn present in the cement from con-

sideration of many experiments seems to point to the fact that it is influenced by two distinct reactions. One of these is due to the influence of gum, which, when present, seems to increase the linoxyn at the expense of the petroleum-ether extract. With the exception of cement No. 4 it will be seen that only those compositions containing gum have materially decreased in petroleum-ether extract during the cementing process. The other reaction appears to be an exchange of linoxyn for ether extract during the cementing process, the amount thus exchanged being proportional to the total resin present and the gum kauri having a decidedly stronger effect than the rosin.

Such hypothesis afforded me a clue to a further investigation in which I endeavor to submit analogy with the phenomena mentioned earlier in the communication. I refer to the continuous solubility of linoxyn in certain solvents (ether, acetone, etc.) together with the complete solubility in amyl alcohol and acetate. It will be interesting to mention that other solvents were tried, among them being coal-tar naphtha, turpentine and benzene, and in none of these cases was

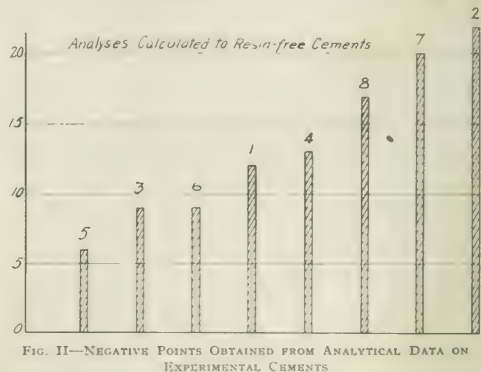


FIG. II.—NEGATIVE POINTS OBTAINED FROM ANALYTICAL DATA ON EXPERIMENTAL CEMENTS

it possible to obtain solution as in the case of amyl alcohol and acetate. A generalization as to the class of compounds which effected solution as distinct from the others, I have hitherto failed in, beyond the general statement that a body to act as a solvent must contain oxygen in its molecule. An experiment in which rosin at a temperature of 120° C. was used showed that it behaved in a manner exactly similar to amyl alcohol and acetate. The mass obtained was perfectly transparent and was soluble to a clear solution in ether, but in petroleum ether showed an insoluble fraction of an oily nature. The two fractions obtained may possibly be identical with "ether extract" and "petroleum-ether extract," which would indicate that the reaction occurring in the cement pan is very far-reaching and complex. A similar experiment with rosin as a solvent and employing polymerized wood oil showed perfect analogy with the other solvents, an insoluble residue being obtained nearly equal in amount to the solid oil originally used. This, I submit, completely confirms my other experiments and shows that solidified wood oil undergoes no transformation during the cementing process. Con-

sideration of the figures will show that this is fully borne out, those cements containing wood oil being decidedly inferior in every way to those containing gum. The direct comparison of gum with wood oil is easily seen by comparing compositions Nos. 6 and 7, although I should like to state that rosin has its own

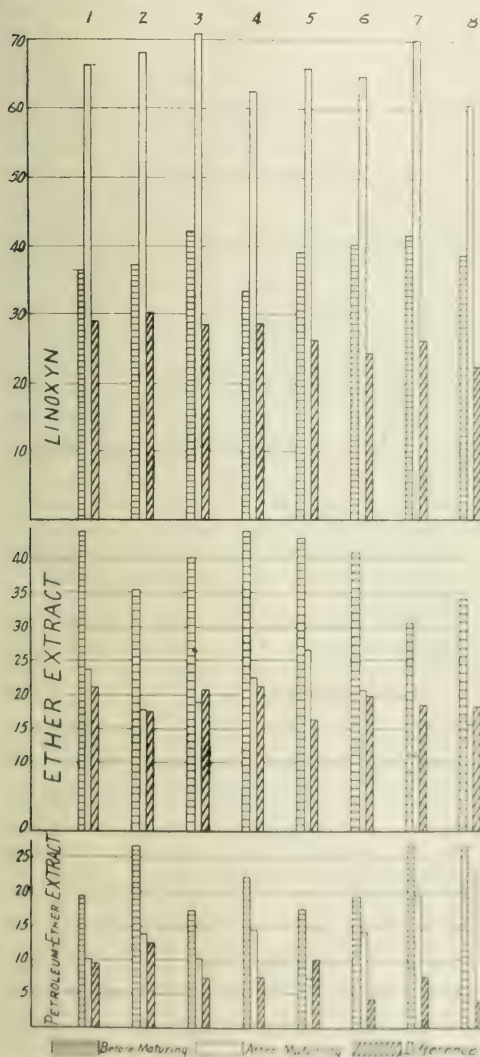


FIG. III. COMPARISON OF PERCENTAGE COMPOSITIONS IN THE LINOLEUM IN CEMENTS BEFORE AND AFTER MATURING IN LINOLEUM.

particular decided function, especially in the form of gum rosin mixture.

A further statement is necessary to the effect that on account of the necessity of experimenting with compositions containing no added gum (Nos. 2 and 3) it was expedient to employ an artificial oil which is

rather higher than would correspond with a good skin, and it may be remarked that the gum vs. wood oil differences would be far more apparent if an oxidized oil with an extract just sufficient to run down had been chosen.

ETHER EXTRACT—The formation of ether extract by means of resins is well demonstrated here, the resin-free compositions 7 and 8 being markedly deficient in this respect. The comparatively small increase (see difference column) in the case of No. 2 is probably accounted for by the wood oil diminishing as it were the concentration of the rosin by its presence.

PETROLEUM-ETHER EXTRACT—Here the effect produced by economy of gum as predicted earlier is well shown. The compositions containing no gum (Nos. 2, 4, 7 and 8) are remarkable in showing a high percentage of the petroleum-ether extract, while Nos. 2 and 7 have actually gained in this constituent during cementing. It should be mentioned that No. 5 is the standard composition used by most linoleum manufacturers.

ETHER III

LINOXYN—It is necessary here to state that this constituent should be high in a matured linoleum, the body or hardness of the product being dependent

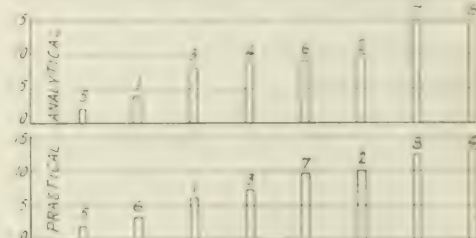


FIG. IV. NUMERICAL FIGURES COMPARED FROM ANALYTICAL TESTS TAKEN WITH THOSE CALCULATED FROM THE MEAN RATIOS OF THE ETHER CONSTITUENTS IN THE CEMENT.

on this. Some of the linoleum, containing a very great degree of resistance to water and has the advantage of being resistant to atmospheric influences and spontaneous decomposition. The wood oil linoleum here shows up rather better on account of the hardened wood oil consisting of about 40 per cent of linoxyn.

ETHER EXTRACT—The quality and amount of the finished linoleum is absolutely dependent on the proportion of this constituent and the loss during maturing should be as little as possible, the loss of linoxyn during maturing should depend as far as possible for its formation on the petroleum-ether extract. It will be seen that the smallest loss occurs in the case of No. 5 which composition also shows the highest proportion. It will also be noticed that the typical good quality wood oil linoleum, No. 1, shows up at a disadvantage in this important case. No. 3 shows up as a disadvantage but less so than the No. 4 "small" composition.

PETROLEUM-ETHER EXTRACT—The table is very important in that it indicates that a high percentage of this constituent will give a comparatively soft body to "cure" but not so at very considerable figures. The standard good quality linoleum, No. 5, shows up

pears first in this table while the typical wood oil rosin linoleum, No. 2, appears distinctly inferior to it. Looking at 7 and 8, the failure here appears to be not so much wood oil as absence of resins.

FIG. IV.—The comparison of agreement between the analytical data and the practical tests in these tables cannot, it must be remembered, be quite perfect owing to the fact that the former takes no cognizance of the properties intrinsically conferred on the linoleums by the physical properties of the non-oily constituents of the cements. Taking into account my previous statements as to the advantages accruing from the presence of the gum itself (within certain definite limits, No. 5 composition being considered the ideal mixture) any tendencies to show the gum cements as favorable in the upper table ought to be amplified in the lower table.

FIG. V.—It will be seen that generally speaking the

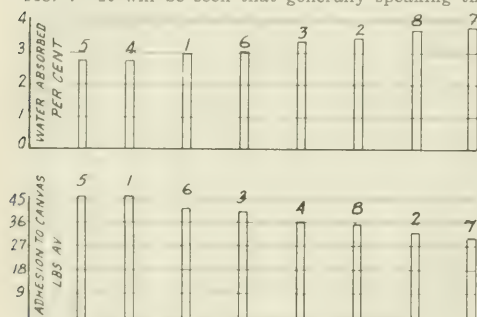


FIG. V.—TESTS OF EXPERIMENTAL LINOLEUMS

more resinous linoleums are less porous (and thus more resistant to disintegration by damp) than the others, the standard No. 5 linoleum being the best in this respect. The impermeability of No. 4 is explained by the fact that the low melting point rosin has been brought to the surface by the hot rolling treatment to which the cloth was subjected. Indeed on rubbing lightly with the hands, the presence of a sticky coating was made apparent.

The adhesion to canvas is an important consideration, separation of canvas and body, especially in the case of "granular inlays" linoleum, being more common than is generally supposed when the cloth is laid on a floor which has a tendency to dampness. Lack of adhesion is due to both absence of gum and a low "ether extract" and the table bears out well the superiority of linoleums containing gum.

The general conclusions to be derived from these analytical data are therefore summarized as follows:

(1) The presence of resins to a full 20 per cent of the cement is essential to obtaining the maximum transformation of the oily matter during cementing to a material with high binding power.

(2) The said transformation is too far-reaching if the oily resin present is rosin, in that the body (as measured by linoxyn) is liable to diminish to below the limit fixed by working conditions.

(3) The presence of gum is essential to secure the diminution in greasiness (petroleum-ether extract).

(4) The chemical influence of wood oil on the cement pan transformation is nil, the apparent disadvantages from its presence being merely made up of the diminution of action taking place, owing to the smaller amount (lower concentration) of oxidized oil present.

(5) The best balance of oil-gum-rosin is in the proportion of roughly 80 : 10 : 10, no advantage being obtained by diminishing rosin and consequently increasing the cost.

These conclusions apply merely to the chemical properties, the general physical qualities of the various compositions being further influenced according to the particular non-oily matter present. The concluding test to which the several linoleums have been subjected was that of actual wear under standard conditions. It may be remarked that in order to get strictly comparative results of such wearing tests a good deal of difficulty is experienced in according equal conditions to all of the several products examined. The best method is to map out a ground plan carefully, and to subdivide the pieces into many units, repeating individual samples two, three or even more times. After a period depending on the heaviness of the traffic, a careful examination is made and comparisons noted between each particular piece and the one immediately adjacent. By a process of classification the result of observation in the form of "A in better condition than B, B in better condition than C, etc.," and collating together duplicates, a résumé can be arrived at which shows the relative order of resistance to wearing. It may be stated that in these particular tests another series of samples was arranged on stairs attached to a building out of doors. These latter tests yielded more marked results than the indoor tests.

The results appear in the following order, the linoleum showing the highest resistance being placed first:

1st	2nd	3rd	4th	5th	6th
No. 5	Nos. 1 & 6	No. 3	No. 4	No. 2	Nos. 7 & 8

Apart from the foregone conclusion showing the necessity for the presence of gum in linoleum, the result is interesting in that it shows that the standard composition No. 5, consisting of a cement made with 10 per cent each rosin and gum kauri to be the best, in spite of the fact that Nos. 1 and 6 are made with more expensive materials, *i. e.*, the cheaper constituent rosin is highest in the case of No. 5.

It being beyond the purposes of this communication to deal with a description of the mechanical processes involved in the manufacture of linoleum, I think it however necessary to qualify my previous statement as to the necessity for employment of gum-rosin cements from "shower bath" oxidized oil in the new Walton inlays. These products will be familiar to all as the inlaid or "solid right through to the back" linoleums which have as their distinguishing feature a sharpness of outline of the individual figures or units. I exclude, however, under this denomination, imitations of parquet flooring which are made by stamping the figures out of a sheet, reuniting them by hand on a table and consolidating a new sheet under a hydraulic

The calculated elementary analyses of these bodies when oxidized according to the hypothesis would be

	(a)	(b)	(c)	(d)	(e)	(f)	(g)	(h)	(i)	(j)
C	77.4	74.8	72.5	70.3	72.5	68.1	64.3	70.3	66.1	68.1
H	11.7	11.2	10.6	10.0	10.6	9.6	8.6	10.0	9.1	9.6
O	10.9	14.0	16.9	19.7	16.9	22.3	27.1	19.7	25.6	22.3

On comparing these figures with those agreeing the more nearly with those obtained and having chosen these, appending the approximate iodine values of "theoretical" and "found" together with the oxidized acids theoretically yielded with that found actually, we have, assuming the maximum yield of oxidized acids from an unsaturated chain to be 61 per cent:

		2	2	4	6
		6	6	6	6
THEORY					
C	72.5	68.1	66.1	64.3	
H	10.6	9.6	9.1	8.6	
O	16.9	22.3	25.6	27.1	
Iodine value	80.8	76.0	73.7	71.6	
Oxidized acids	20%	40%	61%	61%	
FOUND					
Petroleum-Ether Extract					
"Soluble"	73.00	68.74	65.97	63.35	
"Insoluble"	10.45	9.65	9.50	8.75	
Iodine value	16.55	21.61	25.53	27.90	
Oxyacids	85	79	58	52	
	17%	38%	52%	57%	

The iodine value comparison I consider to be of little value as obscure reactions probably occur on such complex molecules. This is borne out by the lack of agreement in values obtained by the use of different methods (see above).

That on taking another oxidized oil, fractionating by extraction, and performing elementary analyses of the fractions, slightly different results would be obtained is highly probable; in fact it is likely that the suggested formulas submitted as approximating to the theoretical glycerides are mixtures of which the most that one can say is that one particular member is distinguished by preponderating in linolenic as distinguished from oleic acid glyceride. Common sense would support the view that the insoluble fraction linoxyn is likely to preponderate in linolenic while inferior or semi-drying oils yield relatively large proportions of the less oxygenated fractions.

The transformation of one fraction into another as shown in the experiments merely presupposes partial exchange of acidic groups, a phenomenon already suggested in the case of polymerization at high temperatures by Morrell.¹

DUNDRE, ROSEFIELD ROAD
STAINES, ENGLAND

THE REMOVAL OF BARIUM FROM BRINES USED IN THE MANUFACTURE OF SALT

By W. W. SKINNER AND W. F. BAUGHMAN

Received October 18, 1916

The impurities which are found in rock salt and in natural and artificial brines are many, but for the most part are not substances of such a markedly deleterious character from a food standpoint that they are to be regarded as seriously objectionable if, in the manufacture of salt, small quantities of them are permitted to remain in the finished product. This is not true, however, of the salts of barium which occur in certain brines in notable amounts, as, for instance, in the brines from the Ohio Valley District of West Virginia and Ohio, also known as the Kanawha District.

That the Ohio Valley brines contain barium has been known for many years. Hunt in his "Chemical and Geological Essays"² says, quoting Leney, that the presence of barium salts is a constant characteristic of the

Allegheny River brines and Dr. Stieren in the *American Journal of Science*¹ gives the analysis of a brine from Tarentum, Pennsylvania, which contained 0.00612 part of barium chloride, 0.00378 part barium carbonate, 0.00959 part strontium chloride, and 8.586 parts calcium chloride in 1000 parts of brine. Dr. Robert Peter reports in the Kentucky Geological Survey² for 1878 the analysis of a brine from Clay County, Kentucky, which was found to contain 23 grains of barium chloride per wine gallon, equivalent to 0.393 part per 1000.

While it has not attracted much attention, the poisoning of animals by salt has frequently been noted and reported. Howard in 1889³ reported the examination of a sample of salt which was supposed to have caused the death of mules and which was found to contain a considerable quantity (per cent not given) of barium chloride. The same year he reported the poisoning of two horses, arsenic being suspected. An examination of the viscera showed no arsenic, but a quantity of sodium salts, and the precipitant for the calcium group gave an especially marked reaction (possibly barium). Several cases of poisoning of stock were reported from Kentucky.⁴ No poison could be found in the samples of salt examined. Two cases of fatal poisoning of horses and cattle from salt have come to the attention of the authors, the trouble being due undoubtedly to the presence of barium chloride in the impure salts fed to the animals. This salt was produced in the Ohio River District.

In 1913 a number of dairy cows in Cincinnati were killed, death being attributed to the use of salt in the ration. Upon examination it was found that the salt used contained a considerable amount of barium chloride. The salt was produced by a salt works in the Ohio River Salt District.

OBJECT OF THE INVESTIGATION

Owing to the meager information available, it seemed necessary and desirable to investigate the character of the brines of the Ohio Valley to determine: (1) their normal constituents, especially their content of barium; (2) the efficiency of the elimination of barium by the methods now employed in the manufacture of salt; (3) the normal amount of barium chloride to be expected in the several grades of salt manufactured from these brines, and if, by ignorant or careless methods of manufacture, an excessive amount of barium was likely to occur in the salt; also to study briefly the methods of production with the idea of suggesting, if possible, either some modification of the present process or the development of some new method of treatment by which the barium chloride could be entirely removed from the brine or reduced to such a small amount that the salt obtained, especially those grades known as No. 1 "Fine," "Common Fine" and "Table and Dairy," which enter so largely into products used for human food, or of grades of salt which might be substituted for them, should contain at most only traces of barium.

¹ Vol. 34 (1862), 86.

² Chem. Rept., [1] 4, 2nd series, 52.

³ West Virginia Station, Bull. 103.

⁴ Kentucky Station Report, 1892, 20.

¹ J. Soc. Chem. Ind., 1915, Feb. 15th.

² 4th Ed., 1891, p. 121.

SOURCE OF THE BRINE

The Ohio River or Kanawha Salt District is composed at the present time of Kanawha and Mason Counties, West Virginia, and Meigs County, Ohio, all of the producing salt works being located in these three counties. Formerly, the district was much more extensive than it is at present; according to report, there were at one time about 30 works in operation. However, the natural advantages in the production of salt in the Michigan District and the Northern Ohio District are such that the Ohio River salt makers cannot successfully compete unless peculiarly well located regarding fuel supply, etc., the result being that salt making in the latter district has declined until in 1914 but 5 works were in operation. The industry, however, has recently shown signs of recuperation. One old works has been re-established and a practically new and extensive plant has been erected on the site of an abandoned property at Mason City, West Virginia. From data gathered directly from the producers, the production of salt in this district in 1915 is estimated at approximately 500,000 barrels.

The salt in the Ohio River District is produced from natural brines obtained from bored wells. Originally, the wells were from 450 to 1000 ft. deep and yielded a rather weak brine. When it was discovered that brine of a higher degree of salinity could be had at lower levels, deeper wells were bored. Most of the newer wells are about 1100 to 1300 ft.; one well, however, was reported to be about 1600 ft. The salinity of the brines directly from the wells varies from about $8\frac{1}{2}$ to 10° Bé. at 20° C., and when first pumped is clear if an ordinary valve pump is used. When, as in one case, an air lift is used, the brine is cloudy, due to the decomposition of the ferrous bicarbonate present.

To determine the character of the brines, several representative samples were collected and analyzed, the results appearing in Table I. For purposes of comparison there has been included in the table an

analyses which is of particular interest in the consideration of the treatment of the brine for the removal of the barium is the content of ferrous bicarbonate, the importance of which will be discussed later.

TECHNOLOGY OF SALT PRODUCTION

A brief description of the technology of the production of salt in the Kanawha District seems desirable to a proper understanding of the application of the method and an interpretation of the results of the treatment of the brine for the removal of barium. No attempt will be made to give in detail the complete treatment of the brine for the production of salt and the separation and recovery of the several valuable by-products. As previously stated, the brines are natural and pumped from deep wells. In most cases it is practically pumped directly from the wells to the evaporators; in one or two cases a small amount of storage for the brine is provided. However, in the largest works in the district, storage capacity was provided for only about one-fourth of the daily capacity of the plant.

All of the salt in this district is produced by the steam-heated or direct-fired pan or evaporator and the grainer system. The kettle process, formerly largely employed in this district, has been entirely abandoned and the vacuum pan has not been introduced because, as claimed by the most experienced manufacturers, the corrosive action of the concentrated brine and the bittorn or mother liquor is so great as to make the use of the vacuum pan impracticable. In the evaporator, the brine is boiled and the steam later utilized for further concentration of the brine in the settlers and grainers. The salt is removed from the grainers either by manual labor, shovels being used to remove the accumulated salt on the bottom of the grainer to draining racks immediately above the same, or, as in two instances, by a mechanical scraper and conveyor belts. The brine is usually drawn directly into the evaporator, heated to boiling, and concentrated to about 50° Bé. and then

TABLE I ANALYSES* OF BRINES FROM THE OHIO RIVER DISTRICT

LAB. No.	WORKS	LOCATION	DESCRIPTION	SP. GRAV. 20° C.	NaCl, %	Ca, %	Mg, %	Fe, %	SO ₄ , %	CO ₂ , %	SiO ₂ , %	Other, %	Total, %
16078	A	Malden, W. Va.	Direct from well	1.036	61.24	0.16	0.46	0.01	0.01	0.01	0.01	0.01	61.89
16081	D	Hartford, W. Va.	Direct from well	1.036	61.24	0.16	0.46	0.01	0.01	0.01	0.01	0.01	61.89
16080	B	Pomeroy, O.	Direct from well	1.0746	80.11	13.54	0.36	0.01	0.01	0.01	0.01	0.01	103.49
W. L. 8	R	Pomeroy, O.	Direct from well	1.0361	61.24	0.16	0.46	0.01	0.01	0.01	0.01	0.01	61.89
W. L. 7	C	Pomeroy, O.	Direct from well	1.0361	61.24	0.16	0.46	0.01	0.01	0.01	0.01	0.01	61.89
W. L. 9	F	Pomeroy, O.	From brine tank	1.0361	61.24	0.16	0.46	0.01	0.01	0.01	0.01	0.01	61.89
(a)		Pomeroy brine		1.036	61.24	0.16	0.46	0.01	0.01	0.01	0.01	0.01	61.89
(b)		Malden brine		1.036	61.24	0.16	0.46	0.01	0.01	0.01	0.01	0.01	61.89

* Small amounts of iodine, bromine, silica, lithium and arsenic.

* * Potassium not separated, included with NaCl.

a) Analysis by Prof. C. W. Foulke, Ohio State Univ. Chem. Lab., Columbus, Ohio.

b) Analysis by C. D. Howard, W. Va. Expt. Sta., No. 103.

analysis of a Pomeroy, Ohio, brine made by Professor C. W. Foulke, and an analysis of brine from Malden, West Virginia, made by Professor C. D. Howard. It will be noted that the Malden brine contains about twice as much barium chloride as the brine from the vicinity of Pomeroy which is the center of the salt production district on the Ohio River. It is to be noted also that the barium chloride is the case of the Malden brine is equivalent to about one-eighth of the sodium chloride and a little less than a per cent of the total salt in solution. The composition of the

brine from the evaporator. When the brine from the well is pumped through the well and then into the settling tanks about 100 ft. above the evaporator, it is usually, although when the brine is very high in iron, it is pumped directly into the evaporator. The brine is then pumped into the evaporator, where it is heated to boiling and concentrated to about 50° Bé. and then

exists in the brines pumped from the wells as ferrous bicarbonate which is broken down in boiling and is partly removed by the filters, a further amount being precipitated in the settler. The brine from which the greater portion of the iron has been removed is concentrated to from 20 to 21° Bé. at a temperature of about 170° F. and run into what is known as the "draw settler" where just a little of the salt is allowed to crystallize out and in so doing removes with it the last visible trace of iron in suspension. The clear brine with a pale straw color is then drawn off to the crystallizing tanks technically known as "grainers," where it is evaporated by a system of copper steam pipes as in the settling tanks.

The first crop of salt is obtained at about 23° to 24° Bé. at a temperature of from 175 to 180° F. maintained in the grainer. As the salt is removed and the volume of the brine reduced by evaporation, more brine is run into the grainers, which is continued until the gravity is increased to about 30° Bé., the concentration at which it is considered advisable in the best salt works practice to discontinue the production of No. 1 salt, although some producers run up to 32° Bé.,

while off-grade salt comes from the others. The course of the brine in the works may be briefly summarized as follows: Well, storage tanks, preheater, evaporator, collecting well, filters, mud settler, draw settler, No. 1 salt grainers, No. 2 salt grainer, bittern concentrator, bromine works, calcium chloride works.

With either of the above systems of salt making, one would expect that as the degree Baumé increased, the yield of salt would be proportionately more impure, but from the analysis of the samples obtained from the grainers of different concentration, there appears to be very little increase in the amount of impurities, at least of barium chloride, until the concentration reaches about 30° Bé., provided the temperature in the grainers is maintained and salt of uniform grain is produced. In the best works, therefore, it has been the practice to use only brine under 30° Bé. for the production of No. 1 or table and dairy salt.

As the object of the preliminary work was to determine the character of the salt produced and the impurities which it contained rather than a technical study of the production of salt, only such samples of

TABLE II—ANALYSES SHOWING COMPOSITION OF SALT OBTAINED FROM UNTREATED OHIO RIVER VALLEY BRINES

Lab No.	WORKS	SALT	GRADE	SOURCE	Per cent Moisture	PERCENTAGES ON WATER-FREE BASIS				
						CaCl ₂	MgCl ₂	NaCl	NaCl	NaCl
16086	A	No. 1	Course	Warehouse	4.07	1.22	0.39	...	0.20	98.19
16087				Warehouse	3.32	0.89	0.27	...	0.03	98.81
16088				Warehouse	2.30	0.74	0.07	...	0.30	96.69
16089				Table and Dairy	6.05	2.05	0.74	...	0.09	97.12
16090				Table and Dairy	10.17	2.22	0.70	0.09	0.09	96.90
16091	B	No. 1	Table and Dairy	Draining board of No. 1 Grainer	11.45	2.32	0.78	0.07	0.08	96.75
16092				Draining board of No. 2 Grainer	6.40	2.71	0.82	0.07	0.23	96.17
16093				Draining board of No. 3 Grainer	10.41	1.86	0.78	...	0.04	97.32
16094				Grainer	7.35	1.63	0.70	...	0.04	97.63
16095				Warehouse	2.26	0.56	0.24	...	0.01	99.31
11232 K	C	No. 1	Table and Dairy	Market	1.97	0.51	0.11	...	0.03	98.24
16097				Warehouse	9.76	2.19	0.98	0.09	0.06	96.68
16098				No. 3 Grainer	8.55	2.02	0.86	...	0.05	96.97
W. L. A				Warehouse	8.33	1.85	0.76	...	0.02	97.42
21416				Grainer	5.23	0.78	0.31	...	0.02	98.89
16101	D	No. 1	Table and Dairy	Market	6.64	1.27	0.54	...	0.04	98.34
18242-L				Warehouse	6.88	2.17	0.91	...	0.05	96.86
W. L. 156				No. 4 Bin	11.64	1.95	0.81	...	0.05	97.18
W. L. 157				No. 1 Grainer	19.71	1.86	0.79	...	0.04	97.29
W. L. 158				No. 3 Grainer	20.38	2.10	0.88	...	0.05	96.94
W. L. 159	E	No. 1	Table and Dairy	No. 5 Grainer	11.90	3.38	1.40	...	0.13	95.06
W. L. 160				Market	3.69	0.51	0.22	...	0.01	99.27
18225-L				Warehouse	10.57	3.38	0.94	1.19	5.17	89.25
16093				No. 7 Grainer	6.33	2.32	1.02	0.37	1.46	94.92
16096				Warehouse	11.32	4.22	1.96	0.11	0.95	92.65
21417	F	No. 2	Table and Dairy	Warehouse	12.55	5.54	2.60	0.16	1.15	90.51
16099				Warehouse	7.35	2.58	1.10	0.09	1.18	95.04
16100				Shed salt from conc. bittern tank	5.49	16.48	7.12	0.69	5.47	70.23
16102				Warehouse	5.66	3.68	1.13	1.46	1.02	92.70
W. L. 155				Warehouse	19.98	4.31	1.99	0.31	10.75	82.67
(a)	G	Cattle Salt	Off	Warehouse	...	1.86	1.42	...	16.18	80.54
(a)				Agricultural Salt	...	3.44	1.11	...	18.52	76.93

(a) Analysis by C. D. Howard, W. Va. Bull. 108, p. 291.

and possibly more. From the grainers in which the No. 1 or Table and Dairy salt is made, the brine, when it has reached 28 to 30° Bé., is drawn off to the "bitter water grainer" in which the No. 2 or "off-grade" salt is made and in which the concentration is carried to 38 to 40° Bé. The bittern is then drawn off to the by-products works and further treated for the recovery of bromine, calcium and magnesium chlorides.

In some cases instead of filling each grainer with fresh brine as the volume is reduced, the brine is run from No. 1 grainer to No. 2, then to Nos. 3, 4, 5, 6, 7, as the case may be, throughout the system, the new or least impure brine being always introduced at the No. 1 grainer. The concentration of the brine gradually rises in each grainer as the impurities increase, the No. 1 table and dairy grade salt being obtained generally only from grainers 1, 2, 3 and 4,

brine and salt were obtained as it was considered would afford data of value upon this particular phase of the question.

Samples of salt were collected representing the product of the five plants in operation at the time, and were taken from the salt stored in bulk in the warehouses, where possible, as such samples represent the mixed salt from the several grainers and are representative of the product as placed on the market. Samples were also obtained in the works either directly from the grainers or from the draining boards and bins. Samples of both the No. 1, "Table and Dairy" grade and the No. 2, "Off" grade salts were obtained. Table II gives the results of the analysis of the several samples. There have also been included for comparison the analyses of two samples of off-grade salt reported by Howard.

It will be noted that the content of barium chloride

in the 22 samples of No. 1 salt varied from 0.02 to 0.23 per cent expressed on the dry basis. Four of these samples, Nos. 16087, 16095, 16097, and W. L. 156, taken from the warehouses of four different salt works may be taken to represent fairly the character of the high-grade table and dairy salt, well drained and ready to be barreled. The barium chloride content of these four samples is 0.03, 0.04, 0.03 and 0.05 per cent, respectively. The samples taken from the draining boards and bins, or when recently removed to the warehouse, show a higher content of barium chloride than does the finished product, because the mother liquor which contains the impurities has not sufficiently drained off. Salt requires a storage of from 10 to 15 days to be properly cured. In the state of New York, a storage of 14 days is required by law.

By reference to the table it will be observed that the barium chloride content of the off-grade salt, including the two samples quoted from Howard, varies from 1.02 to 18.52 per cent. The largest amount found by the authors was 10.75 per cent. The off-grade, or No. 2 salt, constitutes from 7 to 10 or 12 per cent of the total salt produced by a works, the quantity depending upon the concentration at which the brine is drawn to the bitter water grainer and to which it is concentrated before backing off the mother liquor to the bromine works.

The No. 2 or off-grade salt is not sold for table or dairy purposes or for packing meat, but is used largely in the manufacture of ice, salting of hides, glazing and agricultural purposes, and in recent years has been quite generally labeled "*Nor for food purposes*" or "*Do not feed to stock*," or in some other manner to indicate that it is not intended for food. The demand for this low-grade salt, however, is quite limited. Consequently, there is a great temptation to utilize it by substitution for, or mixing with a higher grade salt or by "melting" it in the settlers in order to bring the brine more rapidly to the saturation point. Where this is done, of course, the impurities in the brine in the grainers from which the table and dairy grade salt is obtained are greatly increased and No. 1 salt produced from a brine so fortified will invariably show a high content of barium chloride. It is also a great temptation for the works manager to run up the concentration in the first grainers as high as he dare in order to increase the yield of No. 1 salt and decrease the yield of No. 2 or off-grade salt, resulting in an increase of impurities, including barium chloride, in the No. 1 salt. Furthermore, the No. 2 salt is frequently almost as white and as fine a grain as the No. 1 salt, and although it may be labeled or invoiced when shipped in bulk "*Nor for food purposes*," it is a great temptation to the unsupervised jobber, or a dealer ignorant of the nature of deleterious matter, to substitute the inferior and unsound for the better grade and, of course, higher priced salt. The problem, therefore, was one of removing the barium from the brine before it is drawn into the grainers for crystallizing out the salt. This is possible by eliminating it completely from any of the treated brines, provided a method of treatment could be de-

veloped within the narrow margin of profit of salt making; in other words, producing a greater yield of No. 1 salt for a given quantity of brine, since if the barium were removed the concentration of the hot brine could be raised considerably above the 28° or 30° Bé. found to be the limit for the production of a high-grade salt by the technique of salt manufacture as heretofore employed.

METHOD OF TREATMENT

The removal of the barium as sulfate was considered as probably the most practicable method of treatment, primarily because of the insolubility of the compound and also because sodium sulfate, commercially known as salt cake, which it was thought could be used, is one of the cheapest of the heavy chemicals, a by-product of several industries, being quoted in 1915 at \$12 per ton delivered at points in southern Ohio. It can be obtained in bulk and in granulated form, therefore easy of solution, and may be had free from any significant impurities.

The critical points in a method attempting to remove the barium as sulfate were considered to be:

(1) The practically complete removal of the precipitated barium sulfate formed before the salt crystallized out of the brine; otherwise any suspended barium sulfate would be carried down with the salt.

(2) While adding sufficient sulfate for this purpose, the formation of any calcium sulfate should be avoided, or at least if formed, the amount should be kept within the solubility of calcium sulfate in the brine and bittern, thus preventing the formation of scale, which, because of its insulating effect, would seriously interfere with the efficiency of the whole works, since for the most part thin copper pipe of large diameter is used throughout the evaporation system, the cleaning of which from any accumulated scale, it was thought, would be a laborious and costly undertaking.

(3) The cost of treatment must be low, since the margin of profit in the manufacture of salt is so small that unless the cost of treatment were very low or offset by an increased value of the product, the method would be impracticable.

(4) The application of the method of treatment must not interfere with the present general plan of operation and management, which has been found by experience to be suited to the production of salt in this district.

The first condition was deemed the primary, because the method by which the brine is treated is the basis of the management of the works largely depends.

From some preliminary experiments, and on the recommendation of barium as sulfate from the report made by some salterns in 1910, it was learned that in treating the brine of the salt works and in concentrating the same to about one-third of its original volume in order to the evaporating, only about 1/10 of the salt in the brine could be removed, when an excess of salt was added which was chemically equivalent to the sodium present in the brine. It was pointed out, however, that an excess of sodium carbonate was added, but it was suggested that

the excess must be kept within the limit of solubility of calcium sulfate in the complex bitter water solution of the last grainers in order to prevent calcium sulfate scale formation. To determine the effect of adding the precipitant in excess, the following experiment was performed:

To one 500 cc. portion of the original cold brine was added sodium sulfate just equivalent to the barium present, and to succeeding 500 cc. portions was added an excess of sodium sulfate amounting to 15, 30, 45, 60 and 75 per cent, respectively; the solutions, after standing from 3 to 4 hours, were boiled and evaporated to one-third their original volume, thus simulating the process in the works. The brines, as before noted, contain very considerable quantities of ferrous bicarbonate, averaging about 100 mg. per liter. The presence of the iron as bicarbonate and in large amount is a fortunate circumstance, since it may be broken down either by aeration or boiling, yielding a "flock" which materially aids in the rapid deposition of the barium sulfate formed. It was also found that the precipitated barium sulfate had a mutually beneficial action on the rapid deposition of the iron which will be referred to further under the application of the method. The results appear in Table III, and are shown graphically in Fig. I.

TABLE III. PRECIPITATION OF BARIUM FROM BRINE WITH SODIUM SULFATE

Mr. Barium. in 500 cc. of original brine.	Na ₂ SO ₄ Wt. Mr.	Added Per cent excess	Mr. Ba left in solution	Barium precipitated as BaSO ₄	
				Direct det'n Mg.	By difference Mg. Per cent
122	126.1	0	22.3	101.9	99.9 81.9
122	145.0	15	12.3	110.5	109.7 89.9
122	163.9	30	7.7	111.4	114.3 93.7
122	182.8	45	4.9	113.8	117.1 96.0
122	201.8	60	2.8	118.6	119.2 97.7
122	220.7	75	2.4	118.6	119.6 98.0

The requisite amount of sodium sulfate to add to remove the maximum amount of barium and at the same

time to produce the minimum amount of scale, could only be approximated, because of a lack of reliable data regarding the solubility of calcium sulfate in the complex bittern composed of chlorides, bromides, and iodides of sodium, potassium, magnesium, strontium, calcium and iron at the varying temperatures of the solutions while in the bitter water grainer, and while consideration was given to the determination of such data, it was finally abandoned as being probably unprofitable, since its value would depend upon accurate volume determinations of the bittern which, it was found, would be exceedingly difficult

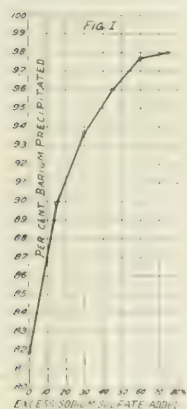
to obtain. An approximation of the requisite amount of sulfate to add could be made, however, by determining the amount of barium remaining in the salt by the old process of manufacture. A representative sample of bitter water was found by analysis to contain 2164 mg. of barium per liter. As the quantity of bittern at this time was approximately 3,000 gals.

per day, this was equivalent to 54.2 lbs. of barium which is carried on through and removed in the bittern. The original brine contained per liter 241.6 mg. of barium which, based on a consumption of 158,000 gallons per day, gives approximately 319 lbs. The difference, 265 lbs., is, therefore, the amount of barium which has remained in the salt and represents approximately 83 per cent of the total barium in the original brine. It was evident, therefore, that the treatment to be efficient must remove approximately this amount.

It was surmised that the efficiency of the treatment in the plant would be less than shown by experiments in the laboratory and therefore it would be advisable to add an amount of sodium sulfate which would remove about 90 per cent of the barium. From the table it will be noted that a 30 per cent excess gave a precipitation efficiency of 93.7 per cent. It was decided, therefore, to use this amount in the experimental application in the plant. From the table it will be noted further that, theoretically, it required 126.1 mg. of sodium sulfate per 500 cc. of brine to precipitate the barium, and that a 30 per cent excess required 163.9 mg. of sodium sulfate, a difference of approximately 76 mg. per liter. It was estimated that brine which flows from the salt grainer to the bitter water grainers represents a concentration of about 15 to 1. It is apparent from the above, therefore, that the excess of sulfate in a liter of brine drawn into the bitter water grainer is equivalent to 770 mg. of SO₄, which is equivalent to 1.091 g. of calcium sulfate per liter, an amount which it was anticipated would form some scale. To determine if calcium sulfate scale was likely to be formed in the No. 1 salt grainers and to what extent in the bitter water grainers from using a 30 per cent excess of sodium sulfate and also to study the character of the barium sulfate and iron hydroxide deposited in the evaporators by the proposed treatment, a small improvised salt works was constructed and operated in the laboratory. The salt produced was of a high grade and after a run of about 10 days, no scale could be observed in the grainer, while the precipitated barium sulfate and iron hydroxide, most of which was kept in suspension by the boiling, was almost completely removed when the brine was drawn off, the small amount of deposit formed being quite soft, having very little the character of scale.

APPLICATION OF THE METHOD FACTORY TEST

The preliminary experimental work and the calculations regarding the cost of treatment were such as to lead to the conclusion that a method of treatment using salt cake was both practicable and profitable. The manager of one of the large salt works having become thoroughly interested in the matter, kindly offered to furnish the necessary equipment and place his works at our disposal for a factory test to determine if the method could be applied in such a manner as to remove the barium without seriously interfering with the production of salt or of the profitable by-products from the concentrated mother liquors or "bitterns." Accordingly there was installed the neces-



sary solution and dosing tanks, dosing device and meter for the daily treatment of 200,000 gals. of brine, the maximum capacity of the plant. The test continued for a period of about 7 days, the estimated output of the plant for the period being from 375 to 400 bbls. of salt of all grades per day.

The brine as it flowed from the two wells contained, respectively, 243.7 and 239.6 or an average of 241.6 mg. of barium (Ba) per liter. The laboratory experiments had shown that by adding an amount of sodium sulfate equivalent to the barium content of the brine it was possible to remove only 82.0 per cent of the barium and that a 30 per cent excess removed approximately 93.7 per cent: 241.6 mg. of barium are equivalent to 250 mg. sodium sulfate, or 0.002086 lb. sodium sulfate per gal. of brine. Using a 30 per cent excess, one gallon of brine required 0.00271 lb. of sodium sulfate.

A meter placed on the outflow pipe of the brine supply tank showed that 158,000 gals. of brine was the daily consumption of the plant at the time. The cocks were, therefore, set so that exactly the above amount of brine would flow to the evaporators every 24 hours during the 7 days. Using 30 per cent more sodium sulfate than the amount equivalent to the barium present in the brine required 428 lbs. sodium sulfate for a 24-hour treatment. The sodium sulfate employed in the experimental work was ordinary salt cake of commerce such as is used in glass making, etc., and sells for 55 to 65¢ per 100 lbs. The salt cake used was found upon analysis to have the following percentage composition:

NaCl	NaHSO ₄	CaSO ₄	Fe ₂ (SO ₄) ₃	Moisture	Insoluble	Na ₂ SO ₄ , Pb & As
0.28	1.93	0.78	0.30	0.21	0.10	98.69. None.

The absence of lead and arsenic is important since they are impurities which may be anticipated in salt cake and which it would be highly undesirable to introduce into the salt.

The requisite amount of sodium sulfate for the treatment of one day's supply of brine was dissolved in condenser water, which was used instead of river water because an ample supply was available, it being used as feed water for the boilers. The fresh brine could not be used for making the solution of sodium sulfate because the brine contains approximately 14.5 g. of calcium chloride per liter and a precipitate of calcium sulfate would result. It was also found necessary to neutralize the acidity of the salt cake, the 428 lbs. requiring theoretically about 4 lbs. of calcium oxide; 5 lbs. of good burnt lime were used as its equivalent of hydrate.

In order to obtain full advantage of the effect of iron hydroxide resulting from the decomposition of the ferrous bicarbonate naturally present in the brine in a large amount, it was found advisable to add the sodium sulfate as early as possible in the process and before the brine was heated.

It was decided, therefore, to dose the brine at the point where it was drawn from the storage tanks into the first preheater. Here the content of barium in a given volume of brine is constant, which is not the case later in the process, the concentration in the brine

at a given point varying from time to time. This is a matter of vital importance in the addition of just the right amount of precipitant to remove the barium and yet not a sufficient excess to produce scale.

To check the results of the dosing and to determine where and to what extent the barium was removed, analyses were made of the treated brine at various points in the works. The character of the brine taken from the draw settler before and after treatment, it was considered, gave the most certain indication of the efficiency of the removal of the barium. At this point the brine is clear, all suspended matter having been removed, and the composition is practically constant, being just at the crystallization point of sodium chloride. These results

Before treatment		After treatment	
NaCl	Na ₂ SO ₄	NaCl	Na ₂ SO ₄

show that an average of 88.6 per cent of the barium in the original brine was removed by the treatment before the concentrated brine was drawn into the grainers. This apparent efficiency was considered highly satisfactory in view of the fact that an appreciable quantity of impurity, including barium chloride, was being constantly returned to the mud settlers from the drainage bin, which could not be provided for in the treatment. Table IV gives the analysis of salt made from the same brine after treatment, compared with salt produced by the same works before treatment.

TABLE IV. Salt Made from Brine Drawn into Settlers Before and After Treatment at Various Points

Before treatment		After treatment	
No. 1	No. 2	No. 1	No. 2

No. 1. 1.8 1.1 1.1 1.1
No. 2. 1.8 1.1 1.1 1.1

1.1 From draw settler of process.

1.1 Sample taken from 24-hour No. 1 salt run, showing percentage treated.

Salt taken directly from the grainers always contains a higher percentage of impurities than salt from the warehouse because the salt is drawn in the former has not had a chance to drain off thoroughly. Consequently, the results for the above-treated salts are higher than they would have been had the taking of the samples been delayed until the salt had seasoned for ten days or two weeks in the warehouse. The results show that the No. 1 salt after treatment contains only about half the amount of barium which it does before treatment, while the quantity of barium in the No. 2 salt is increased by approximately 50 per cent. Treatment, not only improves the quality of the No. 1 salt improved, but the increase of the No. 2 is of great value in its greatly improved as far as the content of crystalline barium is concerned, and is greatly improved as far as the quality of the No. 2 salt.

The small quantities removed, averaging 10 to 20 per cent of the total, and the low cost, make it believe that the effect of the process could be extremely increased. The increase in the amount of the salt, the number of barrels containing the impurities, was reduced 50 per cent before and was found by analysis to contain 14.5 g. of calcium per liter of brine. The results of the treatment of the brine before the

the experiment was tried, it was not thought advisable to complicate the operation by attempting to treat this drainage liquor, since the barium in it would gradually decrease as a result of the treatment.

The brine in the "bitter water grainer" contained, before treatment, 2164 mg. barium per liter and 7 days after the treatment began, 903 mg. barium. All of the old brine was drained out of the bitter water grainer before it was filled with treated brine, but there still remained a considerable quantity of the old impure salt from previous runs on the bottom and sides of the grainer, which undoubtedly increased the barium content of the liquor, but which could not be conveniently removed without closing down the plant. Similarly, there was an accumulation of old salt in all the draw settlers and grainers. If the treatment had been continued long enough to have removed from the system all the accumulated barium salts that remained from the old method of treatment, or if the plant had been thoroughly cleaned and started with treated brine, there is no doubt but the removal of barium would have been more complete and a higher efficiency shown by the method during the preliminary test.

Previous to the treatment, the brine in the grainers was of a light yellowish green color and the salt sometimes had a yellow or slightly red tint from the traces of iron present. After treatment, the brine in the grainers was almost colorless, having only a faint greenish cast, and the salt was snow-white and sparkling. The brine in the bitter water grainer before treatment was red in color and the salt also had a red color; after treatment the brine had very much less color and the salt was almost as white as the No. 1. In fact, it was difficult to distinguish by the color between the No. 2 made after treatment and the No. 1 made before treatment.

The danger from overdosing and the formation of a hard scale of calcium sulfate and the serious effect the deposition of such hard scale upon the elaborate copper pipe evaporating system would have upon the efficiency of the salt works has been referred to before. The preliminary laboratory work indicated that barium sulfate precipitated with the iron hydroxide would not form a hard scale, and it was thought that the residual barium sulfate and ferric hydroxide not eliminated in the preheaters would be prevented from sludging the evaporators by the violent boiling to which the brine is subjected in the evaporators. It was found, however, that while there was very little increased accumulation of sludge in the evaporators the barium sulfate had a tendency to adhere to the steam pipes. In the preheaters the barium sulfate and iron hydroxide settled as a soft sludge on the pipes as well as on the sides and bottom. Most of this could be easily swept off with a broom, but a deposit about $\frac{1}{32}$ in. thick remained quite firmly attached, not as a hard scale, but as a friable sediment which could be easily scraped off with a knife.

After the works had been run for 7 days with the treated brine, the evaporators were drained and examined. A deposit of barium sulfate and iron was

found on the copper steam coils of the same character as that found in the preheaters. There was no deposit on the iron shell of the evaporators, but a small amount of barium sulfate and iron hydroxide sludge had settled out on the bottom. No trouble was apparent from the formation of any calcium sulfate scale.

The deposit of barium sulfate and iron hydroxide could be removed from the pipes with wire brushes, but it was appreciated that if it accumulated to such an extent as to cause insulation of the pipes, the evaporators would have to be shut down occasionally and cleaned. This would be quite a serious difficulty, as ordinarily the evaporators are cleaned only once a year. From the experimental run of 7 days the full significance of the difficulties could not be satisfactorily estimated. Some idea of the amount of barium sulfate remaining in the evaporators and mud settlers is shown by check analyses made of samples of the treated brine taken just before entering the evaporators and again just before being drawn to the grainers. These analyses show that 50 per cent of the barium is deposited in the preheaters before the treated brine enters the evaporators and since 88.5 per cent of the total barium has been removed by the time the brine reaches the grainers, it is evident that the difference, or 38.5 per cent, has been deposited between these two points; that is, in the evaporators, on the filters, and in the mud settlers. What portion of this remains in the evaporators when the brine is boiled, it was impossible to estimate accurately.

It was concluded from the laboratory work and from the preliminary test in the works that the most effective method of treatment was to add the sodium sulfate solution, the acidity of which had been neutralized with lime, to the cold brine and by decomposing the ferrous bicarbonate to obtain a fairly rapid precipitation, the iron flock very materially aiding in settling out the barium sulfate, which, it was found by experiment, required about 16 hours. The results obtained were so encouraging that the manager of the salt works decided to employ the process for the permanent treatment of the brine and the necessary equipment outlined by us was installed, consisting of four 50,000-gal. settling tanks to take care of the estimated maximum daily capacity of the works, a 500-gal. solution tank, pump, blower, the necessary pipe lines, etc. The volume of each of the storage tanks was determined to a point about 8 in. from the top and found to be 47,700 gals. The procedure as finally worked out was as follows:

The accurately weighed charge of salt cake for treating the above amount of brine was transferred to the 500-gallon solution tank nearly filled with condensed water. The mixture was occasionally stirred and live steam was forced through until the sodium sulfate had dissolved, requiring usually about 30 min. Lime which had been slaked and rubbed to a paste was then added to neutralize the acidity of the salt cake. To stir the brine thoroughly after treatment with the neutralized sodium sulfate solution, air was blown through the mixture, by placing in the bottom of each

tank a cross made of $\frac{3}{4}$ -in. iron pipe; in each arm of the cross were drilled $\frac{1}{4}$ -in. holes about 12 in. apart. This cross was connected with the compressed air system under about 75 lbs. pressure, and proved to be a most effective stirring device. Air was forced through the mixture for one hour, by which time the ferrous bicarbonate had been broken down and a flocc formed. The solution was then permitted to stand for 16 hrs., tests showing that practically all of the barium sulfate in suspension and a large part of the iron had settled out by this time. The treated brine was then ready to be drawn to the preheater or evaporator as needed.

Careful control and observation were maintained in the plant during the first 10 days of operation under the new method and periodic inspections have been made since. Samples collected during the control period from various places in the plant were analyzed to show the efficiency of the process. Some of the results are shown briefly in Table V.

TABLE V—DATA ON CONTROL OF PLANT

Barium content of original brine, unconcentrated—Mg. per liter
Upper well..... 243.71 Av. 1
Lower well..... 239.61 (21.6) = 14 lbs. per gal.

STORAGE TANKS

Treated brine as it flows from tanks into preheaters

Treatment, 130 lbs. salt cake per tank

No.	Date	Time	Barium in solution, Mg. per liter	Barium in solution, per cent	Removal efficiency, per cent
1	9/17	After standing 16 hrs.	None	2.2	91.9
2	9/18	After standing 16 hrs.	None	2.1	87.1
3	9/19	After standing 16 hrs.	None	2.1	90.1
4	9/20	1 hr. after starting to draw off	1.8	12	7.0
5	9/20	From same tank as (4), 3 hrs. after starting to draw off	1.8	12	7.0
6	9/22	1 hr. after starting to draw off	Trace	1.8	18
7	9/23	After standing 16 hrs.	1.8	18	1.4
8	9/30	Treated with 125 lbs. salt cake per tank	None	27	11.2
9	9/22	Treated brine as it flows from preheaters into evaporator, same time as (6)	None	27	88.8
10	9/23	Same as (7)	None	1.2	26

DRAW SETTLERS

Brine after treatment 130 lbs. salt cake per tank	Barium in solution, Mg. per liter	Barium in solution, per cent	Removal efficiency, per cent
11 9/19	19.6	8.1	91.9
12 9/20	13.3	5.8	94.8
13 9/21	10.6	4.4	98.6
14 9/22	10.8	4.8	98.8
15 9/23	11.8	4.9	94.1
16 9/30 (125 lbs. salt cake per tank)	15.4	6.4	93.6

The results show that after standing for 16 hrs., practically all of the barium sulfate in suspension is deposited in the tanks, accompanied by a large portion of iron. The small amount of barium sulfate found in suspension in several instances may be attributed to a leaky valve on the air system. The outflow of the tanks was placed 1 ft. above the bottom so as not to disturb the deposit when the brine was drawn to the preheater. It has been found necessary to flush the tanks of the accumulated sludge once a week. The removal efficiency in the tank of 91.9 per cent is an average of 5 determinations representative of a period of 6 days. There was an additional removal from the loading of the treated brine in the evaporator and its further concentration in the final settler. The determination of the barium in solution at the time as it is drawn from the draw settler, produced at the point of crystallization of the salt, shows that the average percentage removal was 94.8 per cent. The

result, while slightly higher than the efficiency obtained in the laboratory experiments, may be regarded as practically identical with it and quite satisfactory.

The works were operated for 3.5 months, using brine treated as outlined above with a 10 per cent excess of sodium sulfate. The operation of treating the brine was reduced to a system whereby the additional labor involved was almost a negligible factor in the cost of operation and without interrupting or interfering with the regular work of the plant. However, at the end of the 3 1/2-month period, considerable scale had deposited on the sides of the water grainer and scale was also beginning to show quite distinctly on the pipes in the grainer. It was decided, therefore, to reduce the amount of sodium sulfate to approximately the equivalent amount necessary to combine with the barium. Some of the pipes were removed from the water grainer and cleaned. The removal of the scale, which was about 1/16 in. thick and rather soft and friable, did not prove to be as difficult an operation as was anticipated. The labor of removing the scale with wire brushes was relatively easy. The works were then run for another 3 1/2 months, using an equivalent amount of sodium sulfate at the end of which period the plant was shut down for inspection and cleaning. The pipes in the water grainer at the end of the second period showed only a very slight deposition of scale, an interesting observation being that some few lengths of hard drawn copper pipe used to replace some of the older soft copper pipe showed no scale whatever. No noticeable evidence of scale could be detected on the grainer pipes which had been cleaned at the end of the first period. Some sludge composed of barium sulfate and ferrous sulfide accumulated in the one evaporator of the horizontal type upon the floor in the pool near the bottom of the brine and water lines one-fifth the length of the evaporator. This deposit was soft and spongy and easily removed by a wire brush. No deposit formed in the evaporator of the vertical type.

The No. 1 and the No. 2 salts produced as a result of the treatment were immediately white due to a more complete removal of the iron from the brine than was possible formerly. The salt apparently crystallized from the grainer and would give a greater yield from a given amount of brine and from, though this could not be definitely determined in the absence of any reliable data on yield. The character of the salt produced is shown in Table VI.

From the grainer, No. 1 salt and the second quality represented by the third No. 2 salt, as shown, it will be noted that the entire output of the plant is of a quality equal to or superior to the best and heavy grade of salt produced by the same plant prior to the installation of the method of treatment. In fact, the salt from the latter would give a lower percentage of salt grade, to wit a quality so low as to render it useless for commercial purposes as much of the No. 1 salt produced by other plants of the same class. In other words, application of this method to the brine, having ferrous sulfate present from the

TABLE VI—ANALYSIS OF SALT PRODUCED AFTER TREATMENT OF BRINE WITH SODIUM SULFATE

		Per cent Moisture	Per cent Insoluble	NaCl	PERCENTAGES ON MOISTURE-FREE BASIS						SrCl ₂
					MgCl ₂	CaCl ₂	CaSO ₄	BaSO ₄	BaCl ₂		
No. 2 Salt, the first produced after treatment.	1909/15	10.06(a)	0.035	95.62	1.24	3.00	0.09	0.02	0.00		
No. 2 Salt, the first produced after treatment.	Sept., 1915	8.425(a)	0.038	95.44	1.30	3.01	0.18	0.03	0.00		
No. 2 Salt, 12 days after beginning treatment.	10/16/15	15.52	0.008	92.68	2.13	5.16	0.09	0.03	0.00		
No. 2 Salt, 19 days after beginning treatment.	10/23/15	13.12	0.018	93.84	1.81	4.38	0.11	0.01	0.00		
No. 2 Salt, 27 days after beginning treatment.	10/31/15	16.00	0.008	91.98	2.42	5.61	0.10	0.02	0.00		
No. 2 Salt, representative sample of sludge taken from warehouse											
11/1/15		5.91	0.023	97.22	0.80	1.97	0.08	0.04	0.00		
No. 1 Salt, after treatment.	9/19/15	5.247(a)	0.013	97.38	0.78	1.78	0.03	0.02	0.00		
No. 1 Salt, after treatment; collected in open market.	10/22/15	7.70	0.010	97.94	0.61	1.42	0.02	0.02	0.00		
Mixed Salt, No. 1 and No. 2 as delivered to warehouse.	Jan., 1916	10.22	0.010	96.54	1.00	2.39	0.01	0.01	0.00		
Mixed Salt, No. 1 and No. 2 after seasoning in warehouse.	2/16/16	3.73	0.010	97.58	0.72	1.68	0.00	0.02	0.00	0.05	
Mixed Salt, No. 1 and No. 2 from warehouse.	9/6/16	6.89	0.010	97.56	0.70	1.72	0.00	0.01	0.00		
No. 2 Salt, after treatment with equiv. Na ₂ SO ₄ .	Jan., 1916	14.01	0.037	93.80	1.80	4.30	0.00	0.04	0.01		
No. 2 Salt, after treatment with equiv. Na ₂ SO ₄ 1 mo. later.	2/16/16	10.55	0.035	95.30	2.83	6.70	0.00	0.02	0.04	0.14	
No. 2 Salt from grainer, after treatment with equiv. Na ₂ SO ₄ 9 mos. later.	9/6/16	16.15	0.010	95.06	1.43	3.48	0.00	0.02	0.00		
ANALYSIS OF SALT BEFORE TREATMENT OF BRINE WITH Na ₂ SO ₄											
No. 1 Salt.	From market. (11232-K)	2.26		99.31	0.24	0.56				0.01	
No. 1 Salt.	From warehouse (16097)	5.97		98.24	0.51	1.22				0.03	
No. 1 Salt.	From No. 3 grainer (16098)	9.76		96.68	0.98	2.19				0.06	0.09
No. 1 Salt.	From warehouse (W. L. A)	8.55		97.42	0.86	2.02				0.05	
No. 1 Salt.	From warehouse (21416)	8.33		97.42	0.76	1.85				0.02	
No. 2 Salt.	From warehouse (21417)	11.32		92.65	1.96	4.22				0.93	0.11
No. 2 Salt.	From warehouse (W. L. B)	12.00		90.51	2.60	5.54				1.15	0.16
No. 2 Salt.	From warehouse (16099)	7.35		95.04	1.10	2.38				1.18	0.09
No. 2 Salt.	Sludge salt from conc. bitter tank (16100)	5.49		70.23	7.12	16.48				5.47	0.69

(a) Moisture by difference.

market food salt which contains an appreciable quantity of barium. The highest content of barium found in the No. 2 salt has been 0.06 per cent, expressed as mixed barium sulfate and chloride. A sample, representing the mixed No. 1 and No. 2 salts, obtained from the works in February, showed 0.02 per cent barium sulfate. Since the installation of the process, the estimated production of salt by the works has been about 100,000 bbls. or approximately 14,000 tons.

The cost of treatment is low. Based upon the maximum capacity of the plant, 400 bbls. of salt per day, the actual cost of treatment, not including cost of original installation of tanks and equipment, and using an amount of sodium sulfate equivalent to the barium present, is approximately 0.5 cent per barrel, based on salt cake at \$12 per ton delivered at the plant. The cost of equipment, tanks, pumps, blower, pipe lines, etc., could not be definitely determined, since part of the equipment, for instance the compressed air system, had been installed previously for other purposes. A careful estimate places the cost of equipment and installation at about \$2,000. This is somewhat higher than a similar installation would cost at other plants, since the installation described necessitated an unusually high cost for foundation and emplacement of the storage tanks, due to the location of the plant on a very steep hillside. The interest on this investment and the depreciation of the equipment plus the labor cost, which it has been difficult to estimate, will not, it is believed, make the total cost of treatment over 1 cent per bbl., which is more than compensated for by the increased value of the product.

SUMMARY

The results may be summarized as follows:

I—The process enables the salt manufacturer to eliminate from the total product of the plant all but insignificant traces of an impurity which has been a constant source of concern.

II—The difference in the price of the heretofore off-grade salt, but which now forms a part of the first-grade salt, will more than offset the entire cost of the treatment.

III—The installation of the necessary equipment is a comparatively simple matter and does not necessitate any material change in the equipment at present employed in salt works.

IV—The application of the method eliminates the production of an off-grade salt and therefore removes from the market a potentially dangerous food product.

V—There is produced about 400 lbs. per day of barium sulfate as a by-product, for which it is expected to find a satisfactory market, although this has not yet been definitely determined.

BUREAU OF CHEMISTRY, WASHINGTON

THE USE OF THE COTTRELL PRECIPITATOR IN RECOVERING THE PHOSPHORIC ACID EVOLVED IN THE VOLATILIZATION METHOD OF TREATING PHOSPHATE ROCK

By W. H. ROSS, J. N. CAROTHERS AND A. R. MERZ

Received October 26, 1916

The basis of nearly all mixed fertilizers is phosphoric acid in so-called available form as indicated by its solubility in water or in solutions of certain organic compounds. In this country phosphate rock constitutes by far the principal source of the phosphoric acid used in the manufacture of fertilizers. Other sources of relatively much less importance are bones, basic slag and certain organic wastes, such as fish scrap. The relative amounts of these different materials which enter into the fertilizer trade are governed by their supply rather than any difference in the fertilizing value of the materials. At present only one firm in this country is producing basic slag of sufficiently high grade to be used as a fertilizer. The supply of bones and fish scrap is also entirely inadequate to meet the present demands of the fertilizer trade. In the form of rock phosphate, however, phosphorus occurs in this country in such immense deposits that this source will undoubtedly continue to supply for an indefinite period the phosphoric acid used in the manufacture of commercial fertilizers.

The treatment to which phosphate rock is subjected in the manufacture of commercial fertilizers is still almost entirely limited to digestion with sulfuric acid

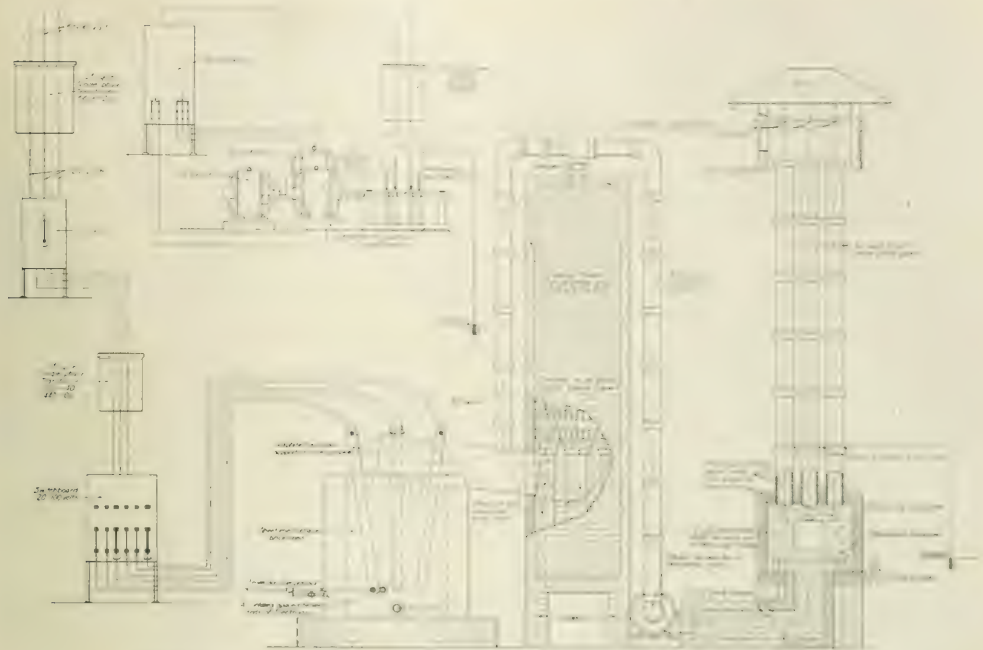


DIAGRAM OF PLANT LAYOUT THE CLEVELAND PHOSPHATE AND FERTILIZER MANUFACTURING CO.

for the preparation of so-called superphosphate or acid phosphate. This process is a comparatively simple one and where cheap sulfuric acid is available or can be produced cheaply in districts where fertilizers are used in largest quantities, this method of making available the phosphoric acid in phosphate rock can be operated at a comparatively low cost.

There are many disadvantages, however, in making phosphoric acid water-soluble in the form of superphosphate:

- 1.—Such a product is not suitable for mixing with considerable quantities of certain other fertilizers, such as lime, calcium cyanamid and sodium nitrate. Lime compounds have the property of reverting the acid phosphate back again into the insoluble form. Sodium nitrate does not have this effect on superphosphate but the acid properties of the latter, particularly if an excess of sulfuric acid is present, have a tendency to set free nitric acid from the nitrate with which it is mixed.

- 2.—When continuously applied to barren soils deficient in lime the acid properties of superphosphate may tend to counteract in a measure the beneficial effects which the phosphate present might otherwise produce.

- 3.—In the manufacture of superphosphate, chamber acid (50% HCl) and ground phosphate rock are thoroughly mixed in equal proportions by weight and the mass allowed to react for 24 to 36 hr. The percentage of phosphoric acid in the final product will thus be only one-half as great as in the original

phosphate rock. It thus happens that the richest superphosphate that can be made by a single acid treatment of the highest grade phosphate mined in the United States contains only about 30 per cent of phosphoric acid. The remaining 70 per cent consists of gypsum, water of combination and the impurities occurring originally in the phosphate rock. This mixture, and being mixed in a fertilizer only about 50 with a soil substance, it follows that material of the nature of superphosphate will not stand so long shipped to places remote from where it is manufactured. For this reason, then, the greater measure of phosphate available to us by fossil almost purely in the eastern States, the superphosphate method is not considered to be applicable for the utilization of the extensive phosphate deposits occurring in the States of Utah, Idaho, Wyoming and Montana.

These disadvantages in the manufacture of superphosphate have been recognized and a great many processes have been proposed and patented with a view to producing soluble phosphates in a cheaper and in a more satisfactory way than was obtainable with the superphosphate method. A comparison of these various processes has recently been made by Waggoner and Tyrol of the Bureau of Agriculture in England, showing the processes employed. The treatment proposed and the acid solutions obtained by the processes. These processes, which have to do with the final kind of phosphate rock, are described by them as follows: (1) acid treatment which involves the use

ufacture of superphosphate and phosphoric acid; (2) combined heating and acid treatment; (3) double decomposition by means of a silicate or an alkali; (4) processes used in connection with the steel industry; (5) processes in which the phosphorus or phosphoric acid is volatilized; (6) treatment dealing with the production of two or more fertilizer elements; (7) electrolysis; (8) enrichment or concentration of phosphates; (9) processes and apparatus for the mechanical treatment of phosphates; (10) miscellaneous processes.

As Waggaman and Fry have pointed out, the claims made for some of these processes are not justified while many other processes are entirely impractical from a commercial standpoint.

The processes which have attracted most interest during recent years, and which give most promise of replacing, in part at least, the sulfuric acid method, belong to Group (5) and have to do with the volatilization of the phosphorus from phosphate rock. All are based on the method long in use for the manufacture of elementary phosphorus and consist in igniting phosphate rock at a high temperature with or without one or more reagents such as coke and silica. The main advantages in this procedure lie in the fact that from rather impure raw materials there may be obtained comparatively pure phosphoric acid of high concentration which may readily be adapted to the preparation of fertilizers containing two or more fertilizing elements in concentrated form. Such a fertilizer would admit of shipment to places remote from where it is manufactured. The chief disadvantage of the superphosphate method in the utilization of the western phosphate is thus overcome by the volatilization method. As this method, moreover, is particularly adapted to the use of hydro-electric power it is probable that phosphoric acid prepared by volatilization will in the future compete as a fertilizer with that prepared in the form of superphosphate.

The processes of Wing,¹ Ruymbeke,² Landis,³ Washburn,⁴ Haff,⁵ and Hechenbleikner,⁶ all call for the ignition of phosphate rock with coke and silica in an electric or blast furnace at such temperature that the phosphate radical is replaced by the silica and in the presence of the reducing atmosphere caused by the coke, the phosphorus is first volatilized in the elemental form to be at once changed into phosphoric acid by oxidation with air and absorption in water.

In the processes proposed by van Denbergh,⁷ De Chalmot,⁸ Levi,⁹ Haff,¹⁰ Haff and Willson,¹¹ and Willson and Haff,¹² the use of coke is omitted and the phosphate rock is simply ignited with sand or some other siliceous material as feldspar.

In Morehead¹ and Duncan's² processes, on the other hand, for producing elementary phosphorus the siliceous material is omitted and the phosphate rock ignited with coke or other reducing material.

According to Maywald,³ phosphorus pentoxide may be volatilized from phosphate rock by simply passing an electric current through the latter in a furnace to which air is admitted.

The processes proposed by Machalske⁴ differ from any of the others in that the ground rock is ignited with a mixture of sodium chloride and coke. The phosphorus chloride formed is led off and treated with water to form phosphoric acid and hydrochloric acid. It is suggested that the carbide remaining in the furnace may be used in the fixation of atmospheric nitrogen.

Of these different processes for treating phosphate rock those which apparently offer most promise involve the use of both silica and coke. In experiments made in this laboratory it was found that when the rock was ignited with these two reagents, the phosphorus was driven off much more readily and completely and at a lower temperature than when the ignition was made with either of them alone.

The feasibility of the process as a method of extracting phosphoric acid from phosphate rock has been demonstrated by the large scale operations which have been carried on in a commercial way at Mt. Holly, N. C., under the rights of the Hechenbleikner⁶ patents.

The furnace used in this plant has a capacity of 5,000 kw. and is operated by a 3-phase alternating current at 250-500 volts. The charge consists of a mixture of phosphate rock, sand and coke in such proportions that the quantities of silica and carbon in the charge are about 20 per cent in excess of that required by the equation:



This charge is fed into the furnace through openings around the electrodes. In this way the double purpose is served of permitting the electrodes to be adjusted without allowing the fumes of phosphorus to escape, and the cool charge likewise forms a protection against too rapid oxidation of the electrodes. As the phosphorus is driven off it is first oxidized with air in an oxidizing tower and then passed through a series of scrubbing towers where absorption of the oxides takes place. By circulating the solution through the towers a solution may finally be obtained containing as high as 50 per cent of phosphoric anhydride. With the solution thus recovered there may be prepared ammonium phosphate by neutralizing with ammonia; or by treating a fresh lot of phosphate rock with a quantity of acid equivalent to the phosphoric acid in the quantity of rock taken, there may be prepared double superphosphate which contains upwards of three times the percentage of phosphoric

¹ United States Patent No. 435,821.

² United States Patent No. 540,124.

³ United States Patent No. 859,086.

⁴ United States Patents Nos. 1,044,957, 1,047,864 and 1,100,639.

⁵ United States Patent No. 1,084,856.

⁶ United States Patent No. 1,112,211.

⁷ United States Patent No. 669,271.

⁸ United States Patent No. 689,286.

⁹ United States Patent No. 984,769.

¹⁰ United States Patent No. 1,018,186.

¹¹ United States Patent No. 1,076,499.

¹² United States Patent No. 1,103,910.

¹ United States Patents Nos. 862,092 and 862,093.

² United States Patent No. 733,316.

³ United States Patent No. 902,725.

⁴ United States Patents Nos. 89,438, 89,439 and 89,440.

⁵ United States Patents Nos. 1,112,211, 1,167,755 and 1,173,960.

anhydride that is contained in superphosphate made in the ordinary way from the same phosphate rock.

A number of disadvantages, however, attend the scrubbing tower method of recovering the oxides of phosphorus when volatilized in the way described:

(1) Notwithstanding the extreme hygroscopic nature of phosphorus pentoxide it is nevertheless not readily absorbed by water when volatilized from phosphate rock and complete absorption can be effected only by a more or less extended series of towers provided with a system of baffle plates over which water is made to circulate.

(2) The acid has an injurious effect on all metal parts required in the pumping system necessary for maintaining a circulation of the solution through the towers.

(3) The hydrofluoric acid evolved in the process from the fluorine occurring in the phosphate rock also acts injuriously in the case of any extensive absorbing system, and it is considered by those engaged in the practical operation of this process that the hydrofluoric acid has a retarding effect on the absorption of phosphorus pentoxide as evidenced by the observation that the absorption of the pentoxide from phosphate rock free from fluorine takes place more readily than from rock which contains fluorine.

(4) By use of scrubbing towers it has been found impractical to obtain a solution containing more than 50 per cent phosphoric anhydride. When such a solution is neutralized with ammonia gas to make mono-ammonium phosphate the product obtained will contain about 25 per cent of water and will consequently have to be dried before being placed on the market. Drying is also necessary in the manufacture of double superphosphate, which adds considerably to the cost of manufacture.

It has occurred to the authors that by the use of the Cottrell precipitator in place of the scrubbing tower system now used for collecting the fumes evolved from the furnace, most if not all of the disadvantages cited might be avoided.

The results which have now been obtained with the precipitator in experiments undertaken on a fairly large scale have justified expectations, and it has been found that the chemical and physical properties of phosphorus pentoxide are such that the Cottrell precipitator is particularly adapted to its precipitation in the form of phosphoric acid.

The furnace used in these experiments consisted of an iron cylinder lined on the inside with fire-brick and provided with an opening near the bottom for the removal of the slag. The exhaust gas ducting system used was stepped down from 36 in. to 12 in. by the shaft phase 75 K. V. A. transformer. This transformer was provided with a split primary and by using in different combinations in series and in parallel the coils in the secondary different voltages could be obtained, varying from 40 to 1100 volts at 60 and 110 cycles of these voltages.

In the preliminary experiments there was used as absorbing tower a 4 ft. sq. and 4 ft. meter pipe section with an effective absorption surface of about

3,000 sq. ft. These experiments demonstrated the difficulty of recovering all of the phosphoric acid by this means.

When the Cottrell precipitator was installed the gases in the first series of experiments were still allowed to pass through the tower, but with no water present. This then simply served as a baffle tower and as a means of cooling the gases, thereby permitting experiments to be made on the precipitation of the phosphoric acid at temperatures but little above the ordinary temperature.

The power used in the precipitator was provided by a 110 volt, 60 cycle, alternating current motor-generator set, and was stepped up by an 8 K. V. A. transformer capable of yielding voltages of 10,000, 20,000 and 40,000 volts. In these experiments the highest voltage only was used. From the transformer the current was changed to intermittent d. c. by a small mechanical rectifier attached to the shaft of the generator and so adjusted as to operate in synchronism with it. The positive lead from the d. c. side of the rectifier was earthed while the other terminal was connected to the wires suspended in multiple, one in each of the pipes used in the precipitator. Each pipe was then earthed. In the accompanying diagrammatic sketch is represented the equipment used in these experiments.¹

In the preliminary experiments made with the precipitator, sheet iron pipes were used, 6 in. in diameter and 10 ft. high. The precipitated acid, however, had such a corrosive action on the pipes that they had to be abandoned. Pipes were then constructed from ordinary 6-in. glazed terra cotta tile, 5 sections being taken for each pipe. The precipitated acid gave to the inside of the pipes an effective conductive surface and in grounding the pipes it was found sufficient simply to bring the ground wire to the inside surface of each pipe at one point. Arranged in this way the terra cotta pipes could be used just as efficiently in the precipitation of the acid as metal pipes and they had the very important advantage of being unaffected by phosphoric acid. When a metal mesh was found to be most useful some wire suspended in the pipes had sufficient wire but proved unsatisfactory. Weights were suspended at the ends of the wires and multivolt connections were furnished by a wire connecting all the weights.

The furnace evolved from the charge in the furnace was drawn off by the current of an exhaust fan, constructed of agricultural wood, through which the gases passed before entering the precipitator. The outlet of the fan was closed with flanges secured in perfect communication of the acid by the means of the lathe. Entrance of air into the furnace was allowed in order that the gases could be cooled, and the charge fed in ground was at many of the voltmeters. In this way variations of the collected phosphoric acid obtained in the furnace as it passed down the charge.

The quantity of the acid used in drawing off the fumes from the furnace was 100 to 110 lbs. per hour.

The apparatus described in this paper is a preliminary one and is subject to many improvements.

As shown later, this flow of air was much in excess of that necessary to oxidize the phosphorus evolved from the furnace. Using a fan of this capacity it was found necessary to use 6 pipes to bring about complete precipitation of the fumes. By cutting down the volume of air treated the number of pipes necessary might be reduced in proportion. Moreover, with a higher potential than was available, pipes of even double the diameter might be used. In a plant of commercial size, therefore, the increase in the capacity of the furnace over that which we used should call for a much less proportionate increase in the number of pipes.

Since the phosphorus passes off from the furnace for the most part in the form of phosphorus pentoxide it might be expected at first thought that it would be collected as such in the precipitator. A simple calculation will show, however, that this is not practical for there will always be enough moisture in the charge used and in the air required to oxidize the phosphorus evolved to convert the phosphorus pentoxide either in whole or in part into phosphoric acid.

Thus in air saturated at, say 20° , and of sufficient volume to supply the gram molecules of oxygen called for in the equations, $\text{Ca}_3(\text{PO}_4)_2 + 3\text{SiO}_2 + 5\text{C} = 3\text{CaSiO}_3 + 5\text{CO} + 2\text{P}$; $\text{CO} + \text{O} = \text{CO}_2$ and $2\text{P} + 5\text{O} = \text{P}_2\text{O}_5$, there are 9.9 grams of water, sufficient to convert 18 per cent of the pentoxide into orthophosphoric acid. If it be assumed, moreover, that the phosphoric acid in the phosphate rock amounts on an average to 19 per cent of the charge used, and that the moisture in the latter amounts to, say, 5 per cent, then this source of moisture will be equivalent to a further 69 per cent of the phosphorus pentoxide.

By increasing the quantity of water vapor passing into the precipitator, acid of any dilution may be obtained; conversely, if the air is dried before entering the furnace and likewise the charge used, the evolved phosphorus pentoxide should be precipitated in the solid state, but from a commercial point of view there would be little or no advantage in collecting the phosphorus pentoxide as such on account of the extremely hygroscopic nature of this material.

This hygroscopic nature of phosphorus pentoxide makes it particularly adapted to precipitation with the Cottrell precipitator. If it precipitated in a flocculent state as it occurs in the anhydrous form, or in a pasty condition too thick to run down the sides of the pipes its recovery with the precipitator would be a matter of difficulty. In our experiments, however, it was found that there was always an excess of moisture in the air drawn through the furnace and in the charge used above that necessary completely to convert the phosphorus pentoxide into phosphoric acid. This was then precipitated in the form of a solution which ran down the sides of the pipes and was collected in a continuous stream from the delivery tube leading from the stoneware receiver, which also served as a baffle in the box which supports the precipitating pipes as shown in the sketch.

When the fumes were passed through the tower and precipitation thus made at a temperature but

little above normal, the concentration of the acid first collected was in the neighborhood of 60 per cent phosphoric acid. The moisture content of the charge used amounted to only about 1 per cent. From the calculation already given it must follow therefore that the rate of air which was passed through the furnace to carry off the fumes must have been much in excess of that necessary to oxidize the phosphorus evolved. On cutting down the flow of air somewhat the concentration of the acid was increased to about 80 per cent, and it is quite evident that with the humidity of the air remaining the same a still more concentrated acid might be obtained by still further limiting the flow of air through the furnace. It was thought, however, that without changing the rate of flow of the air through the furnace a more concentrated acid might also be obtained by increasing the temperature at which the precipitation was made.

In carrying out experiments on the precipitation of the acid at higher temperature, the baffle tower was cut out and the fumes passed directly into the precipitator through the terra cotta by-pass as shown in the sketch. Under these conditions the fumes from the furnace entering the precipitator reached in the course of two or three hours a temperature of about 175° and remained fairly constant at this temperature for several hours longer. In passing through the pipes the temperature of the gas fell to about 100° . As shown in Table I, the concentration of the acid collected in this way, with either a maximum or minimum flow of air passing through the furnace, was considerably in excess of that collected in a corresponding way at a lower temperature.

TABLE I—VARIATION IN CONCENTRATION OF ACID WITH THE TEMPERATURE OF PRECIPITATION AND WITH THE FLOW OF AIR THROUGH THE FURNACE

Temperature of Precipitation	Flow of Air through Furnace	Sp. gr. 25° 25° of Acid Collected	Concentration of Acid, Per cent H_2PO_4
About 30° C.....	Maximum	1.448	63.07
About 30°	Minimum	1.530	80.23
About 100°	Maximum	1.766	90.82
About 100°	Minimum	1.800	95.23

In Table II are given analyses of two samples of phosphoric acid collected on different dates and which are thought to represent extremes as regards impurity in the samples of acid so far collected.

TABLE II—ANALYSES REPRESENTING EXTREMES AS REGARDS IMPURITY IN THE PHOSPHORIC ACID COLLECTED IN THE COTTRELL PRECIPITATOR

	A	B		A	B
H_2PO_4	63.68	63.07	$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$	0.06	Trace
H_2SO_4	0.21	0.04	Arsenic.....	Trace	Trace
HF	0.49	Trace	Heavy metals.....	None	None
HCl	0.04	None	Residue on igniting to redness.....	0.85	0.11
SiO_2	0.26	0.03			
CaO	0.03	None			

The rock used in these experiments consisted of Florida land-pebble phosphate and was used without grinding. The phosphorus present amounted to 32.14 per cent expressed as P_2O_5 and the fluorine to 2.33 per cent. If all the fluorine as well as all the phosphorus were volatilized and precipitated, then the hydrofluoric acid in a phosphoric acid solution of the concentration of, say, Solution A, Table II, should amount to 3.52 per cent. Likewise, since the coke used contained 2.56 per cent of sulfur expressed as SO_2 , the percentage of sulfuric acid in the

same phosphoric acid solution, if all were volatilized and precipitated, would amount to 0.75 per cent. Since the amounts of hydrofluoric and sulfuric acids found even in Solution A form only a comparatively small part of that which would be present in the phosphoric acid if all were volatilized and precipitated, it is evident that under the conditions of the precipitation the greater part of the hydrofluoric and sulfuric acids pass through the apparatus in the form of gas and are therefore not acted upon by the precipitator.

The acid collected when the fumes were passed through the baffle tower contained in suspension a slight amount of insoluble material consisting mostly of volatilized silica, but when this was removed by filtering, or by decantation on settling, the acid obtained was then perfectly transparent. When the baffle tower was cut out, the acid collected naturally contained a larger amount of suspended matter with a consequent small increase of bases in solution and was somewhat colored, due, no doubt, to carbonaceous matter carried over with the current of air.

By operating the furnace continuously and by reducing the amount of heat radiated, it should be possible to pass the fumes from the furnace through an efficient baffle tower and yet make the precipitation at temperatures above 100°. Judging from the results already obtained, the acid collected under these conditions should be of sufficient purity for use in those industries where a relatively pure acid is required. To prevent contamination of the acid in its preparation the precipitator must be made of stoneware or porcelain and all metal must be avoided in all parts of the equipment that come in contact with the fumes. In the manufacture of phosphoric acid for use in fertilizers these special precautions for collecting pure acid would of course be unnecessary.

SUMMARY

An investigation on a semi-commercial scale has been made of the use of the Cottrell precipitator in recovering the phosphoric acid evolved in the volatilization method of treating phosphate rock by ignition with coke and silica in an electric furnace. A current of air which was passed over the charge in the furnace served the double purpose of oxidizing the fumes of phosphorus to phosphorus pentoxide and of carrying the latter to the precipitator. In one series of experiments the fumes, before entering the precipitator, were passed through a tower provided with baffle plates which had the effect of cooling down the gases to about ordinary temperature. In a second series of experiments the tower was cut out and the fumes passed directly into the precipitator at a temperature above 100°. In each case the phosphorus pentoxide, which takes up water from the current of air passing through the furnace and also from the moisture arising from the charge, is precipitated in the form of a solution of phosphoric acid. When the precipitation is made at temperatures at about 100° or above, the concentration of the acid is greater than when collected

at a lower temperature, but by reducing the flow of air through the furnace, acid of high concentration may also be obtained with low temperature precipitation.

The advantages of this method of collecting the phosphoric acid over the scrubbing tower method now in use are as follows:

1—The equipment required is simple in construction and automatic in operation.

2—The simplicity of the construction of the precipitating pipes decreases the difficulties arising from the corrosive action of the phosphoric and hydrofluoric acids evolved from the phosphate rock.

3—In this way there may be recovered phosphoric acid of a high degree of purity suited for direct use without further purification in those industries where a relatively pure acid is required.

4—A more concentrated acid can be obtained in this way than is possible to prepare directly by any other commercial process, and when this acid is used in the preparation of concentrated fertilizers, such as mono-ammonium phosphate, a dry product may be obtained directly without the necessity of evaporating solutions, or of drying the resultant product.

This is the first time that the Cottrell precipitator has been used for the precipitation of a product which has been purposely volatilized with a view to its recovery in this way.

RECEIVED BY THE EDITOR

J. S. LITTLE & COMPANY, INC., MANUFACTURERS
WASHINGTON, D. C.

EMULSIONS AND SUSPENSIONS WITH MOLTEN METALS¹

By H. W. BAKER

The object of this paper, which is written at Prof. Bancroft's request, is not to present any new information, but to suggest a line of thought.

In the refining of aluminum chips to ingot a loss of 30 per cent of the metallic content is common and a 15 per cent loss represents very good practice. In a study² of these losses it was found that the cause for the high loss is not primarily the loss of oxidation of aluminum, but the failure of the phosphorus to remove the oxide film on the surface of the chips. The latter is removed satisfactorily by adding sufficient sodium flux and is lost practically by smelting. Commercial aluminum chips from the molten slags of the electrolytic manufacturing plants show as at 24 per cent of the total weight flux will give a product more than 90 per cent of metal. There is considerable loss here, a few more and somewhat 75 per cent in volume of the completed and usually are less than a few mill and sometimes 25 per cent of very fine dirt, part of this percentage mixed with the chips.

If we take an iron making situation, chips in the molten slags would be similar. The larger the chips

¹ Presented at the 10th Meeting of the American Chemical Society, New York, N. Y., September 10, 1916.

² "The Losses in the Refining of Aluminum," by H. W. Baker, in the Bulletin of the American Chemical Society, Vol. 34, No. 1, 1916, p. 10.

chips melt down to fairly large globules that succeed in breaking through the skin of dross, getting into true metallic contact with each other and coalescing into a pool of metal that can be poured satisfactorily. But the tiny droplets formed by the melting of the smaller chips are so microscopic in size and so infinitely light in weight that they cannot break through the honeycomb of oxide and dross about them. So, instead of going down where they are wanted, they remain in the dross.

In order that as many of the medium sized drops as possible may not be too viscous to flow down, the temperature is raised far above the melting point. When the very hot dross, which is dry and powdery, is skimmed off and reaches the air, the tiny entangled globules burn up at once, with a thermit-like behavior. The pool of coalesced metal, even in the open air, takes on a thin coat of oxide which then protects it from further oxidation.

So while oxidation (and, nitridation as well) is the ultimate cause of the loss, this oxidation would not take place save for the very finely divided physical state of the metal.

Two methods serve to reduce the loss by promoting coalescence, and both are in commercial use, though the details of the methods appear to be known only by a few refiners. One is the "puddling" process where the chips are melted in an open iron pot, small amounts being added at a time, and each addition being thoroughly stirred and pushed into the main mass, the temperature being very carefully kept only just above the melting point, so that the mass is pasty, but not truly fluid.

By the constant working over of the mass, the tiny globules are squeezed together with enough force to break the entangling film and bring them into metallic contact. Finally, after the mass of metal surrounds the particles of dirt and oxide instead of the honeycomb of dirt surrounding the globules, *i. e.*, the disperse phase of the emulsion—using this term loosely to include suspensions also—has been reversed, and the mass is heated up so that the dross will rise. The other method is to mix large amounts of NaCl with the chips, as a menstruum to dilute or soak up the envelope phase of dirt, preferably using with the NaCl a small amount (say 15 parts to 85 parts of NaCl) of some fluoride, such as CaF_2 , to dissolve the little Al_2O_3 present and heating without much stirring. This method also breaks up the emulsion and the tiny globules settle satisfactorily. Of course the best method is one of prevention, that is, collecting the chips without contamination by dirt. Removing the dirt by washing and screening is possible, but troublesome and expensive.

There are many other cases where a molten metal or alloy forms an emulsion or suspension with a solid, a liquid or a gas.

"Floured" or "sickened" mercury, where globules of mercury refuse to coalesce when coated with talc, graphite, grease, etc., is one, and dirty molten sodium, another example of a liquid and a solid. Blue powder is an interesting example, and the problem of

melting it is quite analogous to that of aluminum chips. Roeber¹ distinguishes between "physical" blue powder, or "zinc snow," which consists of particles of zinc uncoated by foreign materials, and which coalesces on melting, and "chemical" blue powder, in which each particle is coated with a skin of ZnO and probably a little SiO_2 . The methods of separating the phases in this case are, distilling the volatile zinc away from the non-volatile impurities, heating under pressure, to break up the enveloping skin, as in the old Montefiore system, or dissolving off the skin by the process of Bleecker,² who adds the blue powder to an electrolytic bath of fused ZnCl_2 kept above the melting point of zinc. The ZnCl_2 has some solvent action on the coating and the particles migrate to the cathode and coalesce.

Another case where a small amount of a solid phase distributed through, or emulsified with a molten metal, is in defective fusible boiler plugs, where Burgess and Merica³ find that a network of oxides may prevent the plug from blowing out although the metal of the plug is fully molten.

Entangled oxides, the bane of the foundryman in steel, brass, bronze, and aluminum, are, in a sense at least, emulsions of a solid phase with the liquid metal which are not broken up, but freeze into place and result in unsound castings. Here one either reduces the oxide chemically or attempts to collect it in a slag by means of some flux.

The retention of metal by slag in reduction and refining processes is a case of an emulsion of two liquids. In the Pattison process we have another case where the breaking of the emulsion is essential. Metal fog in the electrolysis of fused salts is still another example.

Richards⁴ has recently brought this out in the cases of strontium and cerium.

The emulsion of a gas in a metal gives rise to a problem no less serious to the foundryman than that of a solid or a liquid with the molten metal, for if the emulsion is not broken, we have blowholes and porous castings.

Sometimes it is desirable to maintain an emulsion or suspension of a metal with another phase. Examples of a suspension of some solid with a liquid metal (or, more strictly, of a solid with a plastic mixture of solid eutectic and liquid metal) are the "near alloys" of Friedrich⁵ where such materials as cobalt silicate are mixed with an alloy of 90Sn 10Cu kept within the eutectic range. Here the cobalt silicate is probably the disperse phase. But there are useful cases where the metal is the disperse phase within a solid.

In sherardizing, zinc dust coated with enough oxide to prevent coalescence is a necessity. In calorizing, aluminum oxide is mixed with the aluminum powder for

¹ E. F. Roeber, *Met. & Chem. Eng.*, **10** (1912), 481.

² W. F. Bleecker, "The Electrolytic Method for the Reduction of Blue Powder," *Trans. Am. Electrochem. Soc.*, **21** (1913), 389.

³ G. K. Burgess and F. D. Merica, "An Investigation of Fusible Tin Boiler Plugs," *Trans. Am. Inst. Metals*, **9** (1915), advance copy, 3 pp.

⁴ J. W. Richards, "The Metallurgy of the Rarer Metals," *Met. & Chem. Eng.*, **15** (1916), 26; *This Journal*, **8** (1916), 736.

⁵ K. Friedrich, "Near Alloys," *Met. & Chem. Eng.*, **8** (1910), 191.

the same purpose. Here an "emulsion" of solid metal and solid oxide, if the process is run below the melting point of the metal, is required to prevent the welding together of clean metal surfaces below the fusion point of the metal, or one of liquid metal and solid oxide to prevent coalescence of the globules, if run above the fusion point.

Emulsions of two liquid metals find a notable example in the mixture of half copper and half lead used for packing bearings, brake bands, etc. Molten copper and lead, in equilibrium, form a two-liquid layer system, being immiscible. Yet it is possible, by the use of sulfur or nickel as an emulsifying agent, to produce a quite uniform mixture of the two metals, though it is as ticklish a job as the foundryman often attempts. To a lesser degree, the liquation of lead or of some other low melting, immiscible phase in brass and bronze casting, offers the same problem.

Could we obtain stable emulsions of metals normally immiscible in the liquid state surely some of them, after solidification, would be industrially useful. Useful emulsions of gases with metals are hard to find. Yet uniformly porous metals or alloys might be useful. Hannover¹ has shown that lead, made porous by an indirect method, makes a storage battery of four times the capacity for the same weight as one with solid lead plates.

The chemistry of colloids is proving of immense use to industry. It is right that the colloid chemist should deal with the system water, benzene, soap at room temperatures at the start, for seldom is much gained by attacking the more complicated problems before the simple ones are solved. Yet when he has flocculated and peptized, frothed and floated, long enough to bring some semblance of order out of chaos and to get some working hypotheses on the mechanism and causes of emulsions and suspensions, he may find it of use for the clarification of the present somewhat emulsified theories, as well as of practical value, if he will remember that there are other systems than water and oil and other temperatures than 0 to 100° C. Molten metals and alloys, from mercury to tungsten, also offer their problems of colloid chemistry. And when the colloid chemist shall have solved only a few of the problems waiting for him in that field, the foundrymen and metallurgists, at least, will rise up and call him blessed.

MORRIS HALE
ITHACA, NEW YORK

SIMILARITY OF VITREOUS AND AQUEOUS SOLUTIONS²

By ALEXANDER SIEGEMUND

Received September 12, 1916

The striking similarity of properties of vitreous and aqueous solutions, both as to appearance and behavior, has led the writer to refer to them together in lectures on glass. They are collected here, with introduction to a series of papers, covering somewhat on individual cases, which will appear from time to time.

¹ H. I. Hannover, "The Production of Porous Metals," *Mech. Eng. Inc.*, **10** (1914), 509.

² Presented at the Third Meeting of the American Chemical Society, New York City, September 10-12, 1916.

Zsigmondy, in his work on "Colloids and the Ultra-microscope," calls attention to the size and properties of small particles in solutions. When gold is introduced into the batch as element or in compounds, the melt results in a yellow vitreous solution resembling aqueous solutions of the chloride. When the glass is reheated the unstable compound breaks up and the red colloid results. This again resembles the aqueous solution in appearance. If reheated a number of times the glass mass becomes brown by reflected light and blue by transmitted light, just as the oxalic acid reduction of an aqueous chloride solution yields a brown precipitate and blue supernatant liquid. That the particles are of colloidal size is evident from the researches on glass by Siedentopf and Zsigmondy.¹

Copper is introduced into the batch as Cu_2O or CuO or as a cupric salt. Reducing agents are added. The resulting glass resembles aqueous solutions of cuprous salts in appearance. On reheating, the glass turns red and with continuous heating and greater reduction it assumes a liver-color. As in gold solutions the red color is due to the colloid; the liver or red-brown mass consists of the coarser precipitate.²

Selenium enters the batch as element, sodium selenite or sodium selenate, together with a reducing agent. The resulting vitreous solution is black while hot and changes to a colorless, yellow, red, or dark mass on cooling, depending upon the quantity of selenium present. When the colorless or light solution is heated it again turns dark and if the correct amount of selenium is present becomes red on cooling. Fenaroli³ has shown that the red solution consists of polyselenides resembling the polysulfides in sulfur-amber glasses. The writer examined some selenium ruby glasses for colloids while the Fenaroli experiments were under way. Besides the similarity of behavior of gold, copper and selenium glasses on heat treatment, but found no obstruction to the passage of light rays in the ultra-microscope. A peculiar fluorescence or bloom on the surface of the glass prior to reheating was attributed to partial reduction of the compound, as the glasses were high in iron. The steel, when Fenaroli subsequently examined some specimens, proved to be essential to the same results, which is the product of reducing agent in the bath. In a reducing bath heated continuously with the solution in the glass. As selenium solution is introduced into the bath there is a possibility that they become high in iron content, as the yellow or red color formed from the by other elements in the bath.

On reheating the solution the glass mass again becomes transparent, but the glass is much more yellow and dark and becomes a dusky brownish. The writer examined these specimens by aqueous solutions of various elements, which at a single reheating of the solution in glass, and in a further reheating, turned red.

³ Fenaroli, *Comptes Rendus Acad. Sci. Paris*, **191**, 1916.

⁴ *Ann. Phys.*, **18**, 1916.

⁵ *Ann. Phys.*, **18**, 1916.

⁶ *Ann. Phys.*, **18**, 1916.

relatives. The ferrous silicates are green, the ferric, yellow.

Copper glasses, when the batch contains an oxidizing agent, are blue and here again the color is the same as that imparted to a dilute aqueous solution by the cupric ion.

The color imparted to glass by cobalt oxide is practically identical with that produced by an excess of concentrated HCl in aqueous CoCl_2 solution where the complex CoCl_4 is supposed to form.

The color of vitreous manganese solutions resembles that of aqueous solutions. Similarity in valence was recently shown by Scholes¹ in his article on "Trivalent Manganese in Glass."

In opal and alabaster glasses we encounter another striking parallel to conditions in aqueous solutions. Opalescence is largely due to finely divided alumina of colloidal size. Just as electrolytes will precipitate such colloids from aqueous solutions, so NaCl or Na_2SO_4 or other chlorides or sulfates will precipitate this colloid from vitreous solution. As a result, a glass which is opalescent without the addition of one of these salts becomes an alabaster glass if they are added, through the precipitation of the colloid by the salt. The light then transmitted is white. When the sulfate ion is present the color is more intense than with the chloride ion.

Effects resembling the Liesegang layers have been obtained in opal glasses to which CoO and selenium were added. The alternating strata are blue and white when the glass gathered from the pot is allowed to cool without reheating.

CONCLUSION

The data presented seem to indicate clearly that much might be accomplished by studying vitreous solutions, in part at least, on the basis of similar phenomena observed in aqueous solutions of some of their constituents. The writer hopes to add evidence through researches which are under way and planned.

SCHOOL OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH

CHEMICAL COMPOSITION VS. ELECTRICAL CONDUCTIVITY²

By COLIN G. FINE

Some years ago, while still at the university, I carried out a number of experiments on the electrothermic production of ultramarine. Powdered mixtures of sodium sulfide, china clay and carbon were interposed between carbon electrodes in a closed crucible furnace. I observed at the time that in order to keep the electrical resistance and the temperature of the charge fairly low so as to avoid decomposition of the ultramarine as soon as it was formed, it was necessary to use very finely divided carbon, such as lampblack. With charges made up of powdered coke which was coarse compared to the lampblack, I could

not get any appreciable current to pass between the carbon electrodes up to potentials of 250 volts.

Subsequently, I have found repeatedly that the electrical conductivity of mixtures of finely divided substances is a function of the relative size of the components.

EXPERIMENTAL

A series of tests was made in order to get values of a more quantitative nature. Two substances were selected, the physical properties of the one as divergent as possible from those of the other: a black metal powder, tungsten, and a white insulator powder, thoria. The advantages in this selection are manifold; both tungsten and thoria will stand very high temperatures and can therefore be made practically moisture-proof. It is a well known fact that in all high-resistance tests adsorbed moisture is a very disturbing factor. Metals such as copper and silver were not serviceable since they cannot be heated to high temperatures without partial vaporization, which though slight was sufficient to cover the surface of the insulator granules with a highly conductive film. Other factors that decided our selection in favor of tungsten and thoria were: (1) high state of purity; (2) availability of both in extremely fine powdered form (readily sifted through 250 mesh gauze); (3) constancy and stability under ordinary atmospheric conditions; (4) sharp distinction in color; (5) high specific gravities (which reduced the tendency to dust).

All mixtures here recorded were made up of equal weights of tungsten and thoria. As regards the size of the particles, as stated above, the mixtures would pass readily through silk having 250 meshes to the inch. The holes in this silk are about 0.001 in. in diameter.

All attempts to segregate particles of a well-defined size by such methods as suspending water, organic liquids or air, were frustrated on account of the persistent tendency of the very fine particles to form agglomerates.

We finally resorted to the familiar "tap test." This gave us fairly good comparative values of the fineness of the various powders used. Ten grams of the powder or powder mixture were filled into a 10 cc. glass graduate and tapped to constant volume; usually, after 7 minutes no further decrease in volume could be detected. The ultimate volume in cc. divided by 10 gave us the relative volume (v_r) as recorded in Table I. It can easily be demonstrated that the values for v_r are a function of the density and mean particle size. At first there seemed to be a serious objection to the tap test, namely this, that a powder composed of, say, equal parts of coarse and fine particles would give the same figure for v_r as a second powder whose particle size was a mean between the two limiting sizes of the first powder.

This objection to the tap test was automatically set aside since in the ordinary preparation of metal or oxide powders in single small lots by far the greater majority of particles are approximately of the same size. This tendency to form a "standard" size is a universal phenomenon, the dimensions of any particular standard

¹ THIS JOURNAL, 7 (1915), 1037.

² Presented at the 53rd Meeting of the American Chemical Society, New York City, September 25 to 30, 1916.

being dependent upon the physical factors such as temperature, strength of solution, etc., under which the particular powder is prepared. (Compare also, the size of the crystals of granulated sugar and the "Strike pan.")

TABLE I
RELATIVE VOLUME (%) OF

Mixture	ThO ₂	W	MIXTURE		Appearance of Mixture
			Found	Calc	
R.....	0.720	0.113	0.430	0.417	White
P.....	0.720	0.350	0.565	0.535	White
Z.....	0.576	0.235	0.389	0.406	White
S.....	0.305	0.113	0.200	0.209	White
T.....	0.305	0.330	0.275	0.315	Black
X.....	0.238	0.577	0.420	0.408	Black

Referring to Table I, we note that the thorium powders varied in relative fineness between 0.720 and 0.238 and the tungsten powders between 0.577 and 0.113. The calculated value for τ_r of any mixture is equal to one-half the sum of the τ_r values of the ThO₂ and W constituents. These calculated values agree fairly well with the experimental and support our contention that the particles of any freshly prepared powder are of fairly uniform size. If this were not the case no such agreement between the calculated and experimental values would be possible.

As to the appearance of the mixture, if the τ_r value for the white powder is high as compared with the value for the black powder, the appearance of the mixture is light; if the white powder is coarser than the black powder, the appearance of the mixture is dark. In other words, whenever the ratio of τ_r for ThO₂ to τ_r for W is greater than 2, the mixture is white; if less than 2 the mixture is black. [The absolute density of W (19.6) divided by the absolute density of ThO₂ (6.8) = 2].

ELECTRICAL MEASUREMENTS

The powders were pressed into rods 4 cm. long and 0.5 cm. square. They were then placed in a tungsten-hydrogen furnace and fired at 1600-1650° for 2 hrs. This firing caused the rods to sinter together and rendered them practically proof against moisture. The fired rods were kept in a P₂O₅ desiccator. The rods were then mounted between brass clamps and the resistance measured on a Wheatstone bridge with a sensitive galvanometer. Care was taken to make these measurements on days when the humidity of the air was low.¹

In view of the differences in "Color" of the various mixtures in the powdered form, it was not very surprising to find marked differences in the electrical resistances. The firing at 1600°, however, resulted in an almost uniform shade for all of the mixtures. In Table II below are recorded four of the characteristic resistance values found. In the last column are the calculated specific resistance values.

Powder	Found R ₁	Found R ₂	Calculated R ₃
ThO ₂ No. 2	11.5	11.5	11.5
Z	0.951	0.951	0.951
W No. 1	0.000	0.000	0.000

The powders, ThO₂ No. 2 and W No. 1, were pressed up into rods the same size as those for the mixtures; they were likewise fired at 1600° for 2 hrs.

¹ Compare in the connection H. J. Proctor, "Surface Resistance Insulators," *Phys. Rev.* 3, 439.

Our results tend to show that under ideal conditions of mixture relative grain size, uniform distribution, etc., the resistivity values for white mixtures such as Z would be even higher than here recorded. Similarly, the resistivity values for black mixtures such as X would be lower than those found, approaching a limiting value equal to twice that of the 100 per cent metal rod.

CONCLUSION

In general we may say that the electrical conductivity of a substance is primarily dependent upon the shape and the distribution of the fundamental grains or particles comprising the substance and secondly, upon the presence or absence of thin films of secondary material enveloping these ultimate grains.

On the basis of this theory we can account for the comparatively high conductivity of gold that contain but a trace of conducting material. We can also account for the marked difference in resistance of any two samples of commercial copper whose chemical composition is identical depending upon whether the impurity, such as sulfur, is primarily dissolved in the metal or whether it forms a film ("cement") of copper sulfide around pure granules of copper. The latter case is to be regarded, as already suggested, as an enrichment of copper in copper sulfide. The high resistance of these surface films composed of say sulfide or oxide or arsenide accounts for the high resistivity values of copper when but a trace of the impurity is present.

EDISON LAMP WORKS

11 - CLEVELAND, OHIO
1 - CLEVELAND, OHIO (BRANCH)

VARNISH ANALYSIS AND VARNISH CONTROL II—VISCOSITY OF VARNISHES

By MAX V. SEATON, H. J. PROCTOR AND G. B. SAWYER

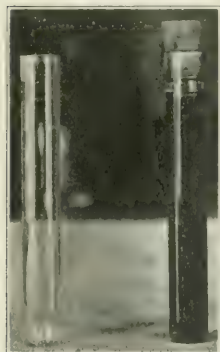
Abstracted from No. 100

The first paper of this series, entitled "Molecular Weights of Varnishes (I)," dealt with a method for determining the apparent molecular weights of oil and varnish products, and pointed out the value of such a determination. The following paper will, in the same way, deal not only with the methods found valuable for determination of the viscosity of varnishes, but will also show some of the difficulties which can be met with in the study of the viscosity of varnishes under varying conditions.

Viscosity of such products as petroleum oils has long been recognized as an important characteristic, and standard methods are specified by many manufacturers of such products. Much information has been published, both as to the viscosity of products of this type and as to the methods suitable for determining viscosities. The Bureau of Standards and the Bureau of Mines having paid particular attention to the subject, routine measurements of viscosity as a specification constant have been made for a number of commercial products, among which, greases and greasy solutions may be cited. It is only of late years that any considerable attention has been paid to the viscosity of the solutions of natural

products, but the importance of the determination is being more thoroughly recognized every day.

The physical constant which is correctly designated as the "viscosity" of a varnish has often been referred to by other names. In most common use is perhaps the term "body" of varnish, by which most varnish manufacturers mean "viscosity." Continued use of this phrase is inadvisable, however, as several writers¹ have recently used the term in designating the amount of solid material present in the varnish, and applied in this manner it is a more accurate and expressive term. The term "gravity" has also been misused by its substitution for "viscosity" and it is still used in this sense by some workers. An example of this use is seen in the phrase "gravity bottles," which is applied by many varnish makers to the small vial in which they place varnishes for observation of the viscosity by following the rate of rise of an air bubble of definite size. Such a bottle is shown in Fig. 1. It is filled with varnish to the lower of the two etched marks on the glass and the cork inserted to the upper



Empty Filled
FIG. 1. VISCOSITY TUBE FOR
VARNISH

mark, thus enclosing air of a definite volume. By inverting the bottle and following the rise of the air bubble, viscosity can be roughly judged. The varnish maker usually has a number of tubes of standard varnishes with which he compares the varnish under test. This method, crude as it is, is in a majority of the cases the only one which is used. It should be noted that the bottles usually sold for this purpose vary greatly in interior diameter so that an assortment of them will not necessarily show the same rate

of rise of air bubble in the same varnish. On this account it is necessary carefully to examine shipments of these bottles and make sure that they are of uniform size.

The use of viscosimeters of various types in the determination of varnish viscosity is coming into practice with most manufacturers. The Tagliabue, Engler and Saybolt instruments, which are familiar to all workers with petroleum products, have been used to a considerable extent. Varnish viscosity is usually determined at about ordinary room temperature. However, many varnishes are far too viscous at this temperature to flow easily through these instruments, and it is often necessary to raise the temperature very considerably before a determination can be made, often, in fact, determining viscosity at the boiling point of water. This is rather unfortunate, for, as will be shown later, the temperature coefficient of viscosity differs greatly with different varnishes. Although it is certain that by the use of any one of the viscos-

imeters noted greatly improved results can be obtained over the results secured by the use of the so-called "gravity bottle," yet these instruments are not pre-eminently suited for viscosity determinations on the general line of commercial varnishes. From the manufacturer's standpoint it is important in most cases to determine viscosity before the varnish has been filtered. Generally, at this stage it will contain a considerable amount of finely divided precipitate or "flock." In a viscosimeter which depends on the measurement of the rate of flow through a small orifice, presence of foreign material of this kind is almost sure to influence results to such an extent as to render accuracy impossible. Any instrument in which this

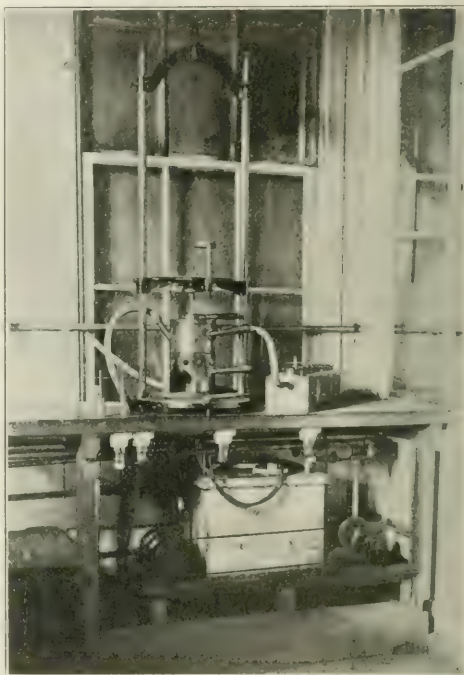


FIG. 11

defect can be avoided will thus have considerable advantage as regards accuracy. Most suitable in this respect are instruments which depend on observation of the rotation of a disk, sphere or cylinder in the liquid, as with such instruments the presence of a considerable amount of precipitate will not influence results. Among the commercial instruments which meet these requirements are the Stormer viscosimeter, the MacMichael torsion viscosimeter, and the Doolittle viscosimeter.

The Stormer viscosimeter undoubtedly has a distinct field in which it is of value, but it has not been found in this laboratory to give results as accurate as those desired in general varnish viscosity determinations, nor is it as rapid as the instrument in use by

the writers. The MacMichael instrument¹ is an interesting one. It is accurate and permits rapid working, but it has not been investigated by the writers, owing to the fact that in this laboratory electric power fluctuations are so excessive that driving the bath at a constant rate of speed would be prac-

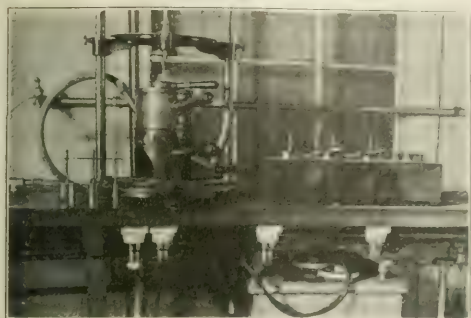


FIG. III

tically impossible. The Doolittle instrument, properly handled, is undoubtedly as accurate as either of the others and, in addition, by proper arrangement of the heating baths is capable of more rapid manipulation than the other two. All of these instruments are free from the error due to suspended flock, and are also capable of giving results on varnishes of widely varying viscosity.

In order to make viscosity of value as a routine determination, it is necessary that the methods employed shall admit of obtaining results with great rapidity. To this end, the apparatus shown in Fig. II and III has been devised in this laboratory. The viscosimeter employed is a standard Doolittle instrument in which the retardation of the rotation of a cylinder of standard size, immersed in the varnish, is noted while this cylinder is swinging under the driving force of a twisted steel wire. As the temperature of this laboratory is often very high during the summer months, and as maintenance of cool baths is always difficult, a standard temperature for viscosity determination has been set considerably above any normal room temperature, and yet not high enough to cause serious error when varnishes possessing different viscosity temperature coefficients are examined. This temperature is 40°C . Many varnishes are so viscous at this temperature that the standard cylinder of the Doolittle instrument, which is 1.2 in. in diameter, cannot be used. In such cases smaller cylinders, either 1 or 1/2 in. in diameter, are substituted for the larger one, and the results thus obtained expressed in terms of viscosity on the standard cylinder by reference to comparative viscosity tables obtained between the different cylinders.

It requires between 10 and 15 seconds for the varnish contained in the small cup of the instrument to come to the proper temperature after being drawn off the length of time would, of course, make viscosity

determinations rather slow. To avoid this difficulty, the viscosimeter is connected, as is shown in Fig. III, with a constant temperature bath which is arranged to supply to the water bath of the instrument a rapid current of water at the unvarying temperature of 40°C . This bath consists merely of a galvanized iron tank, holding about 40 liters of water, and containing several electric heating elements regulated by means of a mercury-toluene regulator through suitable relays. The water is circulated from this bath, placed on a shelf below the viscosimeter, by means of a small centrifugal pump. After passage through the water bath of the instrument proper, the water goes to the varnish preheater, shown to the right in Fig. III. This consists of a long narrow copper box having 4 holes in the cover of a size sufficient to hold a viscosity cup. With 5 cups in use it is possible to fill and place 4 in the preheater and 1 in the main bath of the viscosimeter. As fast as a determination is finished the cup can be emptied, cleaned, refilled with cold varnish and placed in the preheater in the opening previously occupied by the cup which is now removed for viscosity determination. With occasional stirring the cups in the preheater come to constant temperature in 15 minutes. By this method a cup is ready for the operator every 4 or 5 mins. and an experienced man can make a large number of determinations in an hour.

The results of viscosity determinations made with the Doolittle instrument are usually expressed as "degrees of retardation," which factor is read off directly from the revolving disk which is divided into 360 parts. Viscosity is expressed in these terms throughout this paper. In published viscosity tables Doolittle viscosity will often be found expressed in terms of grams of sugar. The factor necessary for transference to this system is obtained during standardization of the viscosimeter. This is done by means of sugar solutions of various percentages. Such a standardization curve is shown in Fig. IV. By use of

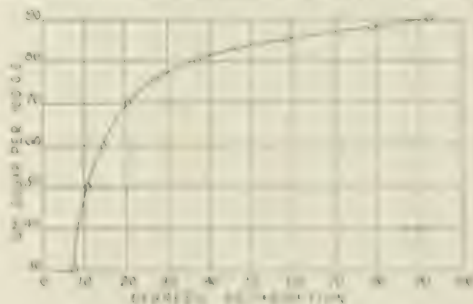


FIG. IV. Standardization curve.

this curve and the reference to the figures published in such a work as "The Analysis of Varnishes" published by the Doolittle instrument can be converted into those common to the Saybolt-Viscometer or any other viscometer.

Determination of the presence of transition would

be valuable if for nothing else than as a method of insuring a material of constant properties. It is very desirable that successive shipments of commercial varnishes leaving the manufacturer possess as closely as possible the same general physical properties, especially as regards to working under the brush. Viscosity plays a very important part in determining this characteristic.

Accordingly, in this laboratory, and in several others, the viscosity of each tank of varnish is determined before shipments are made, and a rigid viscosity specification is adhered to. The greater part of the value of viscosity determinations is lost, however, if only this feature of the determination is seen. The fact is that careful study of viscosity gives probably more information as to the nature of the varnish itself than any other single constant. However, in order for a viscosity determination to be of most value it is necessary that a close understanding and cooperation exist between the manufacturing and testing departments, with a full knowledge in both departments of what changes in viscosity in one direction or another may mean. To this end it is almost essential that a record of the heats used in varnish practice be obtained and compared side by side with viscosity

be traced to a change in the character of the colloids present.

It is fortunate that the colloidal material is usually found in the emulsoid form, for emulsion type colloids possess characteristics so radically different from those found in true solution that it is possible to distinguish fairly readily between the two types. Emulsoids, for example, in certain concentration ranges, vary their viscosity tremendously with slight increase in concentration. It is also usually possible by suitable means to change their degree of dispersion, and whenever such a change can be produced the viscosity of the varnish will vary considerably. Ostwald, Freundlich, Zsigmondy, and other writers have pointed out that colloids of the emulsion type possess abnormal temperature coefficients of viscosity. With a colloid of definite concentration the temperature coefficient may be either higher or lower than would normally be expected in a true solution of about the same percentage composition. The curves in Fig. V show the change in viscosity with temperature of three varnishes which are probably representative of the true solution type. They are, in other words, very high in soluble gum and low in polymerized oil. One of these curves, for example, is that of an ordinary

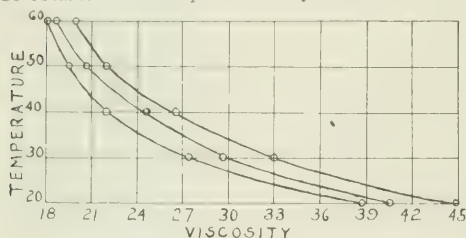


FIG. V—VARNISHES OF TRUE SOLUTION TYPE

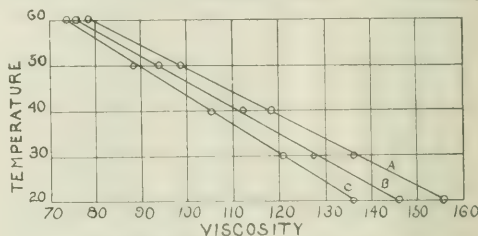


FIG. VI—VARNISHES OF COLLOIDAL TYPE

figures. Such a record is available when, as in many progressive plants, an automatic recording electric resistance thermometer or pyrometer installation is in use. By study of such temperature charts together with investigation of the viscosity characteristics of the varnish produced, it has been found possible in every case not only to discover abnormal conditions but also to predict methods for remedying them rapidly and efficiently.

In considering the viscosity of a varnish we must realize that we are dealing with a material which represents two types of solutions, *viz.*, *true* and *colloidal*. As far as can be judged at present all varnishes contain material of both types, and the viscosity of the complete varnish will be a combination of the viscosity effects produced by the constituent materials. It is interesting to note, also, that the colloids may be of two different types which differ radically in their viscosity characteristics, that is, they may be suspensions, which possess a viscosity very little higher than that of the dispersion means, or emulsoids, the viscosity of which may be very great indeed. The changes in viscosity of varnishes which are found to occur on ageing or which develop to an abnormal extent after the addition of some solvents can usually

rosin gloss oil which does not exhibit colloidal properties. The shape of the viscosity temperature curves should be particularly noticed and the resemblance between the three observed. Fig. VI, on the other hand, shows three varnishes which can be fairly safely said to be colloidal in nature. For example, the varnish represented by Curve A shows the Tyndall effect very markedly, that is, it is strongly opalescent when a beam of light is passed through it, although the individual particles in this particular sample cannot be distinguished by the ultramicroscopic methods available in this laboratory. In the case of this varnish and of those represented by Curves B and C, which are known to contain highly polymerized oil, it will be seen that the viscosity temperature curve is practically a straight line. The method, then, of determining viscosity of a varnish at various temperatures and plotting the results obtained, will often give information as to the nature of the varnish solution.

The writers on colloids, quoted above, also show that change in degree of dispersion of the dispersed phase influences the viscosity of emulsoids in a radical way, viscosity in general rising with decrease in the degree of dispersion. We would predict, therefore, that if we add to the varnish, which is in this case a

colloid of the emulsion type, a true solvent for the dispersed phase, which in other words would increase its degree of dispersion, viscosity would be lowered. Such solvents are found in substances such as rosin acids or acid linseed oil, which will hold in true solution considerable amounts of the highly polymerized oils which occur in varnishes. The radical change which occurs when such a product is added to the varnish containing colloidal material soluble in such a substance, is shown in Fig. VII. Curve *A* indicates the change in viscosity produced on an overcooked wood oil varnish which undoubtedly contains a considerable amount of colloidal material, while Curve *B* shows the very slight effect produced by the same addition on a varnish of more normal composition. This method of addition of a solvent for polymerized products followed by observation of the change in viscosity can furnish a great amount of information as to the physical nature of the varnish solution which, in the belief of the writers, is even more responsible for the practical

is of value to the manufacturer is an observation of the changes which occur during ageing. The meaning of the complex changes which occur has always been obscure as the change in the usually determined constants was not sufficient to account for the radical differences observed in brushing, drying and luster. Observations of varnishes of radically different types during ageing periods of many months, and in some cases, years in this laboratory, have indicated that in many cases the changes in properties must be due to a gradual change in the degree of dispersion of the colloidal material present. A typical example of this is found in a black baking japan which when incorrectly cooked rose from an original viscosity of 83 to a final viscosity of 110 in one month. This heavy material was greatly reduced in viscosity by the addition of some rosin solution, which is a solvent for the asphalt used. The presence of asphalt in colloidal solution is indicated, and the gradual change in degree of dispersion is undoubtedly the cause for the constantly

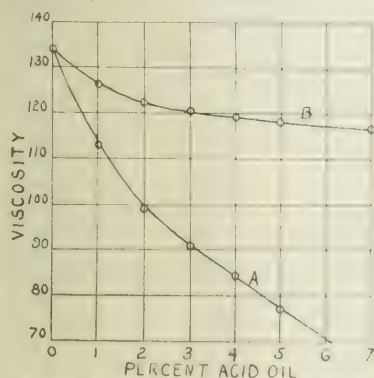


FIG. VII. EFFECT OF ACID LINSEED OIL ON VISCOSITY OF TWO COLLOIDAL VARNISHES

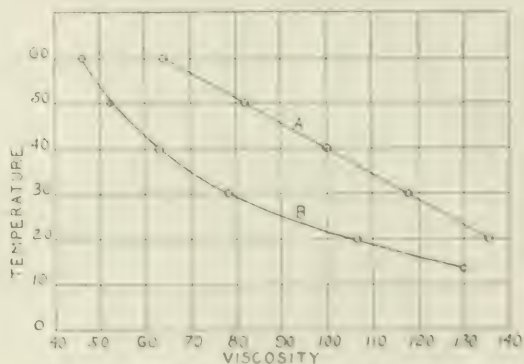


FIG. VIII. VISCOSITY TEMPERATURE CURVES OF A VARNISH BEFORE AND AFTER ADDITION OF LITHOGRAPHIC LINSEED OIL

service characteristics of the varnish than is the actual chemical composition of the products occurring in it.

We have assumed above that addition of a suitable solvent might be expected to change the type of solution existing in the varnish, that is, from colloidal to true solution, and we have previously indicated the difference in the temperature viscosity curves exhibited by the two types of varnish. A simple proof is at hand, then, as to the nature of the change we have produced in Varnish *B* of Fig. VII. We can take the temperature coefficient of viscosity of this varnish before and after adding active thinner. If our theory is sound, we shall expect the viscosity-temperature graph to be a straight line before the addition, but to be curved after the thinner has been added. That this is actually the case is shown in Fig. VIII, where *A* is the viscosity-temperature curve of the varnish before any addition, and *B* that after addition of acid linseed oil has been made. This is, we believe, a fairly definite proof of the existence of colloidal solutions in varnishes of this type, and of the change which can be produced by the use of active thinners.

One other feature of viscosity measurements which

increasing viscosity. A slight change in the method of manufacturing gave a product which fell from a viscosity of 91 to one of 71 during one month, at which point the viscosity remained constant. The second material showed little change in viscosity when additional active solvent was added.

Another example of the type of change which we assume, that is, increase or decrease in degree of dispersion, is found in an emulsion type of the viscosity of lithographic linseed oil during ageing. It is possible by proper treatment to produce oils which will either increase or decrease in viscosity. One sample, for example, had an original viscosity of 91 which fell to a point of 71 (instead of one month and remained at that figure for some time). A somewhat different type of oil of about original viscosity of 91 had a value of 76 in one month, at which point it remained constant. The second oil had considerable more active solvent than the first and would not be too subject to change in a point of several values. However, it should be noted that even the period of ageing of two samples changed, giving such a large amount of product of an engine, running under stress,

the viscosity remained approximately constant, rising only three points during a further three months' ageing. The changes in other physical and chemical characteristics which accompany this interesting viscosity change in lithographic lined oils are being further investigated and additional information will be published as soon as the results are complete.

With many varnishes very great viscosity changes occur during the first 24 hrs. Surprise has often been expressed that a batch of varnish, a sample from which was removed and tested when hot, did not have the proper viscosity when the entire batch had cooled, say about 24 hrs. later. A sample removed from a fresh batch and cooled rapidly almost invariably shows a much lower viscosity than one taken later when the entire batch has fallen to room temperature. This is undoubtedly merely an extreme case of the general phenomena which occur during the ageing of varnishes. In general a review of the ageing processes shows that with stable varnishes viscosity approaches a constant value at the end of about one month's time. If viscosity continues to rise to any considerable extent for longer than this period trouble with the varnish must be feared as it will usually be found that this increase will go on for a long time until finally the consistency of the varnish will become such as to make it unsuitable for general use.

The results quoted above have shown in a very brief way some of the values of viscosity determinations. It is not intended to intimate that these are by any means the only lines along which this determination can prove of value. They merely indicate that continued study of such factors as this can teach the varnish manufacturer the general nature of the products occurring in the various materials which he manufactures, and can also show him in what direction changes in the physical nature of the constituents will influence the practical characteristics which he is attempting to obtain. The generally recognized fact that varnish drying is closely related to the phenomena of jelly formation shows at once how important a knowledge of the nature and amount of colloidal matter present in the liquid varnish is. Study of this and other factors will end by proving the most instructive work possible and will well repay all the time and expense spent on it, as it will enable the producer to construct varnish formulas and indicate heat treatments which will give him practically any characteristic which he desires in the completed product.

RESEARCH LABORATORIES, THE ARCO COMPANY
CLEVELAND, OHIO

THE CRACKING OF AN AROMATIC BASE OIL THE TEMPERATURE FACTOR AT CONSTANT RATE UNDER PRESSURE

By GUSMAN EGGLESE AND ROBERT J. MOORE

Received November 10, 1916

The greatly increased demand for the aromatic hydrocarbons, benzene and toluene, due to their use in explosives and dyes, has led to a systematic review of their sources with the object of obtaining new or greater yields of these two fundamental sub-

stances in the production of picric acid and trinitrotoluene, and the varied dye compounds. This activity towards increased efficiency in method and better utilization of by-products, although fostered by present immediate demands brought on by war conditions, has nevertheless been in accord with the ideals of conservation of resources, lately taking root in our American industries. A number of communications for the production of the above-mentioned hydrocarbons from paraffin and naphthene base oils have already appeared.¹ In the present paper the formation of benzene and toluene from an aromatic base oil—solvent naphtha—at temperatures from 500 to 800° C. at the rate of oil flow of 15 gals. per hr. and 11 atmospheres pressure has been studied. These results are then compared with the percentage yields of benzene and toluene from other hydrocarbon oils.

EXPERIMENTAL PROCEDURE

The apparatus used in the following series of experiments was one which has been described in some detail.² It consisted essentially of an 8 in. diameter steel tube 11½ feet in length, gas-heated in a muffle type furnace. The temperature, pressure and rate of oil flow was controlled with care, since any change taking place in one of these factors would give widely different percentage yields of products resulting from the reaction.

The temperatures used were 500, 550, 600, 650, 700, 750 and 800° C., at a pressure of 11 atmospheres and rate of oil flow of 15 gals. per hr.; 20 gals. of solvent naphtha were used in each experiment.

The analyses of the recovered oils for their benzene and toluene content were made by means of fractional distillation in a Hempel column, specific gravity determinations and nitrations of the fractions. Three hundred cc. of the oil were distilled to 170° C. This cut was redistilled to 105° and 105 to 135°. The cut to 105° redistilled to 95°. This 95° cut was the benzene fraction. The residue from this distillation was then added to the 105 to 135° cut. The latter fraction, 105 to 135°, was in turn redistilled from 95 to 120°. This cut represented the toluene. The benzene was further determined as the dinitrocompound, and the toluene as trinitrotoluene.

TYPE OF OIL USED

The oil used in the following experiments was one derived from the thermal decomposition of coal, and was the cut known as solvent naphtha. The solvent naphtha gave upon sulfuric acid treatment only a slight yellow-lemon in the acid layer. The per cent of *o*-, *m*-, and *p*-xylenes was 70 per cent; the other 30 per cent was composed of higher methyl and isopropyl derivatives of benzene. A trace of naphthalene was also present and was detected as a white solid at the end of the condenser at the completion of the distillation. The melting point of the naphthalene was 79.8° C.

¹ Egloff, *Met. & Chem. Eng.*, **15**: 1916, 125; Egloff, Twomey and Moore, *This Journal*, **8**: 1916, 1102; Egloff and Twomey, *J. Phys. Chem.*, **20**: 1916, 597; *Ind. & Met. & Chem. Eng.*, **15**: 1916, 523.

² Egloff and Twomey, *Met. & Chem. Eng.*, **16**: 1916, 15.

The distillation analysis (Table I) was made by means of a Hempel distilling head and conducted at the rate of 2 drops per sec. at the end of a 24 in. Liebig condenser. The sp. gr. of the oil and fractions were taken by means of a Westphal balance at 15.5° C.

TABLE I
DISTILLATION ANALYSIS OF OIL USED
Specific Gravity 0.868/15.5° C.

Temperature ° C.	Per cent by Vol.	Specific Gravity
135 to 145	70.1	0.866
145 to 160	15.0	0.869
160 to 170	12.0	0.869
170 to 183	1.6	
Loss	1.3	

THE RECOVERED OILS—The general phenomena of the thermal decomposition of hydrocarbons is to give a lower percentage yield of recovery of the starting oil with increase of temperature. A temperature change from 500 to 650° changed the percentage yield only 2 per cent, whereas a similar change of 150° (650 to 800°) gave a decomposition of 39.3 per cent (Table II). The greatest decomposition took place between temperatures of 700 and 750°, where a percentage change of 25 per cent is to be noted.

TABLE II
PERCENTAGES BENZENE AND TOLUENE
Basis of Recovered Oil

TEMP. ° C.	RECOVERED OIL Per cent	Sp. Gr.	Benzene Per cent	Toluene Per cent	Benzene Per cent	Toluene Per cent
500	100	0.868	0.0	0.0	0.0	0.0
550	99.5	0.875	1.4	6.5	1.3	6.4
600	99.0	0.878	1.6	8.0	1.5	7.9
650	98.0	0.901	2.4	13.0	2.3	12.7
700	76.6	0.925	8.0	23.3	6.1	17.8
750	51.6	0.940	19.1	39.9	9.8	20.6
800	37.3	0.989	42.5	17.3	15.9	6.5

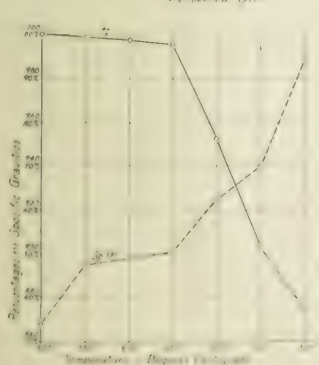
The specific gravity of the recovered oils increased with increase of temperature, which indicated the formation of polycyclic aromatic hydrocarbons of

have been formed at a lower temperature in greater quantities. The toluene formation from the starting oil at temperatures from 550 to 750° shows a higher percentage yield than benzene, while a change of 50° between 750 to 800° shows a percentage increase of benzene of 23.4 per cent and a drop of toluene formation of 22.6 per cent, this drop of 22.6 per cent of toluene formation clearly forming part of the 23.4 per cent increase of benzene formation. This phenomenon gives added experimental evidence as to the course of the aromatic hydrocarbon reaction; in short, the higher alkyl derivatives of benzene of the dimethyl, trimethyl and isopropyl groups, go to toluene and toluene to benzene.

The percentage yield of benzene at 500° was zero and with increase in 50° increments, gave a maximum of 42.5 per cent at 800°. The formation of toluene reached a maximum of 39.9 per cent at 750° and decreased to 17.3 per cent at 800° during a change of 50°. The data have been graphically shown in Fig. 2, which indicates the smoothness of the curve for benzene formation, while a sharp break is to be noted for toluene formation at 750°.

BENZENE AND TOLUENE AS THE BASIS OF OIL FOR PRODUCTION—Upon the basis of 100 gals. of oil used, the percentage yield of toluene, within the limits of practical experimentation, exceeds that of benzene by 4.7 per cent (Table II). The maximum yield of 20.6 per cent of toluene occurred at 750°, whereas at 800° benzene showed a maximum of 42.5 per cent. The critical temperature of maximum formation for toluene occurs between the tempera-

Fig. 1 Percentages and Specific Gravity of Recovered Oil



high molecular weight. The specific gravity changed from 0.868 at 500° to 0.989 at 800°. The data are expressed graphically in Fig. 1.

BENZENE AND TOLUENE IN THE RECOVERED OILS—In the thermal decomposition of hydrocarbons, the formation of benzene apparently invariably increases at a more rapid rate in the recovered oil than toluene, particularly at the higher temperatures (Table II). This is no doubt due to the decomposition of the higher alkyl derivatives of benzene which

Fig. 2 Benzene and Toluene Formation



Fig. 3 Benzene and Toluene Formation



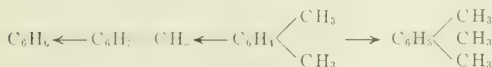
form of 1,2,3,4,5,6-hexamethylbenzene, these temperatures limits a drop of 22.6 per cent of toluene may be noted. This fact indicates the temperature control necessary before aromatic compounds are required for a particular hydrocarbon. A slight increase in the percentage yield of toluene in the case of oil used for production, as is noted in Fig. 2.

In the recovered oil, benzene content is higher than toluene, but, when the temperature increases, the

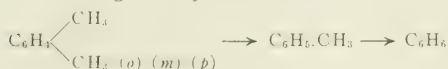
oil is taken into consideration, the conditions reverse and toluene reaches a higher percentage yield, when taken on the basis of oil required for the production of benzene and toluene.

MECHANISM OF THE REACTION

In the thermal decomposition of paraffin and naphthene base oils the mechanism of the reaction is very complex and not thoroughly understood at the present time. But with an aromatic base oil of the type utilized in the present series of experiments the mechanism of the reaction is relatively simple. The course of the reaction has been already worked out in the case of the effect of aluminum chloride upon the methyl derivatives of benzene as the xylenes, trimethyl benzenes and higher derivatives. Anschütz and Immendorff,¹ and Jacobsen² found the following reaction taking place in general when xylene and aluminum chloride reacted:



No quantitative yields are noted in the above experiments. In the present communication, dependent upon the temperature, the percentage yields of benzene and toluene varied. Now since the starting oil was composed mainly of alkyl derivatives of benzene of the methyl group, the course of the reaction was found to go mainly in the direction of:



From two entirely different methods it has been shown that the mechanism of the reaction is essentially as shown above.

DISCUSSION OF RESULTS

The aromatic base oil, solvent naphtha, is without question the most satisfactory oil for the production of benzene and toluene yet studied. In comparing the percentage yields of benzene and toluene from the solvent naphtha, with a paraffin and a naphthene base oil (Table III), an increased yield of benzene of 140 per cent, and, for toluene about 350 per cent, is to be noted.

TABLE III

	PARAFFIN OIL (a)		NAPHTHENE OIL (b)		AROMATIC OIL	
	Per cent Temp. by Vol.	° C.	Per cent Temp. by Vol.	° C.	Per cent Temp. by Vol.	° C.
Benzene	6.6	750	7.2	650	15.9	800
Toluene	4.5	650	6.0	650	20.6	750

(a) Eglöf, Treumay and Moore, *Met. & Chem. Eng.*, **16** (1916), 523.
(b) *Ibid.*, **16** (1916), 387.

Solvent naphtha after thermal decomposition gave a clean water-clear benzene and toluene which lend themselves readily to the formation of phenol or picric acid, and the trinitrotoluene nitration can readily be conducted by the one-step process giving a water-washed trinitrotoluene, with a melting point of 79 to 80° C.

Solvent naphtha opens up a prolific source for benzene and toluene formation, simple to make and of a high degree of purity.

¹ *Ber.*, **17** (1884), 2816.

² *Ibid.*, **18** (1885), 338.

SUMMARY

I—The aromatic base oil, solvent naphtha, has been thermolized at temperatures 500, 550, 600, 650, 700, 750 and 800° C. for the production of benzene and toluene at a pressure of 11 atmospheres and constant rate of oil flow of 15 gals. per hour.

II—In the recovered oil the maximum percentage yield for benzene was 42.5 at 800°, and for toluene 39.9 per cent at 750° C.

III—Upon the basis of 100 gals. of solvent naphtha used the maximum percentage for benzene was 15.9 at 800° and for toluene 20.6 per cent at 750° C.

IV—The mechanism of the reaction from the thermal decomposition point of view is the same as of the reaction of aluminum chloride upon alkyl derivatives of benzene.

Higher → Lower Alkyl Derivatives of Benzene

→ Toluene → Benzene

V—A comparison of the percentage yields of benzene and toluene upon the basis of oil used from a paraffin, naphthene and aromatic base oils, under maximum conditions has been made.

DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY
NEW YORK CITY

THE ANALYSIS OF ANTIMONIAL LEAD

By C. R. McCABE

Received September 11, 1916

The alloy known as antimonial lead contains some 80 to 90 per cent lead. The remaining percentage consists of antimony and tin, the former usually predominating.

For the analysis of this alloy, the writer has found the method of D. J. Demorest,¹ with modifications, very serviceable. The difficulty encountered in applying Demorest's method to this alloy lies in the occlusion or adsorption of antimonious sulfate by the precipitated lead sulfate. A mere decomposition of the alloy by concentrated sulfuric acid leaves the lead sulfate so heavily contaminated that it is discolored, and the error introduced is too serious for any degree of approximation which may be accepted in technical work. In the modified procedure to be described, the purification of the lead sulfate requires only a few additional operations which occasion little delay; otherwise the method is essentially that of Demorest.

The successive steps of the procedure are as follows:

- (1) The alloy is wholly dissolved in a liberal excess of concentrated sulfuric acid.
- (2) The solution is diluted, whereby lead is precipitated as sulfate in a more pure condition than when the alloy is merely decomposed.
- (3) The solution is boiled, which operation further purifies the lead sulfate. Tin is now wholly in solution in the tetravalent form. Antimony is in the trivalent condition and the greater part of it is in solution; however, the lead sulfate still retains antimonious sulfate corresponding to some 7 to 15 mg. antimony per gram of alloy taken.
- (4) The solution is filtered and the filtrate set aside.
- (5) The lead sulfate is dissolved in ammonium

¹ *This Journal*, **5** (1913), 842.

acetate and reprecipitated with sulfuric acid. Antimony is now wholly in solution.

(6) The solution is filtered. Lead is determined as sulfate; antimony is determined in the two filtrates separately by titration with potassium permanganate and equivalent ferrous solution; tin is determined in the first filtrate by the iron reduction and iodine titration method.

PROCEDURE—Weigh 1 g. of the alloy into a 300 cc. flask and add 50 cc. concentrated sulfuric acid. Heat strongly over a bare flame until the alloy is dissolved. Boil 5 minutes after solution is complete in order to oxidize the tin. Only an insignificant quantity of separated sulfates should be visible.

Allow the solution to cool and precipitate the lead as sulfate by the addition of 50 cc. of water. Boil 10 minutes, allow to cool somewhat and again add 50 cc. of water. Shake and let the lead sulfate settle.

Fit an asbestos blanket not less than $\frac{1}{4}$ in. thick in a Gooch crucible, ignite strongly, cool in a desiccator and weigh. Through this crucible filter the supernatant solution, decanting carefully from the lead sulfate. Wash lead sulfate and every part of the inside of flask twice with water, using 25 cc. each time. Decant from lead sulfate and pass the washings through the filter. Transfer the filtrate to a 600 cc. beaker.

Dissolve 10 g. of ammonium acetate in 50 cc. of water. Pour this solution into the flask containing the lead sulfate, washing down the sides carefully. Shake the flask, warming slightly, until the lead sulfate is dissolved. Add 25 cc. of concentrated sulfuric acid, shake, and let the lead sulfate settle 5 minutes.

Filter through the Gooch crucible, bringing the lead sulfate into the crucible with water. Fill the crucible once with water and exhaust thoroughly. Dry the crucible containing the lead sulfate in an oven at 120° C., ignite over a low Bunsen flame 5 minutes, cool in a desiccator and weigh. The increase in weight $\times 68.3$ = per cent Pb.

To the first filtrate add a liberal excess of $N/10$ potassium permanganate solution. Titrate the excess with equivalent ferrous sulfate (or ferrous ammonium sulfate) solution. The end-point is reached when a drop discharges the last shade of permanganate color.

The small amount of antimonious sulfate in the second filtrate is titrated in the same manner. From the total amount of $N/10$ potassium permanganate solution required, deduct 0.3 cc. The difference $\times 0.006 \times 100 =$ per cent Sb.

Add 25 cc. concentrated sulfuric acid to the filtrate, the total volume now amounting to not more than 300 cc. If antimony in the filtrate is less than 0.16 g. sufficient pure antimony is gradually dissolved in the sulfuric acid to make the total amount about 0.16 g.

Place about 1 g iron (nails) in 100 ml of the solution and heat until the iron is nearly dissolved. Add 150 cc. water, cool, filter through a filter, wash with water, and wash with dilute 1% sulfuric acid. Wash the reduced iron with the standard sodium sulfate solution.

liquor as an indicator. The end-point is reached when a blue color is developed which does not perceptibly fade in two minutes.

To standardize the permanganate solution, dissolve 0.20 gram pure antimony in 25 cc. concentrated sulfuric acid; cool, dilute to 200 cc. and titrate the antimonious sulfate in the same manner as in a determination. The derived factor for the permanganate should agree closely with the theoretical.

The iodine solution is prepared and standardized as follows: Place 25 g. potassium iodide and 10.67 g. pure iodine in a beaker, add 25 to 50 cc. water and shake till dissolved. Dilute to a liter. Dissolve 0.10 g. pure tin in 75 cc. concentrated sulfuric acid, cool, dilute to 300 cc., and standardize the iodine against this solution following the procedure described for the determination. One cc. of iodine should equal 0.005 g. tin.

Some experimental results follow. The metal mixtures analyzed resemble antimonial lead. The purity of the metals used may be considered for practical purposes absolute.

	No.	1	2	3	4	5	6	7
Pro...	0.0040	0.0084	0.0091	0.0097	0.0103	0.0109	0.0115	0.0121
So...	0.0040	0.0110	0.0082	0.0082	0.0082	0.0082	0.0082	0.0082
Ph...	0.0040	0.0082	0.0082	0.0082	0.0082	0.0082	0.0082	0.0082
Pb...	0.8035	8568	9130	8523	9104	8036	8524	9074
So...	0.0093	0.0110	0.0110	0.0110	0.0110	0.0110	0.0110	0.0110
Sn...	0.0093	0.0218	0.0530	0.0252	0.0555	0.0057	0.0268	0.0544

A few typical analyses of alloys, representing routine results, follow:

Na	81	80	84	83
Fe	81	56	69	40
Sn	3.35			2.2

1. In improving the method, the following comments are best concentrated in foot-note and should not be hereafter. There were of two problems which could be fixed and no comment should be made to future readers.

While the five determinants are very convincing, it should be noted that non-satisfaction and action stopped for the most part in relation with stopped career when the organisational level was present in our questionnaire and was the consequence brought into relation previous to selection. The author's conclusion is that the career path is difficult to impact completely by action: non-satisfaction needs voluntary commitment of individual actor. Furthermore, if this is the form of such grey collective arrangement, the low self-construction capacity to react with the new fact to develop the career and to ensure the method applicability.

(1) There is a tendency for the two main arguments below to imply other, rather persuasive, conclusions. A serious student of economy is reminded to consider whether or not the fact that he is persuaded matters but not whether he is convincing for it seems he cannot be either. To push this line still further, one can consider whether one's conviction (and its evidence) for the fact is rational. After all, it is not necessary to see what the good reason would be to avoid this line. This reasoning is generalized simply by stating that it is necessary to see how one's conviction (and its evidence) about the rationality of his belief is rational. This reasoning is taken further to conclude that one's conviction is rational. Also, when the student argues, it is necessary to avoid being over-zealous, because rational persuasion can be given by. Hence, the tendency of rational belief is rational.

on proper ignition. The temperature of a Bunsen flame is necessary to complete expulsion of moisture and acid, but this must be moderate and can be safely applied only after a preliminary oven drying.

(5) Presence of the permanganate blank in the antimony titration may be experimentally shown by treating a mixture of about 0.8 g. lead and 0.05 g. tin in the manner of a determination. This blank is possibly due to empyreuma of the acetate, or traces of sulfur compounds formed in solution of the alloy.

(6) Nothing was observed in these experiments to indicate that the temperature of the solution bears any important influence in the titration of antimonious sulfate. The titrations were all made without regard to temperature, though the probable range was from room temperature to 40° C.

(7) An important precaution in the antimony titration is to add sufficient permanganate to oxidize all antimony before the back titration with ferrous solution. If an insufficient amount should be added, the color (which appears before oxidation is complete) vanishes in the usual way upon addition of ferrous solution, and thus a low result is obtained without anything to direct suspicion toward it. To guard against such an error add a drop of permanganate to the colorless solution after titration is presumably complete. The solution is colored if all antimonious sulfate is oxidized, but otherwise it remains colorless. Any unoxidized antimony thus found may be titrated and new readings taken. No impairment of the result follows this correction.

116 SOUTH JAMISON AVENUE
LIMA, OHIO

THE DETECTION OF ADDED WATER IN MILK¹

By HALSEY DURAND

The extreme variability in the fat and water content of milk has necessitated the establishment of very low standards for fat and total solids, the standard in New York being 11.50 per cent total solids, 3.00 per cent fat and 8.50 per cent solids-not-fat.

König, in *Chemie der Menschlichen Nahrungs und Genussmittel*, gives the results of 800 analyses of cow milk as follows:

	Total Solids	Fat	Solids-not-Fat
Minimum.....	9.68	1.67	8.01
Maximum.....	19.68	6.47	13.21
Mean.....	12.73	3.64	9.09

A very valuable paper has been prepared on the composition of milk by Brown and Ekroth to be presented at this meeting.

Assuming a sample of milk to be of the maximum quality, it will be seen that a large amount of water may be added and a large amount of fat removed and still be within the legal standard. From this it becomes apparent that a method for the accurate detection of added water in milk would be of the greatest value.

Two methods have been proposed, viz.:

1—The determination of the refractive index of the serum.

2—The determination of the freezing point of the whole milk.

A third method may also be mentioned, viz.: The determination of the specific gravity of the whole milk and of the serum. This method has been in use for many years.

The first method consists, without going into detail, of the coagulation of the milk by acetic acid of

known strength and the determination of the refractive index by the immersion refractometer and comparing the results with standards determined for whole and adulterated milks. This method has been very carefully tested out in the Department laboratory. It has the advantage of speed, a very important factor when a large number of milks are run each day. It has been found, on the other hand, to be unreliable for the detection of less than 10 per cent of added water which is decidedly too great a margin.

The second method, depending on the elevation (by added water) of the freezing point above the normal established for whole milk, is deserving of careful consideration. This method is incorporated in the Legal Standard for Queensland: Solids-not-fat, not less than 8.50 per cent; fat, 3.30 per cent; total solids, not less than 12.00 per cent. Its freezing point shall not be higher than 0.55° C. below zero.

The work of the department laboratory was carried on, after the method used by Henderson and Meston in their excellent article, "The Freezing Point of Milk," published in *The Chemical News*, 110 (1014), 259. It was found that the form of apparatus suggested in the above paper did not give uniform results with milk of known purity. This was found to be due to the fact that the tube in which the milk was frozen was not provided with an outer tube, to form an air jacket, and thus did not permit of a uniform undercooling. A Beckmann freezing point apparatus was substituted and a considerable number of milks were run and very good results were obtained. All results were run in duplicate as checks in such delicate work are an absolute necessity. In the writer's opinion, the method is an excellent one, but requires the most careful manipulation and constant attention, in the preparation of the freezing mixture, the degree of undercooling, the stirring and the setting of the thermometer. The great objection to this method is the length of time required for its completion. In the Department laboratory it was found that the average time required for a duplicate determination was not less than 45 minutes, a time which would render the method impossible for a routine laboratory.

The fact that the serum of whole milk is constant having been established, by the foregoing methods, the writer has sought for a rapid and trustworthy means of determining changes brought about by the addition of water.

The first method tried was the addition of a weighed amount (3 g.) of anhydrous lead subacetate, the reagent used in Horne's method for sugar analysis, to 100 cc. of milk, filtering the clear serum from the coagulum and the precipitation of the lead dissolved by 25 per cent sulfuric acid with addition of alcohol. The lead sulfate is then filtered in an alundum crucible, washed with alcohol, ignited and weighed. It was conjectured that the serum being constant, a definite amount of lead subacetate would be dissolved, and that this amount would be increased by the addition of water. This proved to be the case, but the results were unsatisfactory as the filtration was very slow and even after a number of washings an amount of soluble pro-

¹ Presented at the Annual Meeting of the American Chemical Society, New York City, September 17, 1916.

tein was retained by the precipitate, which resulted in a reduction of the lead sulfate. The same result was obtained on using 3 g. of normal lead acetate.

The second method tried was the addition of 2 g. of finely divided silver nitrate to 100 cc. of milk and the determination of the silver dissolved in an aliquot part of the serum, by titration with $N/10$ thiocyanate solution, using ferric alum as indicator. This method has proved very satisfactory as far as rapidity is concerned, but a sufficient number of determinations has not been made as yet to establish its applicability.

A third method has suggested itself to the writer; *viz.*, the coagulation of the milk by non-electrolytes, such as saccharin, rennin, etc., and by electrolytes, such as lead acetate, silver nitrate, etc., and the determination of the electrolytic conductivity of the sera thus obtained. As the proper apparatus is not at present available, this investigation has not been undertaken. It is the intention to perform these experiments in the near future, with the belief that the problem may be solved in this way, and a rapid and accurate method for the determination of added water in milk be established.

DEPT. OF HEALTH, E. 16TH STREET
NEW YORK CITY

THE UTILIZATION OF OLIVE POMACE

By W. V. CRUSS AND A. W. CHRISTIE

Received November 9, 1916

In the manufacture of olive oil in California, it is estimated that approximately 4,000 tons annually of pomace remains after pressing. Most of this is wasted, although it is generally known to contain appreciable quantities of oil, and has been thought to have some fertilizing value.

OLIVE CONTENT OF OLIVE POMACE. Samples of olive pomace from a number of olive oil factories were analyzed for moisture and oil. The oil was determined by ether extraction of the dried samples. Later results have shown that ether also dissolves a waxy alcohol known as "oleanol." This is not soluble in gasoline, apparently the most practical solvent for commercial use, and therefore the oil percentages found are slightly higher than the amounts that could be recovered by treating the pomace with gasoline.

The per cent of oil in 18 different samples varied from 7.89 to 20.23 per cent, or from 149.8 to 4161 gals. total oil per ton of pomace. The lowest percentages were found in the pomace from factories equipped with up-to-date grinding and pressing machinery, while the pomace from factories using old style machinery was in most cases high in oil. Since factories with modern equipment are producing the main bulk of the oil, it is probable that the average of 12.41 per cent (11.18 gals. per ton) is too high for the whole state. The average oil content of the pomace from the best equipped plants is 10.22 per cent, a figure which can probably be taken as a maximum average. This corresponds to 2.12 gals. per ton or to approximately 100,000 gals. annually for the whole state. At the price paid for ordinary pump oil, 8 to 12 c. per lb. or 60 to 80 c. per gal., it can be seen

that the recovery of this oil is a matter of considerable importance.

PREPARATION OF POMACE FOR OIL EXTRACTION. It has been found, in the commercial extraction of olive pomace, that the material must be fairly dry to give satisfactory yields. Where time is not important, the pomace may be satisfactorily dried by spreading it out in the sun. The objection to air- or sun-drying is that mold growth develops, destroys oil by oxidation, and produces free acid by hydrolysis. A higher grade of oil and a greater yield could probably be obtained from pomace dried artificially immediately after pressing. The pomace used in the experiments given below was air-dried, no special care being taken in drying to prevent molding.

CHOICE OF SOLVENT.—For commercial use, the solvent must be cheap and easily recovered by distillation. If any great quantity of solvent is lost by volatilization, the cost of production may be prohibitive. On this account, petroleum ether and ordinary ether are not suited to the purpose. Chloroform, ether, carbon bisulfide, and carbon tetrachloride are objectionable because of their poisonous nature. Benzol is a suitable solvent, but is considerably more expensive than gasoline. Gasoline is the cheapest available solvent and has been found to give satisfactory results. Under certain conditions, however, benzol would probably be chosen.

NUMBER OF EXTRACTIONS NECESSARY. To determine the number of extractions necessary to recover most of the oil from air-dried pomace, weighed amounts of pomace were treated with 5 successive measured portions of gasoline, ligroin, and benzol, the amount of oil extracted each time being determined. The amount of solvent used was just sufficient to cover the pomace. The pomace was left in contact with the solvent in closed Mason jars, 2 hours for each extraction, making a total of 10 hours for the 5 extractions. The solvent was strained off after each extraction, filtered and distilled. The amount of oil from each lot was determined by weighing the residue after distillation.

TABLE I.—AMOUNTS OF OIL EXTRACTED BY FIVE SUCCESSIVE EXTRACTIONS OF OLIVE POMACE

EXTRACTION NUMBER	Gasoline		Ligroin		Benzol		Sum of Oils	
	Ex. 1	Ex. 2	Ex. 1	Ex. 2	Ex. 1	Ex. 2	Ex. 1	Ex. 2
1	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
2	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
3	0.07	0.2	0.2	1.20	0.81	0.8	0.91	2.43
4	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.0
Total	1.07	2.2	2.20	3.2	2.81	2.8	2.91	3.43

It is evident from the data contained in Table I. that more than one extraction of pomace that had been extracted with gasoline, 2, 3, 4 and 5 times, respectively. From results as well as those in Table I. indicated that 4 extractions with gasoline practically exhausted the pomace of its oil soluble in this solvent. The last extraction, No. 5 contained more oil than No. 4, due to the difficulty in getting off the gasoline solvent in the same degree in each case.

The yields by gasoline and ligroin were practically the same. The difference observed is that of the losses

being probably within the experimental error. The large yield with benzol is due to its dissolving "oleanol," which is insoluble in the other solvents.

COMPOSITION OF SOLVENT OIL—The solvents were separated from the oil by distillation and the residual oils were analyzed. In Table II are given the analyses of these oils, an oil extracted commercially, and a sample of normal California oil made by the usual pressure

TABLE II. COMPOSITION OF OIL EXTRACTED FROM OLIVE POMACE COMPARED WITH THAT OF OIL OBTAINED BY PRESSING

SAMPLE No.	EXTRACTION BY	Sapon. No.	Per cent Sapon. ifiable	Sp. Gr. 15.5° C.	Free Acid as Oleic Per cent
1	Pressure	189.2	100.0	0.905	0.16
2	Gasoline, Commercially	173.8	91.8	0.903	11.77
3	Ligroin, in Laboratory	182.9	96.4	0.899	36.58
4	Gasoline, in Laboratory	163.2	86.0	0.890	64.63
5	Benzol, Distilled at 100° C.	127.1	52.0	0.866	52.00
6	Benzol, Distilled by Free Flame	175.0	92.3	...	73.40

(a) Based on Normal Olive Oil as 100 per cent.

method. The solvent oils were found to contain less saponifiable matter than pure olive oil and hence their value for soapmaking is correspondingly less. But the differences between the pure olive oil and the solvent oils in this respect are not great, the poorest solvent oil having 86 and the best solvent oil 96 per cent as much saponifiable matter as the pure oil.

The free acid in the extracted oils was very much higher than in normal olive oil. This is due to two factors: Mold growth decomposes the oil in the pomace, giving free oleic acid, and the oil is "cracked" or decomposed into the free acid and glycerin during the heating necessary to distil off the solvent.

Decrease in saponification number of the oils was accompanied by decrease in specific gravity due to increased amount of solvent present.

The quality of the solvent oils was considered satisfactory by soap manufacturers for ordinary grades of soap and soap powders.

RECOVERY OF SOLVENT FROM POMACE—It required 600 cc. of gasoline to cover 400 grams of pomace in a Mason jar. Of this, only 475 cc. could be recovered by draining off the gasoline from the pomace. Attempts were first made to distil off the gasoline by placing the pomace in boiling water or in a current of steam. Both methods were unsatisfactory.

The pomace was then placed in a small copper retort heated by a direct gas flame. The distillation was continued until white fumes began to appear through the condenser. This indicated that all of the gasoline and moisture had been distilled over and that decomposition of the pomace itself had commenced. Practically all of the gasoline was recovered by this distillation. The method is easy to apply and does not require elaborate apparatus.

OLIVE POMACE NOT A FERTILIZER The possible use of olive pomace for fertilizing purposes has been suggested and in fact it has already been so used in some localities to a limited extent. It is well known, however, that the availability of fertilizers, such as fish meal, garbage tankage, etc., is increased by extraction of the oil and fat, thereby making possible more rapid decomposition when applied to the soil. In order to determine the value of olive pomace as a fertilizer, samples before and after extraction of the oil by gasoline

were analyzed for phosphoric acid, potash, and nitrogen with the following results:

AIR DRY SAMPLES USED	Per cent K ₂ O	Per cent P ₂ O ₅	Per cent N
Non-extracted Pomace.....	0.24	0.12	0.86
Extracted Pomace.....	0.26	0.14	1.00

Owing to the removal of the oil, the extracted pomace is found to be slightly higher in fertilizing constituents. The amount of phosphoric acid is no greater than is found in average California soils. These soils contain several times more potash than does olive pomace. Hence the addition of olive pomace to the soil would actually decrease the percentage of these elements in the soil. Furthermore, since the potash and phosphoric acid are combined with the organic material of the pomace, they could not be assimilated by plant roots until such time as decomposition in the soil had released these elements in the water-soluble form required by plants. Therefore, no commercial value as a fertilizer is to be assigned to the potash and phosphoric acid in olive pomace. Tests were made on the extracted and non-extracted pomace by the usual "beaker" method for determining ammonification and nitrification. After two months only very slight gains in ammonia nitrogen were found and no increase in nitrate nitrogen could be detected. In fact, the soils to which pomace had been added showed less than half as much nitrate nitrogen as the untreated soil, indicating that the presence of the pomace had induced denitrification. The extracted pomace gave no better results than the non-extracted. Hence we see that the nitrogen in olive pomace is very unavailable and consequently not of commercial value as a fertilizer.

The return of waste materials to the soil is fundamentally correct. Certain heavy soils, deficient in organic matter, may in time be benefited, both physically and chemically, by additions of pomace, if sufficient time is allowed for decomposition. Organic matter in fertilizers is impossible of commercial valuation, but the organic matter of olive pomace, owing to its very resistant nature, can in no way be compared to manures or cover crops as sources of organic matter in the soil. However, the probable low value of the organic matter of olive pomace prevents any but very local utilization. The foregoing data indicate that olive pomace, either before or after extraction of the residual oil, can in no way be considered as having any commercial value for fertilizing purposes.

SUMMARY AND CONCLUSIONS

I—Pomace from eighteen olive oil factories was found to contain from 7.89 to 20.23 per cent, or 20.98 to 53.81 gallons of oil per ton of fresh pomace.

II—Gasoline was found to be a satisfactory solvent for the recovery of oil from air-dried pomace. Four extractions were found to be sufficient. The air-dry pomace of lowest oil content was found to yield 25.5 gallons of oil per ton by gasoline extraction.

III—The compositions of gasoline, benzol, and ligroin extracted oils compared favorably with that of pure olive oil so far as their value for soapmaking was concerned.

IV—Distillation by direct heat recovers practically

all of the solvent remaining in the pomace. Steam distillation does not give complete recovery.

V—No commercial value as fertilizer should be assigned to olive pomace, either before or after extraction.

LABORATORIES OF ZYMOLOGY AND AGRICULTURAL CHEMISTRY
AGRICULTURAL EXPERIMENT STATION
BERKELEY, CALIFORNIA

MANGANESE AS A CAUSE OF THE DEPRESSION OF THE ASSIMILATION OF IRON BY PINEAPPLE PLANTS

By MAXWELL O. JOHNSON

Received October 30, 1916

The chief pineapple district of the Hawaiian Islands lies on the Island of Oahu on the sloping tableland between the Koolau and Waianae mountain ranges. Through this district there occur various areas of dark or black manganeseiferous soils, and it has been known for ten or twelve years that pineapples on such soils make a very poor growth. At almost any age, but usually about flowering time, the leaves of the pineapple plants gradually become yellow, the plants making slight growth and often dying. The few fruits produced are of small size and poor quality. The unripe fruit, which is pink or red in color instead of the normal green, often cracks open and decays. The flesh of the ripe fruit is hard and white, with considerable acidity. As the dark soils where yellowing of pineapples occurs, aggregate from 6,000 to 10,000 acres of the lowest lying, most accessible, and most easily cultivated land of this region and as the water supply is insufficient for the growth of sugar cane, the profitable utilization of these soils is of considerable economic importance.

ANALYSES OF MANGANESEFEROUS SOILS

Kelley¹ first showed that this yellowing of pineapple plants is directly related to an abnormal amount of manganese in these dark soils. From a number of analyses made by the method of the Association of Official Agricultural Chemists, he gives the average water-free composition of the normal red soils and of the manganeseiferous black soils as follows:²

TABLE I. COMPOSITION OF NORMAL RED SOILS AND MANGANESEFEROUS BLACK SOILS OF OAHU

Average Percentage Composition of	Red Soils	Red Subsoils	Black Soils	Black Subsoils
Insoluble matter.....	12.82	11.17	13.96	81.54
Potash (K ₂ O).....	0.29	0.65	0.91	0.8
Soda (Na ₂ O).....	0.27	0.11	0.11	0.14
Lime (CaO).....	0.46	0.48	0.5	0.18
Magnesia (MgO).....	0.39	0.39	0.47	0.41
Manganese oxide (Mn ₂ O ₃).....	0.17	0.00	0.64	4.69
Ferric oxide (Fe ₂ O ₃).....	21.82	30.10	25.08	11.96
Alumina (Al ₂ O ₃).....	10.04	10.41	11.49	11.00
Phosphoric pentoxide (P ₂ O ₅).....	0.08	0.1	0.11	0.10
Sulfur trioxide (SO ₃).....	0.11	0.08	0.11	0.00
Volatile matter.....	11.14	11.4	11.41	11.80
Titanium oxide (TiO ₂).....	0.01	0.02	0.08	0.08
Total.....	100.00	100.00	100.00	100.00
Nitrogen (N).....	0.13	0.14	0.14	0.10
Acidity.....	1.94	0.00	0.00	0.00

¹ Calculated to pounds of CaO per acre foot.

The writer has analyzed a number of these manganeseiferous soils, the analyses agreeing in the main with those of Kelley. However, a typical example of the "manganese yellow" with the characteristic bad fruit was found to occur on a soil containing only 4.69%

cent manganese (calculated as Mn₂O₃). This manganese was all present as the dioxide.

A number of samples were distilled according to the ordinary Bunsen method for determining available oxygen in pyrolusite, and the manganese dioxide was calculated. Table II shows the results as compared with the total manganese determined by the official method.

TABLE II. COMPARISON OF PRESENTED AND TOTAL MANGANESE WITH THE MANGANESE DIOXIDE IN MANGANESEFEROUS SOILS

Laboratory No.	628	629	630	631	632	633
Total manganese calculated as the dioxide.....	0.35	5.48	5.92	5.89	2.86	6.36
Manganese dioxide calculated from the Bunsen distillation.....	0.35	4.85	5.20	5.15	2.66	5.67

As the Bunsen method gives low results when organic matter and possibly ferrous iron are present, it is safe to conclude that nearly all the manganese in these soils is present as the dioxide.

THE EFFECT ON PLANTS

Kelley¹ and Wilcox and Kelley² made an extended investigation of the effect of these manganeseiferous soils on the pineapple and other plants. Field notes, results of pot experiments, and ash analyses are given, comparing a large number of plants on manganeseiferous and normal soils.

From this investigation, Kelley² concludes:

"That various plants when grown on manganeseiferous soil are affected differently. Some species are stunted in growth and die back from the tips of the leaves, which turn yellow or brown and frequently fall off, and a general unhealthy appearance results. Other species appear to be unaffected and so far as can be judged vegetate normally in the presence of manganese. Microscopic investigations have shown that in certain instances the protoplasm undergoes changes. Occasionally it draws away from the cell wall, the nuclei become brown, and plasmolysis takes place."

"From the ash analyses it was found that manganese was absorbed in considerable quantities, and in nearly every instance was greater in the plants from manganeseiferous soil. The ash analyses also show that a decrease in the percentage of lime takes place. The percentage of lime is increased, while the absorption of manganese and phosphorus is decreased."

"From these analyses we may believe that the effects of manganese are largely indirect and can be explained on the basis of the change in the composition of the elements present in the soil and in the plant, and that the true cause has already been brought about through the modification rather than an actual result of the manganese itself."

COMPARISON OF ASH ANALYSES WITH OBSERVED EFFECTS OF THE MANGANESE

It was thought that it would be of value to attempt some correlation between the ratio of the ash constituents on manganeseiferous and normal soils and the field notes. The ash ratios for the four constituents mentioned by Kelley² together with those for potash and iron, are given in Table III. The field notes are quoted from Kelley² so that some are not used in comparison at this point. The observations for the leaves of the young plants are not necessarily pertinent to the fruit maturity and are not given here. In cases where the normal and acidity in the soils are reported together, it is assumed that to give an iron ratio. The field notes on the downward and olive were kept.

A comparison of Table III shows that there is a possible correlation between the observed effects and

¹ Hawaii Sta. Proc. Bull. 23, 1909.
² Hawaii Sta. Proc. Bull. 23, 1909.
³ Hawaii Sta. Proc. Bull. 23, 1909.
⁴ Hawaii Sta. Proc. Bull. 23, 1909.

¹ Hawaii Sta. Proc. Bull. 23, 1909.
² Hawaii Sta. Proc. Bull. 23, 1909.
³ Hawaii Sta. Proc. Bull. 23, 1909.
⁴ Hawaii Sta. Proc. Bull. 23, 1909.

TABLE III—RELATIVE PROPORTION OF SOME ASH CONSTITUENTS OF PLANTS GROWN IN MANGANIFEROUS AND NORMAL SOILS
Ash percentage on normal soils taken as 1.0

Plant No.	Plants analyzed	MnO ₂	CaO	MgO	P ₂ O ₅	K ₂ O	Fe ₂ O ₃	Observed Effects of Manganiferous Soil on Plants
PLANTS AFFECTED BY MANGANIFEROUS SOIL								
1	<i>Paspalum oblatum</i>	2.09	0.79	0.69	1.09	1.34	0.26	Very sensitive. Suggested by Kelley as a vegetation indicator of nonmanganiferous soils
2	Peanut leaves	6.25	0.90	0.51	0.90	1.70	0.54	Lower leaves brown, subsequently dying and falling away; stem purple, roots brown.
3	Pineapple leaves, 5 mo. old	1.42	1.26	0.75	0.79	0.92	0.73	Seriously affected. Leaves yellow, fruit small and red
4	Pigeon pea leaves	9.54	2.05	0.42	0.37			Less than half the growth on normal soil. Lower leaves brown and dying back
5	Sugar cane	0.75	0.86	0.73	0.80	0.70	0.72	Yellow color on lower leaves developed by young cane during winter
6	Broom corn leaves	3.74	2.22	1.92	0.68	2.32	0.81	Pronounced effect
7	Cowpea vine	3.53	1.33	0.76	0.58	0.93	0.84	Very sensitive. Stem becomes purple, lower leaves turn brown and fall away
8	Corn stover	2.66	2.50	1.66	0.68	0.91	0.87	Seriously affected, stalks and leaf sheath purple, lower leaves brown and dying back
PLANTS APPARENTLY NOT AFFECTED BY MANGANIFEROUS SOIL								
9	<i>Waltheria americana</i> leaves	10.61	1.06	0.70	0.74	0.68	1.20	No effects
10	Crotalaria	28.00	1.62	0.37	0.45	1.25	2.38	Unaffected by manganese, making luxuriant growth
11	Guava leaves	2.93	1.87	0.35	0.58	0.28	6.67	No visible effects. (Found scattered over unplowed portion.)
12	Oat straw	0.86/T.	2.69	1.62	0.08			Slight stunting at first, with later normal growth
13	Mango leaves	9.01	1.93	0.44	0.53			Normal growth
14	Wheat straw	0.22/T.	2.16	1.47	0.53			Fair growth
15	Tobacco stems	0.57/T.	5.04	1.25	0.28			Slight stunting at first, with later normal growth

the plants of manganiferous soil and the variations of the individual ash constituents in the case of manganese, lime, magnesia, phosphoric acid, and potash. It is unnecessary to point out the contradictions which these variations exhibit, as they are apparent at a glance. The lime-magnesia ratio also shows no correlation, but in the case of the iron, a remarkable correlation is easily seen. The assimilation of iron is depressed on those plants to which the manganiferous soil is toxic, while it is increased on those where no toxic effect is observed. This is shown further by Fig. I, where the plants are plotted, according to their

unaffected is considerably increased. Similar graphs for the other ash constituents are without significance. On the basis of this interpretation, the observed physiological derangements are easily explained. The purple, brown, or yellow color, the lack of starch, and other toxic effects are due to deficiency of chlorophyll, for the production of which a proper supply of iron is necessary.

PRACTICAL METHODS OF CONTROL

The theory that this trouble is due to a lack of iron has found striking confirmation in its practical application to the pineapple, the chief economic crop of the region where the manganiferous soils occur. Fields of yellow, unhealthy plants sprayed with solutions of iron salts became green within a very short time. The effect on the fruit was most remarkable. The small, red, stunted pineapples, when sprayed, showed decided improvements within a week, becoming normal dark green and commencing a most vigorous growth within two or three weeks' time. Where iron was applied to one side of the unripe fruit only, that side became green first and made such growth that the fruit soon presented a lopsided appearance. Later the iron appeared to be distributed, as the fruit was fairly symmetrical when ripe. Solutions of iron salts applied to the etiolated leaves of the pineapple plants effected quick relief, while relatively immense quantities of solution and of solid iron salts applied to the soil were without result. Acids applied to the soil and combinations of iron salts with various fertilizing elements were tried without effect. Sodium nitrate gave promising results. Ferrous sulfate sprayed directly on the leaves proved the most economical form of iron to apply. Solutions made slightly acid with sulfuric acid or the waste pineapple juice from the canneries gave slightly better results, the acid tending to prevent precipitation of the basic ferric sulfate.

A convenient and profitable method of treatment has been worked out which has been applied to extensive areas of highly manganiferous soil with immediate success. Good yields of pineapples of excellent size and quality have been harvested from plants sprayed with ferrous sulfate, while on the unsprayed check plats, all the plants were yellow, and many were dead and dying, with fruit of such inferior size and quality as to be scarcely worth picking.

As a result of the writer's experiments, practically

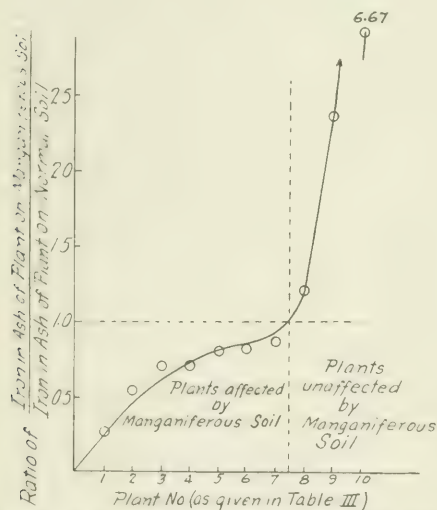


FIG. I. GRAPH SHOWING CORRELATION BETWEEN THE ASSIMILATION OF IRON AND THE EFFECTS ON THE PLANTS GROWN ON MANGANIFEROUS SOIL

number in Table III, on the axis of abscissas, with the ash ratio as ordinates. It would be expected that a significant excess or lack of a constituent would be shown by an opposition of the points plotted in the angles formed by the intersection of the line dividing the plants affected and unaffected by manganiferous soil and the horizontal line for an ash ratio of 1.0.

An inspection of Fig. I shows that the iron content of affected plants is decreased, while that of plants

all the pineapple plantations have now utilized this spraying treatment on the manganiferous soils. Success has everywhere been reported, and at present there seems no obstacle to the profitable cultivation of these extensive areas of manganiferous soil.

These experiments will be given in fuller detail in a forthcoming publication of the Hawaii Agricultural Experiment Station.

MANGANESE AS THE CAUSE OF A DEPRESSION IN THE ASSIMILATION OF IRON

It is well known that excessively calcareous soils¹ may depress the assimilation of iron and even lead to a chlorosis, but this seems the first case where a manganiferous soil has caused such trouble. That manganese is the cause is evident from the fact that the usual calciphilous legumes are among the most strongly affected.

Many fertilizer experiments with different forms of manganese show a stimulation with small doses and a toxic effect with larger applications. Other experiments show no effects.

Loew and Sawa² in 1903 published results of water-culture experiments where they observed a yellowing of pea plants, barley, and soy beans with solutions to which manganous sulfate had been added. The addition of manganous sulfate to the ordinary iron-containing nutrient solution caused an increased growth but later a yellowing took place. This yellow color they think may be due to the increased activity of the oxidizing enzymes. In their conclusions they state that "manganese exerts in moderate quantity an injurious action on plants, consisting in the bleaching out of the chlorophyll. The juices of such plants show more intense reactions for oxidase and peroxidase than the healthy control plants."

Aso³ in similar water cultures with young radish, barley, and wheat plants observed a yellowing with solutions containing (a) 0.02 per cent MnSO_4 + trace of FeSO_4 , (b) 0.02 per cent MnSO_4 + 0.02 per cent FeSO_4 , (c) 0.02 per cent FeSO_4 and as these three solutions diluted with 10 times their volume of water. The ordinary mineral constituents were supplied. With the solution containing only a trace of FeSO_4 and diluted ten times, the yellowing suggested an interference in the assimilation of iron. Pea shoots grown during the first stage of development, without mineral salts, in solutions containing 0.002 per cent of ferrous and manganous sulfates singly and in combination found the greatest stimulation with the manganous sulfate. No yellowing was observed during this first stage of development.

This observation seems to be the only instance where the writer can find from a brief review of the literature of any association of the depression in the assimilation of iron with the toxic effect of manganese.

SUMMARY

I—It has been shown that the manganese of the highly manganiferous soils of the Island of Hawaii is nearly, if not all, in the dioxide form.

II—From a study of ash analyses of plants grown on these manganiferous soils, it appears that the toxic effect observed is due to a depression in the assimilation of iron.

III—The pineapple plant, the chief economic crop grown on these manganiferous soils, has recovered from the toxic effects of the manganese when supplied with iron through the leaves.

IV—A commercially successful treatment has been worked out, and the profitable utilization of these highly manganiferous soils seems assured.

HAWAII AGRICULTURAL EXPERIMENT STATION
HONOLULU, H. I.

THE FERTILIZER VALUE OF CITY WASTE I. THE COMPOSITION OF GARBAGE

BY W. E. COBBEN, AND EDWIN R. TURRENTINE

Received September 8, 1916

In connection with its investigation of the fertilizer resources of the United States, the Bureau of Soils has undertaken the study of the various city wastes to discover if there may be found therein a source of those materials which have value as fertilizer ingredients. The study has involved the origin, composition and methods of disposal of these. It has had to do with the statistical, economic, engineering and sanitary features of the problems of the collection, disposal and utilization of city wastes. Most of the work has been done in the field. In the laboratory various classes of substances have been examined analytically to determine their composition; the availability of the ingredients of potential fertilizer value has been studied and new methods and apparatus for the more economical commercial treatment of these waste materials have been devised. It is proposed to present the results of the laboratory investigations in the present series of papers.

The work has been carried out under the direction and with the collaboration of J. W. Turrentine.

In the commercial handling of city garbage for the recovery of fats and the preparation of tankage for livestock use, the amount of the undesirable material largely on the quality of the raw material. Due to the wide diversity existing between the methods of handling city waste as regards the various cities, it has no small bearing that, because the quantity of the garbage of one city is commercially profitable, that of any other city will be. If separation is effected with much skill and the refuse, portion of the garbage are not, depending from the rendering plant, because in one city possible amount is burned.

The ingredients of unseparated garbage as found in properties, however, to be burned are low, and phosphorus, combined nitrogen and grease. The low interest in the chemical composition, the more value can be recovered. And hence, from it limited commercial combined nitrogen and one valuable value.

The large quantities of garbage available for use as plant food, urban manure, are given as consisting of 10,000,000,000 pounds available from the

¹ See *Cole, Porto Rico, Jour. Sci.*, 11 (1911) and 15 (1912).

² *Proc. Cal. Agr. Expt. Sta. Trans.*, 5 (1903), 100.

³ *Ibid.*, 5 (1903), 100.

proper handling make city garbage a subject quite worthy of the industrial chemist's best attention.

ORIGIN

Garbage may be defined as the waste material arising from the culinary department of a household or other establishment. It then should be made up of the portion of food materials discarded in their preparation for the table and often uneaten remnants. Actually, it contains these, and in addition portions of the containers of food materials, broken porcelain and glass and parts of the various apparatus and appurtenances employed in domestic activities. Thus may be found in it large quantities of the trimmings from green vegetables, such as those coming from cabbage and celery, the parings of fruits and vegetables, the rinds of melons and citrus fruits, in summer, especially of watermelons, and in winter, of grapefruit; meat skins and bones, pieces of fat, the feathers and other waste from the dressing of poultry; containers of food materials, of paper, wood and tin, and portions of them, such as the metal caps of beer bottles, broken glass and crockery, spoons, forks and dish-cloths; oyster, clam and egg shells. Likewise market waste finds its way ultimately into the aggregate collection. This contributes the same sort of material which in general is obtained from households, though it contains more of food remnants, perhaps, than culinary waste, unless the latter is very carefully segregated. It contains, frequently, large portions of materials which have grown stale or spoiled and no longer are fit for food, such as old vegetables and spoiled fish. The trimmings from meat—pieces of skin, fat and bone—usually are collected together and are disposed of more advantageously by sale to fat-rendering establishments. The composition of garbage, then, it may be said, is indeterminate, because of the great variety of materials entering it. Since, as will be shown, it is to the advantage of the municipal collector and, therefore, the resident of the municipality, the householder, to restrict the garbage to the portions of the kitchen waste which are liable to decay and create a nuisance, it is desirable and essential to the best collection and disposal service, that the deposition of cans, broken glass, crockery, and such materials in the receptacle provided for garbage be prohibited. Ordinances usually are in force to this end. Where such are strictly enforced, then, garbage approximates a mixture of animal and vegetable matter; and as such its usefulness, and therefore its value, is greatly enhanced.

COMPOSITION

In the City of Washington, in connection with the investigation of Mr. Irvin S. Osborne for the Commissioners of the District of Columbia, was made the most thorough-going examination of the composition of certain city wastes perhaps so far made in this country. On the results thereof were based the Commissioners' recommendations to the Congress for certain changes in the methods of disposing of the city wastes of Washington. As a part of the investigation the garbage of the city was analyzed in order to de-

termine (1) its true composition in those elements or substances on which its value depends; (2) the variations of these with the season of the year; (3) with the part of town from which collected, and (4) with the class of inhabitants contributing it. The analytical work was conducted in the laboratories of the Bureau of Soils. In order to obtain data on the above points, the analyses had to be made on a large number of samples from the various sections of town possessing different characteristics and had to be prolonged throughout a year.

It is the prevalent opinion that there is a decided seasonal variation in the composition of garbage. This is based on the fact that in summer larger quantities of vegetables are eaten than in winter, from which it is assumed that in summer the garbage is more bulky and wetter because of the large proportion of vegetable matter being contributed thereto; that, correspondingly, the more valuable constituents, meats and bone remnants, are not only relatively less abundant, but absolutely so, because less meat, it is agreed, is eaten in summer. Likewise, it has been assumed that the garbage from those households in which the scale of living is maintained on a more elaborate scale is richer in the valuable ingredients than that from other households. This is based on the two assumptions, that the food in the former household is made up to a larger extent of fats and meats, and that less rigid economy is exercised in its use. While such a distinction actually may exist, it will be shown that it does not necessarily follow that the distinction will exhibit itself in the composition of the garbage.

THE SEASONAL VARIATION IN COMPOSITION

SAMPLING—The samples analyzed to determine the seasonal variation in the composition of the garbage of the City of Washington were taken from the aggregate city collection. This averaged 140 tons per day and varied from 109 tons in February to 198 tons in August. The collection was made by from 50 to 90 wagons. In summer the collection is made daily for the greater part of the city and three times per week for the outlying and thinly populated districts. In the hotel region of the city the collection is daily throughout the year. The wagons in use in this city (removable body, iron tank wagons) hold from 1500 to 3300 lbs. garbage, depending on the nature of the garbage and the manner in which it is loaded. Thus the average daily number of loads sampled was 43. Each wagon employed in this service bears a number and is assigned by number to a definite, prescribed route. Thus by reference to the number of the wagon it is possible to determine the exact neighborhood from which its load has been obtained.

In Washington the various wagons are delivered at a central loading station where the tank bodies are transferred from the running gears to flat cars for transportation by railroad to the rendering plant. It was at this station that the samples were secured.

To make up a sample, about a cubic foot of garbage was taken from each of a chosen list of wagons, a portion being taken from the various parts of the tank, from the center, or bottom or ends. The respective

With the assistance of Mr. F. A. Rammann, Inspector in Charge, Collection and Disposal City Waste, Washington, D. C.

numbers of the wagons sampled were listed, the list being chosen and noted, so that the samples collected from day to day would not be from the same routes. In this way, while no sample represented the entire day's collection from the whole city, the total number of samples covered with fair uniformity all the districts of the city.

The material taken from the various wagons was deposited upon a platform where it was chopped, mixed and quartered, the process being continued until the quantity of material had been reduced to approximately 6 qts. This was divided into 3 samples and an analysis was made of each. Thus the general samples were analyzed in triplicate. The weight of each wagon load of garbage also was determined and noted, so that it was possible to ascertain the total weight of garbage represented by the samples taken. At the time of collecting the sample it was observed from the weather records what the weather conditions had been during the period in which the garbage sampled had been accumulating. In this way it was

being recorded as combustible material and the residuum as ash. Calorific values were determined through the esteemed courtesy of Mr. J. E. Davis, of the Bureau of Mines, who employed the bomb calorimeter method.

In Table I are set forth the results of analysis of the general samples, showing what variation there is in the composition of garbage with the season. In the first column is given the date on which each sample was taken; the second, the number of loads sampled; and the third, the total weight represented by the sample. Analyses are reported both on the dry and the wet basis. Calorific values are reported on the dry basis. Each sample was analyzed in triplicate, the average being recorded here. The analytical data therefore are in each instance the average of three analyses.

DISCUSSION OF RESULTS.—In Fig. 1 the results of the determination of moisture have been plotted to show the variation in that main constituent of garbage with the months. The fluctuation swings from a

TABLE I—ANALYSES OF GARBAGE OF DISTRICT OF COLUMBIA SHOWING SEASONAL VARIATIONS. RESULTS IN PERCENTAGE

DATE	No. of Loads	Total wt Sampled Lbs.	ANALYSES ON DRY BASIS										ANALYSES ON WET BASIS									
			COMBUSTIBLE					ASH					COMBUSTIBLE					ASH				
			H ₂ O	Ash	Oil	K ₂ O	FeO	N	Matter				H ₂ O	Ash	Oil	K ₂ O	FeO	N	Matter			
Dec. 14, '14	69.29	16.89	21.82	0.93	3.76	4.3	86.30	68.00	17.00	21.00	0.90	3.80	4.5	85.30
Dec. 29, '14	72.65	13.72	20.61	1.41	2.85	1.88	86.35	71.00	14.00	20.00	1.40	2.90	2.0	85.10
Jan. 13, '15	75.35	14.63	20.74	1.19	3.32	1.38	86.36	74.00	15.00	21.00	1.20	3.40	1.5	85.30
Jan. 28, '15	73.03	16.75	20.31	1.05	3.10	1.7	86.4	72.00	17.00	20.00	1.10	3.20	1.8	85.30
Feb. 12, '15	74.19	14.22	21.12	0.76	3.08	1.91	86.3	73.00	15.00	21.00	0.80	3.10	2.0	85.30
Mar. 2, '15	40	102,760	70.48	9.40	21.59	1.03	1.13	2.61	86.69	69.00	10.00	22.00	1.10	1.20	2.7	85.30
Mar. 13, '15	35	86,415	69.04	12.00	23.92	0.68	1.20	3.3	86.99	68.00	13.00	24.00	0.70	1.30	3.4	85.30
Mar. 23, '15	37	98,716	71.38	13.13	22.16	1.03	1.60	3.3	86.88	70.00	14.00	23.00	1.10	1.70	3.5	85.30
Apr. 7, '15	33	86,361	65.27	11.41	24.69	0.79	1.13	3.1	88.61	64.00	12.00	25.00	0.80	1.20	3.2	87.20
Apr. 22, '15	35	91,070	71.23	12.32	20.35	1.09	1.18	3.05	86.06	70.00	13.00	21.00	1.10	1.15	3.1	85.85
May 7, '15	33	84,117	71.15	14.57	25.48	1.06	1.59	2.75	85.42	70.00	15.00	26.00	1.10	1.60	2.8	84.40
May 22, '15	38	91,846	72.77	15.13	21.18	1.28	1.88	3.1	86.86	71.00	16.00	22.00	1.30	1.90	3.2	85.86
June 7, '15	51	126,235	74.11	11.18	25.99	1.37	1.08	3.3	88.31	73.00	12.00	26.00	1.40	1.05	3.4	87.35
June 21, '15	33	85,239	73.21	19.80	15.34	1.0	1.03	1.7	84.14	72.00	20.00	16.00	1.10	1.05	1.8	83.85
July 7, '15	33	84,117	71.15	14.57	25.48	1.06	1.59	2.75	85.42	70.00	15.00	26.00	1.10	1.60	2.8	84.40
July 22, '15	66	152,934	78.85	13.61	18.83	1.0	0.92	1.1	83.48	78.00	14.00	19.00	1.00	0.95	1.2	82.05
Aug. 6, '15	51	131,446	79.59	13.17	17.19	1.21	0.87	1.05	85.87	79.00	14.00	18.00	1.30	0.85	1.1	84.85
Aug. 21, '15	50	131,300	77.58	13.72	18.51	0.97	1.64	0.94	86.3	77.00	14.00	19.00	1.00	1.60	0.9	85.30
Aug. 30, '15	86	232,358	79.25	12.95	20.23	0.84	1.54	1.50	86.66	79.00	13.00	21.00	0.90	1.55	1.6	85.66
Sept. 13, '15	43	106,656	71.80	14.43	17.50	1.00	0.96	1.44	88.51	71.00	15.00	18.00	1.10	0.95	1.5	87.55
Oct. 1, '15	29	74,530	78.81	12.72	17.43	0.93	0.98	1.4	87.18	78.00	13.00	18.00	1.00	0.95	1.4	86.18
Oct. 14, '15	40	92,640	73.95	12.30	21.11	0.93	0.69	1.68	87.16	73.00	13.00	22.00	0.95	0.70	1.7	86.36
Oct. 29, '15	40	93,640	71.31	13.18	17.17	1.06	0.74	1.8	84.69	71.00	14.00	18.00	1.10	0.75	1.9	83.69
Nov. 11, '15	39	95,338	73.75	13.01	18.37	1.03	1.1	1.8	86.98	73.00	14.00	19.00	1.10	1.15	1.9	85.98
Dec. 1, '15	34	82,960	70.19	11.99	18.11	0.85	1.83	1.0	88.16	70.00	12.00	19.00	0.90	1.85	1.1	86.16
Average	73.18	13.77	19.97	1.03	1.62	0.9	86.35	73.00	14.00	20.00	1.10	1.60	1.0	85.35

possible to obtain some idea as to the probable changes in composition due to the presence in the garbage of rain water or snow.

METHODS OF ANALYSIS. To determine moisture, and at the same time to dry the samples for further analysis, the material was removed entirely from the jars and mixed thoroughly to counteract the effect of settling on standing or in transportation; portions of 600 to 800 g. in weight were transferred to flat aluminum dishes, of known weight, and were dried practically completely in a vacuum oven maintained at about 90° C. To effect the drying about 60 hrs. were required. The dry material then was ground in an iron mortar to such a fineness as to pass a 2 mm. sieve. Any residual moisture was determined on a small portion of the ground sample.

Feats were determined by the official titration method, likewise total phosphorus and water-soluble potash, and total nitrogen were determined by the official methods.¹ To obtain the percentage of oil and combustible matter, a 5 g. sample was heated to constant weight at a bright red heat, the loss in weight

minimum in April at 68 per cent in a maximum in July of approximately 80 per cent. Whether this is the normal seasonal swing it is impossible to say in the absence of data covering other years. There is no pronouncedly rapid season, say the maxima and minima should fall in those months. April is not the season, it is believed, in which such green vegetables are eaten, nor July the month in which the most are consumed. To be sure, there is no marked difference between July and August, as the material sampled for those months did have as a general rule with preconceived ideas. In Washington, it is to be expected, the most or nearly water-soluble and green corn, the two vegetable materials contributing the largest proportion of waste, are the most abundant, is the one in which the largest proportion of vegetable matter is to be found in the garbage. This seems probably correct. August and September, the months of July and August.

ANALYSIS OF GARBAGE. The analysis of garbage may be derived from the averages in the foregoing results. The minimum gross of garbage, gross, containing 10.1 per cent water-soluble potash, and

¹ Bureau of Chemistry, *Ind. 107*.

of ammonia, bone phosphate and potash in garbage tankage on that date was \$2.00, \$0.10 and \$0.70, respectively, per unit. On this basis, the raw material would carry values of a total worth of \$7.19 per ton. It should be added here that in practice only about 3 per cent grease is recovered, and other ingredients in proportion. Improvements in the technique of rendering garbage are resulting in rapidly increasing yields in all these products. Likewise, the prices obtained for the products have increased, due principally to the enlarged demand for glycerine and potash.

EFFECT OF RAINFALL ON COMPOSITION OF GARBAGE—

An increase in precipitation, either rain or snow, tends to increase the water content of garbage. It is rarely that garbage is handled either by the mass of householders of a city or by the collectors in such a way as to avoid entirely the acquisition of rain water during a rainy season. If the garbage receptacle is not placed where rain or snow will fall therein, the wagons, while being filled, may be open and permit the wetting of their contents. Properly covered receptacles would prevent the wetting of garbage before its collection; and the latest proposed form of garbage wagon provides automatic lids which are removed only at the instant the garbage can is being emptied.

An examination of the accompanying chart in which the rainfall of the District of Columbia for the year 1915 has been plotted, discloses the interesting fact that rainfall practically parallels the moisture content of the garbage of the District, the only sharp divergence from this generalization being during the month of July, the period of maximum moisture content of garbage. The conclusion seems justified, therefore, that the seasonal variation in moisture content is a result not only of a change in diet of the people, but also of the effect of the seasonal rainfall. From *apriori* considerations it can not be concluded that it is the result of either one alone.

It is not at all clear why there should be a divergence in the parallelism of the two curves at the point representing the month of July. The effect of rainfall should be less marked during the summer months because of the nature of the summer rains as compared with those of the winter. The former, as a rule, are hard showers of short duration, and are of such a nature as to drive everyone indoors. During such storms the collectors probably leave their wagons and seek shelter, so that if they observe the simplest precautions for keeping water out of the garbage, by closing their wagons, the material in the wagons, at best, is not exposed to the rainfall. During the winter, on the other hand, the rains are more gentle and of longer duration and the collectors continue their operations without regard to them. It may be possible, too, that a greater effort is made by the householder during the summer than during the winter to keep garbage receptacles closed, on account of the attraction of flies by the exposed waste during the former season and the odors which may arise therefrom. These are problematical, and it may be that the parallelism between rainfall and moisture content of garbage observed for the year 1915 is purely acci-

dental. Attaching a significance to this parallelism, however, leads to the conclusion that the normal seasonal variation in the composition of garbage, that is, that due to the change in diet of the populace, is even less than that observed.

If the observed variation in moisture content is a product of both change of diet and rainfall, as it appears, it might be argued that had the rainfall not decreased during July, the seasonal variation would have been greater than as observed.

The seasonal variation in the most valuable constituent of the green garbage, grease, is shown by the second of the two curves in Fig. 1. The maximum

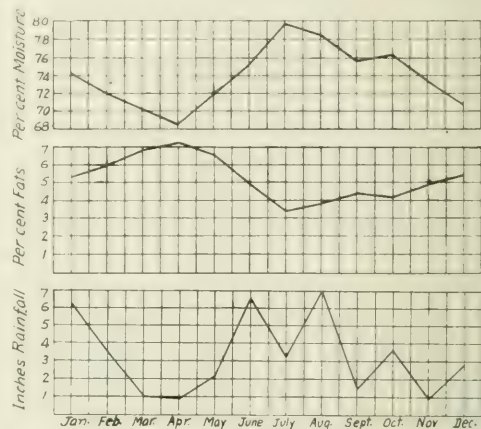


FIG. 1—ANNUAL VARIATION IN PER CENT MOISTURE AND IN FAT CONTENT OF GARBAGE AND RAINFALL

and minimum are 7.2 (average of two analyses), and 3.4 (average of two analyses), respectively, for April and July. From a casual examination of the two curves on this chart it seems evident that the one is the product of the other, reciprocally; that the increase in the content of grease is relatively great because of the lower content of moisture, and *vice versa*. The seasonal variation in content of grease likewise is cut down by the presence of rainwater in the garbage, present in greater amount in winter than in summer.

If it is correct to conclude that the seasonal variation of grease is a product of that of moisture, or moisture-carrying ingredients, it follows also that the same will apply also to nitrogen, phosphoric acid, and to a smaller extent, potash; and such a conclusion seems to be substantiated by the data obtained.

THE SECTIONAL VARIATION IN COMPOSITION

The variation in composition of garbage from various sections of a city is induced principally by the scale of living of the inhabitants of the respective sections. The presence of hotels, restaurants and markets is about the only other factor that introduces such a variation.

For the present investigation the City of Washington was divided into sixteen sections. The division lines were drawn both with regard to class of in-

habitants and conveniences in routing the collecting wagons. It was not possible to make a thorough subdivision of the city on any such basis, but only an approximate one.

The samples were taken in the manner already described, the wagons being chosen by number, since it is remembered, each wagon was assigned to a certain route. It thus was possible to determine with accuracy the area from which each sample was taken.

In Table II are given the results of analyses of 128 samples of garbage, being 8 each from 16 sections of the City of Washington. In the second column, headed "Character," is represented the nature of the section indicated. For convenience the inhabitants of the city have been classified roughly with regard to their style of living in so far as it has been possible to determine this from an entirely superficial observation. The terms, wealthy, medium, poor and colored, have been chosen to describe the characteristics of the four groups resulting, and, as stated, represent approximately the order of the relative elaborateness of the style of living of the respective groups. The period covered by the investigation is indicated in the case of each section; the time covered is inclusive of the months named.

The lack of sharp differentiation in the chemical composition of garbage coming from the different

and undoubtedly, do so to the best of their knowledge. These are tendencies which effect an equalization in the kitchen waste of the respective households.

Likewise, the more wealthy householder, in purchasing materials, secures a higher grade from which as a rule there is less waste. The cuts of meat sent to his kitchen contain less bone and gristle and other inedible parts than does that sent to the kitchens of the poor class; and a similar statement may be made with regard to other food materials. While economy may be practiced in the former kitchen to a lesser degree than in the latter, at the same time there is less of a character that must be discarded in the former than in the latter.

Attention is invited to the conclusions which may be drawn from the analysis of garbage from Sections 10, 11 and 14, the residents of which are largely household servants. These conclusions are of importance in their bearing on the value of city wastes of cities where similar conditions exist. This study of the city wastes of Washington for the first time has made available data which could be applied to the solution of this question, since it indicates that in localities where a large proportion of the inhabitants are household servants garbage can be profitably rendered.

The waste from the kitchens of hotels and restaurants commands a market price as food for swine. Natu-

TABLE II—PERCENTAGE ANALYSES OF GARBAGE OF DISTRICT OF COLUMBIA SHOWING SECTIONAL VARIATIONS (8 SAMPLES IN EACH SECTION)

Section No.	CHARACTER	PERIOD	TOTAL GARBAGE REPRESENTED			ANALYSES ON DRY BASIS						ANALYSES ON BASIS RAW MATERIALS						
			Loads	Lbs.		Ash	Oil	KaO	Fe	N	Comb.	Ash	Oil	KaO	Fe	N	Comb.	
1	1/2 medium to poor, 1/2 colored	Feb.-June	44	126,950	73.48	14.94	18.17	1.14	1.82	2.78	88.03	3.81	1.88	1.41	1.14	1.11	88.540	
2	Mostly colored	Feb.-June	26	66,700	73.91	13.18	18.21	1.27	1.67	3.89	88.3	3.43	1.90	1.12	1.14	1.07	88.500	
3	Medium	Feb.-June	61	151,900	72.49	13.91	20.94	1.02	1.50	80.88	86.9	3.47	1.84	0.29	0.40	0.70	24.03	8.900
4	Medium; slightly poor	Feb.-June	83	206,150	71.83	13.20	20.06	0.99	1.35	2.46	87.59	3.43	1.86	1.11	1.14	1.09	24.18	8.800
5	Medium	Feb.-June	36	84,900	70.64	11.98	23.50	1.18	1.38	1.48	88.02	3.50	1.84	0.11	0.40	0.11	17.88	8.980
6	Medium; poor; colored	Feb.-June	54	126,380	71.06	14.20	19.14	1.11	1.17	2.60	85.81	3.43	1.86	0.11	0.40	0.11	18.91	8.640
7	Medium (suburban)	Feb.-June	34	88,500	71.68	11.72	20.73	1.07	0.94	3.33	88.8	3.43	1.88	0.09	0.60	0.09	13.88	8.600
8	1/2 medium, 1/2 wealthy (Ap's)	Feb.-June	42	107,900	69.70	13.11	20.04	0.99	1.14	2.65	86.80	3.46	1.86	0.09	0.60	0.09	14.88	8.680
9	Wealthy	Feb.-June	80	214,150	71.90	12.05	20.03	0.93	1.33	2.67	87.82	3.34	1.63	0.08	0.88	0.08	18.24	8.700
10	1/2 medium, 1/2 poor, 1/2 colored	Feb.-June	32	85,650	70.60	13.58	13.14	1.01	1.20	2.61	86.42	3.43	1.86	0.11	0.40	0.11	17.88	8.800
11	1/2 medium; 1/2 colored	Feb.-June	41	110,250	70.78	13.46	18.68	1.18	1.48	3.48	86.54	3.57	1.84	0.11	0.40	0.11	23.58	8.760
12	1/2 medium; 1/2 colored	Feb.-June	115	303,650	72.25	11.50	21.17	1.09	0.96	2.88	87.37	3.43	1.88	0.11	0.40	0.11	12.88	8.800
13	Hotels and restaurants	Feb.-June	139	384,100	73.81	15.14	19.08	0.94	0.96	2.73	86.86	3.43	1.86	0.11	0.40	0.11	17.88	8.800
14	1/2 poor, 1/2 colored	Feb.-June	47	118,750	69.58	13.58	19.68	1.04	1.14	2.66	86.42	3.43	1.86	0.11	0.40	0.11	17.88	8.720
15	1/2 wealthy; 1/2 medium (suburban)	Feb.-June	18	49,800	72.11	13.96	19.00	1.10	1.00	3.10	86.96	3.43	1.86	0.11	0.40	0.11	24.09	8.500
16	1/2 medium, 1/2 poor (suburban)	Feb.-June	22	55,300	72.02	13.80	19.11	1.15	0.88	3.88	86.11	3.56	1.86	0.11	0.40	0.11	24.48	8.500

sections of the city and produced by the different classes of inhabitants fails signally to agree with one's preconceived ideas. While the conclusion that no such differentiation exists is unavoidable, it is possible to offer a number of explanations accounting for its failure to appear. An explanation may be based on a study of the diets of the various groups of inhabitants. The diet of the wealthy undoubtedly differs from that of the poor. In winter, for example, the former consists of fruits and fresh vegetables to a larger degree than does the latter. This tends to decrease the value of the refuse from those households, as regarded from the point of view of this study. Aside from the fresh vegetable coming to the kitchen of the rich in winter, an article of food beyond the reach of the poor, it is probable also that the diet of the former is more conscientiously adjusted to the needs of the consumer, this also tending to decrease the amount of reject materials. This would tend to cut down the proportion of oils and fat in the garbage in their food. The poorer classes find it to their advantage to provide for their tables, in more concentrated foods, the more oily and stringy, natu-

rally the hotel and restaurant proprietor prefers to dispose of this material by a method which represents a source of revenue to him, resulting frequently in the more concentrated portions of this being sold to farmers. This is forbidden as a rule in cities where garbage is rendered as a municipal enterprise, an ordinance entirely justified by the benefits accruing to the city from that method of garbage removal. Where permitted, this system operates to lower to the average the value of the more costly high-grade material.

There are other seasonal and largely accidental circumstances which tend further to reduce to a level the values of city wastes. For example, from a survey of Washington, including the suburban lands, garbage was secured when it showed an especially high value. In making an expenditure it was observed that numerous dining cars, comprising their new, were collected in that neighborhood and that their garbage was collected with that of the neighborhood.

CONCLUSIONS

1. The analysis of 128 samples of garbage taken on regular intervals throughout the winter showed that there

was an unimportant seasonal variation in the moisture content, the maximum falling in July and the minimum in April. This seems to be a product of a seasonal change both in diet and rainfall. It fails to show that it is of sufficient magnitude seriously to effect the commercial success of a garbage rendering plant.

II—The analysis of 128 samples of garbage taken from 16 sections, of known characteristics, of the city, through a range of time of 4 or 5 mos. failed to show any marked or consistent variation. The conclusion is indicated that the kitchen refuse from the establishments of the various classes of inhabitants is essentially alike in content of fats and the elements of fertilizer value. This is without regard to relative quantities. Its importance lies in the fact that it tends to refute the prevalent opinion that the garbage of certain cities cannot be rendered profitably because of the nature of its inhabitants.

DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

VALUATION OF WATER-SOLUBLE vs. CITRATE-SOLUBLE PHOSPHORIC ACID

By E. J. PRASKE

Received October 14, 1916

Several of the experiment stations, in recent years, have given a higher valuation to water-soluble phosphoric acid than to citrate-soluble, in their published results of fertilizer inspection. A few stations that have hitherto placed equal values upon the two forms of "available" phosphoric acid seem to be inclined to favor a higher valuation for the water-soluble form. The present paper attempts to show that the higher valuation for water-soluble phosphoric acid is unwarranted by the facts and is inconsistent with the stations' own definitions of valuations.

The New England, New York and New Jersey Stations in the years noted below used the following valuations for phosphoric acid:

TRADE VALUES FOR PHOSPHORIC ACID (CENTS PER LB.)

	1911-1914	1915
Water-soluble	4 1/2	4
Citrate-soluble	4	3 1/2
In iron-bound bone and tankage	4	4
In cottonseed meal and castor pomace	4	3 1/2
In coarse bone and tankage and ashes	3 1/2	3 1/2
In mixed fertilizers insoluble in water or ammonium citrate	2	2

"Trade values" or "valuations" have been defined numerous times in the bulletins, substantially as follows:

"These trade values represent, as nearly as can be estimated, the average prices at which, during the six months preceding March, the respective ingredients, in the form of unmixed raw materials, could be bought at retail for cash in our large markets."¹

The writer wishes to deny emphatically that citrate-soluble phosphoric acid can be purchased "in the form of unmixed raw materials" or in the form of mixed fertilizers at a lower cost than water-soluble phosphoric acid. He will state at once, however, his belief that the lower value given for citrate-soluble is in reality intended to be an expression of certain theories of agricultural value, innocently but inconsistently posing as a trade value.

The market values of water-soluble and citrate-soluble phosphoric are naturally difficult of accurate determination, for in acid phosphate, the great source of water-soluble phosphoric acid, there is a large amount of citrate-soluble, while tankage, bone, fish and cottonseed meal, which contain very little water-soluble, but considerable citrate-soluble, have in addition considerable insoluble phosphoric acid, as well as nitrogen.

It is an easy assumption that a certain percentage of water-soluble phosphoric acid, which represents a higher degree of acidulation, should cost more to produce, and hence sell for a higher price than the citrate-soluble form. As a matter of fact, however, manufacturers of acid phosphate do not strive to produce a maximum amount of water-soluble phosphoric acid from a given amount of rock, but they try to make the maximum amount of "available" at the minimum cost per unit of available. Moreover, in fixing the selling price it is not customary to demand more for an acid phosphate with high water-soluble than for one with lower water-soluble. This will readily be seen from the following table which summarizes the results of all acid phosphate analyses quoted in the bulletins of the Connecticut Station from 1911 to 1915, inclusive, for which retail dealer's prices are given:

Per cent of "available" is water-soluble	No. of Samples	In 100 parts "available" there are		Cost per Unit Available
		Water-sol.	Citrate-sol.	
Less than 70%.....	3	65	35	\$0.98
70% to 79%.....	22	76	24	0.95
80% and Over.....	41	86	14	0.89
Average.....	68	81	19	0.91

It will be noted that we have classified the acid phosphates according to the percentage of their available that is in the water-soluble form. The average 100 parts of available consist of 81 parts water-soluble and 19 parts citrate-soluble, and is worth \$0.91 per unit of available. But contrary to expectation, the phosphates poorer in water-soluble cost more per unit than those with high water-soluble. Obviously, in so far as citrate-soluble phosphoric acid is derived from acid phosphate, either unmixed or in mixtures, it is a more expensive form of available than is the water-soluble form. Its value should, therefore, exceed or at least equal, the value given to water-soluble.

The reason for the greater cost of citrate-soluble in acid phosphate is not entirely explainable by the difference in the grades of acid phosphate. A classification of the above samples on the basis of their guaranteed grades gives the following:

	No. of Samples	In 100 parts "available" there are		Cost per Unit Available
		Water-sol.	Citrate-sol.	
Less than 16% Guaranteed	30	79	21	\$1.00
16% Guaranteed or more.....	38	82	18	0.85

While the grades guaranteeing less than 16 per cent available cost on an average \$0.15 per unit more than the grades guaranteeing 16 per cent available or more, there is only a slight difference in the aver-

¹ New York Bull. 410

age proportions of water-soluble and citrate-soluble phosphoric acid, showing that high water-soluble is not a characteristic of any one grade. At any rate the difference is in favor of a lower price for higher water-soluble. The greater cost of available phosphoric acid in low-grade phosphates is no doubt due to the greater unit cost of handling any low-grade material compared with high-grade, concentrated materials. After all, the cause of the higher cost of citrate-soluble is irrelevant to the present discussion. The trade value is supposed merely to state the facts, not to explain them.

If, then, acid phosphates relatively low in water-soluble and high in citrate-soluble phosphoric acid actually cost as much as or more than acid phosphates high in water-soluble, what is the "unmixed raw material" that supplies citrate-soluble phosphoric acid at a price 10 cents per unit lower than the price of water-soluble, which is even lower than the price of "available" in acid phosphate? The only important sources of available phosphoric acid besides acid phosphate are raw ground bone, tankage, fish, steamed bone and cottonseed meal or castor pomace. What is the market cost of "available" phosphoric acid in these forms?

According to the schedules of trade values given above, 70 to 80 cents per unit is the retail cash value of their total phosphoric acid. How much, then, of the total is soluble in neutral ammonium citrate solution? This is a difficult question to answer. In raw ground bone probably 35 to 50 per cent of the total phosphoric acid is citrate-soluble. In animal tankages and steamed bone the proportion is probably 50 to 65 per cent. In fish scrap it may run from 40 to 80 per cent. In cottonseed meal and castor pomace it is about 94 per cent. In all of the animal ammoniates, therefore, it is evident that the retail cost of "citrate-soluble" is about \$0.80 to \$1.40 per unit or 4 cents to 7 cents per lb. of available phosphoric acid (allowing 40 cents per unit for the insoluble and disregarding the presence of traces of water-soluble).

This leaves, then, only cottonseed meal and castor pomace for consideration. If the total phosphoric acid in these materials is worth 70 cents per unit the available should be worth 75 cents. But it is evident that the valuation of 85 cents per lb. for total phosphoric acid in this form is perfectly arbitrary, for the reason that the supposed value of the phosphoric acid and potash is always included in the fee paid asked for these ammoniates. When values are needed by fertilizer manufacturers for purposes of calculation it is customary to give the available phosphoric acid in cottonseed meal and castor pomace the same value as is taken for available in acid phosphate. The same method is followed by manufacturers in figuring the value of the available phosphoric acid in animal ammoniates. The arbitrary value of 70 cents per unit of bone phosphate of lime is likewise market quotations, for example \$2.64 and \$2.10, is not regarded as truly representing the actual value of the phos-

phoric acid, for actual values depend upon the supply and demand, including that of competitive articles, while it is well known that the arbitrary 10 cents per unit of bone phosphate of lime has not fluctuated in a great many years, even when prices of acid phosphate have risen 100 per cent. The values in retail markets must be judged by themselves, and if an arbitrary value of 2 cents is to be assigned to the pound of insoluble phosphoric acid in animal and vegetable phosphates the citrate-soluble therein must receive a much higher valuation than that given to available in acid phosphate unless the value for nitrogen is arbitrarily loaded out of all proportion compared with its value in other nitrogen sources.

When it is also considered that in the 4,000,000 tons of complete mixtures sold in a normal year there are contained about 34,000,000 units of available phosphoric acid, of which the available tonnage of organic ammoniates is sufficient to furnish only about 3,000,000 units, compared with about 5,500,000 units of citrate-soluble from acid phosphate, it is evident that the latter should be taken into account when figuring citrate-soluble prices.

There is no doubt but that considerations of the supposed agricultural effectiveness of the different forms of phosphoric acid have had more to do with fixing the values under discussion than has consideration of market prices and composition. After the many years of explanation the stations have given of the terms "trade value" and "valuation" it is difficult to understand this bringing in of agricultural considerations. "Valuation does not show the agricultural value of the ingredients."¹ If the stations wish to give a scale of relative agricultural values, that, of course, is perfectly legitimate, but the table should be plainly marked and described. Certainly it is inconsistent to introduce such values into a table of trade values, which are specifically defined as only retail market values. The trade value, according to definition, is intended to state only what the trade price is, not what makes it, or what it ought to be.

DISCUSSION

I. The retail price of "available" phosphoric acid in acid phosphate decreases as the percentage of water-soluble to citrate-soluble increases.

II. As greater quantities of acid phosphate and the impurities phosphoric acid actually more per unit of available phosphoric acid are available in acid phosphate.

III. Agricultural considerations are more in the valuation than in the comparison with trade values which are very different conditions.

IV. There is no basis in fact or chemistry for the prices followed by some of the manufacturers, instead of giving cottonseed meal a lower trade value than water-soluble phosphoric acid.

Received for consideration, February 1, 1916.
and revised March 10, 1916.

LABORATORY AND PLANT

ARTIFICIAL ALKALINITY IN WATER FOR FILTRATION

By A. WADE CLARK

Received November 1, 1916

The very clear and interesting paper by W. Lee Lewis in the October, 1916, issue of *THIS JOURNAL*, p. 914, entitled "Some Features of Swimming Pool Control" is a valuable addition to the literature of the subject of swimming pool waters both from the chemical and bacteriological viewpoint.

The writer notes with interest the discussion of the problem of "conserving the alkaline life" of water that is treated over and over again with alum as is done with that in swimming pools.

The conclusion of the author of the above paper may be summed up by saying that he has shown by his work just how long the alkalinity can be conserved or, in other words, how long the hour of exhaustion of alkalinity can be postponed. With the water of the Great Lakes having a carbonate content of 118 parts per million, it is shown to be possible to postpone this exhaustion long enough to satisfy the requirements of this particular case.

The relatively high carbonate content of the water of these lakes is a fortunate circumstance not met with in many other waters which have to be taken care of by filtration plants and by those in charge of their operation. As the writer of this is one of those so situated it is thought that a few words on the subject will be of interest and assistance to those in control of filter plants as well as of swimming pools.

The writer is in charge of the control work of the water filtration plant of the Company named below and the plant is operating at the rate of somewhat over a million gallons of water per day of 24 hours and running practically 24 hours per day, so that the successful application of the "artificial alkalinity" is a matter of practical large-scale experience covering periods of many weeks of uninterrupted operation.

The raw water scarcely ever contains more than 50 parts per million of carbonates. The pinch comes in periods of heavy rainfall and practically all winter the flood period in the river that is the source of supply, causes the carbonate content to drop so close to zero that there is no reaction with aluminum sulfate and consequently no "floc."

It fell to the writer's lot to wrestle with this problem some years ago and no practical solution of the question of added alkalinity has ever come to his notice in the literature. Moreover, talks with practical filter men have been almost equally barren of definite information. The whole question seems to be in an uncertain and very unsatisfactory condition.

Evidently lime is sometimes used but the objections to it are so great as to make it almost prohibitive. On account of its low solubility it must be added as a "milk" which means using a continuous stirrer and all kinds of trouble in regulating valves and pipes from sedimentation of the lime after leaving the mixer.

Again, it seems to be a tradition among filter men that soda ash (carbonate) is the thing to use. Theoretically, this would seem to be correct. The writer has experimented with it in the laboratory and has personally tried to operate the filtration plant using it, having tried every imaginable combination of proportions of aluminum sulfate and soda ash. It will not work because any excess of soda ash will redissolve the "floc" of aluminum hydroxide. As also any excess of aluminum sulfate will redissolve the "floc" it is not hard to understand that although there may be a theoretical combining proportion, yet the thing is impossible from a practical standpoint. In repeated long-time runs with the writer present and himself adjusting the feed valves, no continuous coagulation could be produced. The redissolved "floc" produced colored water sooner or later.

In casting about for a possible substitute for natural carbonate alkalinity it was thought advisable to try sodium bicarbonate, because it is cheap and is a bicarbonate that might produce an effect similar to the natural calcium bicarbonate of water. The immediate complete success of this procedure and its successful continued use has frequently made the writer desire to publish the results believing that there is sore need for such knowledge among filter men.

The above-mentioned paper on swimming-pool control brought the subject to mind in a forcible way.

The bicarbonate may be added in any excess. It is of course harmless in any needed amounts to the stomach, eyes, throat, and nose. It can be added to the water in bulk by hand or fed in measured quantity by a regulating valve from a solution. It is easily dissolved although not extremely soluble, can be purchased in a high state of purity, in quantity, almost anywhere. The result of the reaction with aluminum sulfate is of course sodium sulfate. This also is harmless in the quantities under consideration. Approximately equal weights of bicarbonate and commercial aluminum sulfate react well, the bicarbonate being practically anhydrous and the sulfate carrying about 50 per cent water. No care need be taken to avoid an excess of bicarbonate.

As for swimming pools, this of course prolongs the alkaline life almost indefinitely or until a taste develops to an objectionable degree.

In filtration plants for industrial or municipal use the old troublesome question of almost complete absence of reaction in cold water stays with us in winter when using bicarbonate of soda, just as without it.

In the plant under the writer's control there is one feature that it is believed could be copied advantageously by some others. Here the water from jet condensers from the power plant is used to supply the filtration plant. This water is kept at 60 to 70° F.

in winter. It contains only a few per cent of condensed water. It seems as if in building filtration plants, in conjunction with pumping stations, some of the heat from exhaust steam could, either by the above method or some other, be used to raise the temperature of the water to be filtered, even if only a few degrees.

The striking advantage of warming the water supply is well known, but, of course, coal cannot be burnt solely to heat the water.

Where swimming pools are to be supplied with water that is originally of such low alkalinity as to give practically no reaction with alum, it is of course difficult to devise a way to fill them the first time. If the raw water supply could be first fed into a pair of capacious tanks and there treated with bicarbonate using alternate tanks, it would solve the problem easily. This could be done except for the probability that so much space could rarely be provided.

Where the city water supply is of sufficient purity and clearness to be used without filtration for the first filling of the pool, this trouble is eliminated.

Where alum and bicarbonate solutions can be fed into the running feed water by gravity from tanks with regulating valves as is done in larger filtration plants, there would be no question at all, but as far as the writer knows, swimming pools are usually supplied with alum-feeding devices and filters all under city water pressure. This works fairly well with waters of high enough alkalinity and also will be satisfactory for refiltering water from the swimming pool because the bicarbonate can be added to the pool before re-filtration. Such plants use potash alum in large crystals which are packed in a closed tank under water pressure and the water, in slowly passing through the tank full of alum, becomes a saturated solution. The undissolved alum retains its massive condition on account of its relatively slight solubility. The tank therefore does not choke up.

Sodium bicarbonate cannot be used in any such device because of its solubility and fineness. A solution of it in such a pressure tank would be constantly changing in strength by progressive dilution and any undissolved bicarbonate would pack tightly in the tank so as to stop the flow. For the same reason aluminum sulfate cannot be used in such pressure filtration system.

It is a strange fact that makers of pressure filters will contract to provide filtration plants for swimming pools in the face of the above difficulties and make no provision whatever for supplying sufficient alkalinity. They must know very well that the alkalinity will be exhausted after a definite number of refiltrations and that raw water with low alkalinity will not reach it all. It is generally conceded among water men that one grain of aluminum sulfate per gallon of water is the minimum and that each grain per gallon requires 2 parts bicarbonate per million. On this basis it would require in the neighborhood of 400 pounds of bicarbonate for each turn-over of a 100,000 gallon pool.

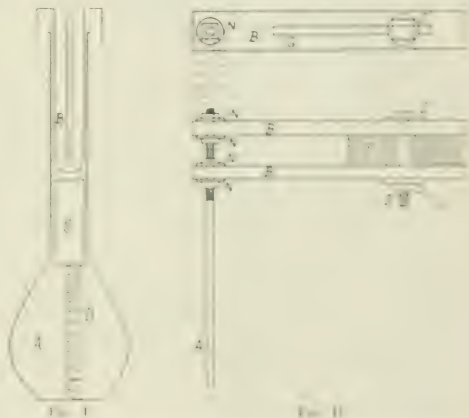
SOME LABORATORY CONVENIENCES

By A. E. PERKINS

Received November 27, 1916

Fig. I illustrates a flat bottomed Kjeldahl flask used to replace the special flask described in connection with the writer's extraction apparatus.¹ In these days when all kinds of hand-made and special glass apparatus is so expensive and so difficult to obtain, the advent of any simple but efficient home-made substitute should be welcome. Fig. I is self-explanatory. The coiled spring *D* may be satisfactorily made from No. 20 brass spring wire. We make use of alundum extraction capsules, *C*, but there would seem to be no good reason why other forms could not be used equally well. We are also now making use of the regular stock size test tube 10 in. \times 1 in., for the condensers *B* instead of the special size specified in the original description referred to above.

Fig. II illustrates a simple, convenient, and very satisfactory home-made burette support. The support is attached to the overhead shelf *E*, on which the bottles



of standard solutions are kept. This arrangement keeps the table top free from encumbrances. The exact points of the support are here described and be suitably varied as follows: *A*, the rail to which the burette clamps are attached, is at $\frac{1}{2}$ in. diameter and may be of any convenient length. It is threaded for about 6 in. on the upper end. *B*, *B* are bush-pieces of 10 \times $\frac{1}{2}$ in. \times $\frac{1}{2}$ in. bush in a suitable distance from the rail to permit the passage of the bulb *B* in their vertical position. A bar that passes has provided along the back end of the support *B*, *B* at distance *A*. These three bush-pieces back the rail and strips securely in place, the distance between *B*, *B* being measured according to the thickness of the rail. *A* may be grooved, as the width and so long as it is not interfering with the other part of work of the strips. *B*, *B* are a half of grooved bush, as provided with a washer, and a line with standard bush, as provided with a washer, *B*, *B* grip the support, to only be the other

The support is most rigid and substantial and can be quickly and easily adjusted to any desired position above the table. The Allihn, Lincoln, or Hoffman burette clamps, as listed by dealers, are satisfactory for use with this support.

TWO CONVENIENT PIPETTES FOR SAMPLING MILK AND MILK PRODUCTS

The writer has had in use for some two years a special form of pipette as shown in Fig. III, for the measurement of milk samples for chemical analysis. For most determinations a pipette is employed which is graduated on the stem in 0.01 cc. to contain 0.6 to 0.8 cc., making it easy and practicable to measure out samples of milk weighing exactly 10 g., whatever the specific gravity of the milk. The specific gravity is always determined in advance and the volume of the sample taken is governed accordingly. In use the pipette is filled to the desired point, the milk is allowed

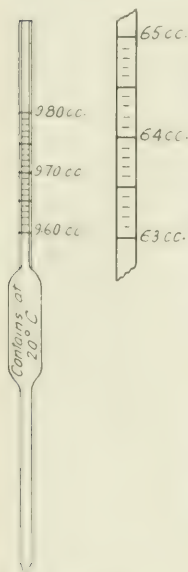


Fig. III

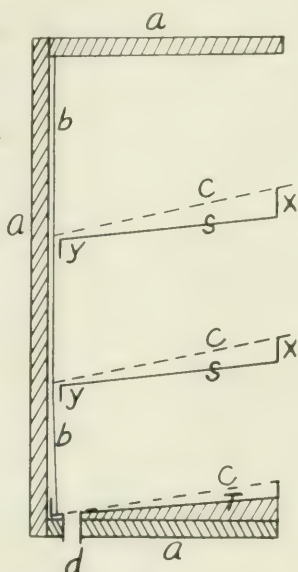


Fig. IV

to run out, and the pipette is then rinsed with water. Before measuring the next sample the water is rinsed from the pipette with a portion of the milk which is being sampled. The use of samples weighing exactly 10 g. very greatly facilitates the work of calculating results.

A pipette of the same general nature graduated on the stem in 0.1 cc. from 63 to 65 cc., as also shown in Fig. III, proves a great convenience in measuring samples of milk or milk products, for the determination of lactose by a polariscope provided with the Ventzke sugar scale. These pipettes were most carefully and accurately made for the writer by Louis F. Nafis, Scientific Glassware Manufacturer of Chicago, Ill.

A NOVEL AND CONVENIENT DRYING RACK FOR LABORATORY GLASSWARE

The frame of this drying rack *a, a* (Fig. IV), which is made of wood to match the interior woodwork of the laboratory, is in the form of a wall case with open front, and may be made of any convenient dimensions. A vertical transverse section is given, showing the arrangement of the shelves. The exact dimensions and spacings must again be left to the judgment of the user. The back of the case is covered with galvanized sheet iron as shown at *b, b*; the shelves *s, s*, also made of the same material, are supported at the ends by wooden cleats, and slope toward the back. A small space is left between the shelves and the back of the case. A double hem about $\frac{1}{2}$ to 1 in. wide is turned upward at right angles to the surface of the shelf along its front edge, and a similar hem *y* is turned downward at the back edge; these serve to make the galvanized iron shelves rigid. A piece of galvanized wire cloth resting on the top of this hem, and on the back of the shelf, as shown by *C*, forms the surface on which the beakers, dishes, funnels, etc., are inverted after washing. The drip from these dishes runs to the galvanized iron shelf, to the back of the case and thence to a shallow metal tray, *T*, at the bottom of the case. This tray is inclined towards one corner where a connection to the drain is provided as shown at *d*. No drip from the dishes on one shelf reaches the dishes on the shelf beneath. Moreover, this arrangement is very economical of space, which is so often at a premium about the laboratory sink, and the dishes, particularly beakers, drain much better than when they are inverted on a level surface.

DAIRY CHEMICAL LABORATORY
OHIO AGRICULTURAL EXPERIMENT STATION
WOOSTER, OHIO

HANDLING A STANDARD SOLUTION OF BARIUM HYDRATE

By W. C. HAYNES

Received November 9, 1916

In handling a standard solution of barium hydrate here in the laboratory of the Union Pacific R. R. Co., considerable annoyance was caused by the usual arrangement of having a siphon tube leading from the supply bottle to the bottom of the burette, and attached to the same by a piece of rubber tubing, and closed by means of a pinchcock. The constant cracking and consequent leaking of the tubing at the pinchcock was so troublesome that the following piece of apparatus was substituted with much success. As it is original so far as is known, the writer thought it would be a good idea to publish it.

The only materials needed are: a small "T" tube, a piece of glass rod about 8 in. long, a small piece of wire about the same length, one small rubber stopper, and 3 in. of small, heavy-walled rubber tubing, a flame, and about one hour's time.

Referring to the accompanying sketch, the apparatus is made as follows: first, close the end of the T-tube at *B* by heating in the flame, leaving the opening *H*

about one or two millimeters in diameter. The glass rod *A* should be selected so as to slide closely but smoothly inside of the T-tube. It must then be rounded at one end, *B*, flattened at the other end, and bent as illustrated. The nick *K* is put in with a file, and is to keep the wire spring from slipping off. Now take a little moist emery flour and grind the rounded end of the rod against the partly closed and thickened tube at *B*, so as to make a tight joint. When this is done the rest of the apparatus is quickly assembled as illustrated by closing the joints at *D*, *D* by means of the heavy-walled black rubber tubing, attaching the spring *E* (made by winding a piece of small wire around a pencil), connecting to the siphon *G*, and inserting in the burette by use of the rubber stopper *F*. (For our purposes this stopper has a small groove to allow

sides of the T-tube and out through the opening *H*, thus filling the burette. When the upward pressure of the thumb is released, the spring pulls the rod down and closes the orifice *H*.

If the siphon tube and the apparatus are dry and connected up as described, the rubber tubing will be protected from the liquid by the air caught above the joint at *T*, in the vertical part of the T-tube, and by the air space where the siphon *G* runs into the side-arm of the T-tube. The latter condition is aided by bending the side-arm slightly upward.

119 N. 114th Street
OMAHA, NEBRASKA

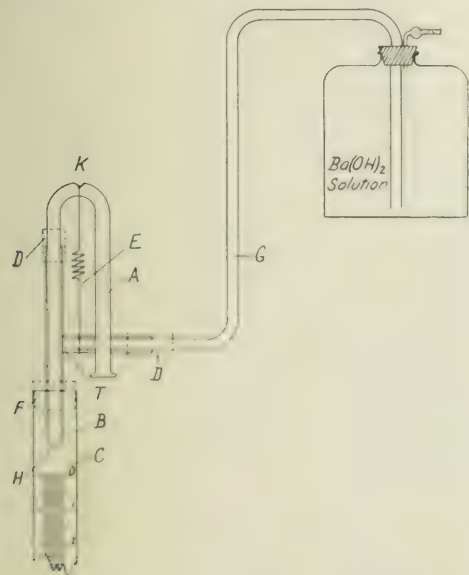
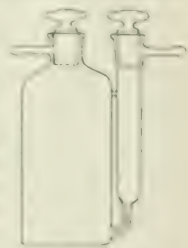
CARBON DIOXIDE ABSORPTION APPARATUS

By J. G. Wessley

Received November 17, 1916

While engaged, about three years ago, at the Bureau of Standards, Washington, D. C., on research work which involved the making of a considerable number of organic combustions, the writer designed and used the form of apparatus first mentioned in the report on that work,¹ and now more fully described.

A cylindrical bulb of thin glass contains the carbon dioxide absorbing agent (soda-lime). Connected with the lower part by a short, thick-walled capillary tube, is the smaller arm which contains the drying agent (calcium chloride, alumina,² or phosphorus pentoxide). The capillary serves to separate the moist soda-lime from the calcium chloride. This form combines lightness and simplicity of construction with a good absorbing capacity and ease of refilling. The stopper's surface and weight are small, so may be pulled from the cylinder. Empty, the separator (about 4 in. in length) weighs so that it will hold 25 g. of soda-lime and 7 g. of calcium chloride and will absorb 25 g. or more of carbon dioxide without renewal.



the passage of air, but the insertion of a small guard tube would improve it.)

By a slight pressure on the flattened end of the glass rod, the solution passes between the rod and the

United States of America
U. S. Patent No. 1,200,000

U. S. Patent No. 1,200,000
U. S. Patent No. 1,200,000

ADDRESSES

THE GERMAN ALARM CLOCK

By H. E. Howe

Although I have been living but a short distance out of the country for the last few months, it has given me a chance to see ourselves as others see us, and there is a temptation to make a few comments along that line. Also having been in a country seriously at war there is an impulse, upon facing a body of men gathered together to launch upon a reciting speech. The would not necessarily be contrary to law and neutrality, for I

have been reliably informed that it was highly necessary to take the case of the German people into consideration. It is a well known fact that the German people are not a happy people, and it is a well known fact that the German people are not a happy people.

I have thought of bringing a resolution of some kind and asking that the house of the German people be brought before it, and I thought that it would be difficult to persuade the representatives of the German people to do so. I have thought of bringing a resolution of some kind and asking that the house of the German people be brought before it, and I thought that it would be difficult to persuade the representatives of the German people to do so.

¹ Bulletin of the Bureau of Standards, Vol. 1, No. 1, 1915.
² 1915.

definitely in mind using conditions growing out of the war as a basis of what I shall try to say.

Prior to August, 1914, Germany was making a quiet, energetic and successful conquest of the industrial world. Her agents were to be found everywhere, learning the language of the country in which they worked, overrunning these countries with representatives, agents and travelers, and placing the German employees in high and low positions all over the country, in industrial and commercial concerns. Market and trade conditions were carefully studied, and unfortunately fair means of competition were not always used. Through the coöperation which existed between the government, manufacturers and banks, the German salesmen were often able to offer terms of credit quite impossible with a manufacturer not having such beneficent coöperation.

This is particularly shown in South America, where goods were often placed upon the merchants' shelves to be paid for after they had been sold to the consumer, while instances of credit up to two years are by no means uncommon.

The stocks of merchants were frequently kept filled so that competition was largely prevented. Since the beginning of the war, agents in various lines traveling in South America have found dealers to have been loaded up previous to August, 1914, with sufficient merchandise to care for their customers until 1917.

Reports from all over the world were received in Germany, and this information gathered by members of the diplomatic corps, by travelers and others, and put into such shape to allow the commercial conquest to go forward under the best possible conditions.

At home great attention was paid to research experiments and efforts to utilize all by-products, and much of the work accomplished would have been impossible without government aid in the form of subsidies and direct contribution, and the great advantage derived from the assistance of the banks, upon whose boards were technical men with voting power.

GERMAN CONTROL OF BASE METAL INDUSTRY

It may not be generally known to what extent Germany had succeeded in controlling the base metal industry of the world. This was particularly felt in Australia, where lead, zinc and copper were in the hands of powerful German trusts. It is not too much to say the German world control over lead, zinc, and copper was well-nigh complete, and affected not only the producer and the consumers in Britain and elsewhere but fixed the world's price for these commodities, limiting the output where necessary and directly controlling and affecting employment and wages.

In certain instances the refining of concentrates and matte was carried on in Germany in order that such refining processes might be kept as secret as possible, and to prevent their establishment in other parts of the world.

German workmen have not been slow to seize upon the advantages offered through the inventions of others, and in many instances have forged to the lead by effecting refinements and improvements in the inventions of other countries. Examples of this are the machine gun, the aeroplane and the submarine. Another notable example is the fixation of atmospheric nitrogen by means of which a final day of reckoning is being postponed, and the first commercial process for fixation was developed by two Americans.

When the woeful mistake was made of starting the present war, it soon began to be demonstrated that by turning the same forces to account, as had been used in commercial conflict, Germany could very nearly carry on a successful conquest of Europe. Many problems had been worked out in advance, and real research work had been employed to develop totally new weapons for offense and defense. The ex-

tent to which chemists were depended upon is well illustrated by the nitrate question. I have been reliably informed that it was not expected that all nitrate would be excluded from Germany, but that quantities could be imported by way of Italy, it being thought that that country would not enter the war. When it was found that a miscalculation had been made, orders were issued to the various organizations of chemists that they simply had to find ways of providing sufficient nitrates. This has been accomplished, and I have no doubt that after the war we will learn of greatly improved processes for the fixation of atmospheric nitrogen.

Now all of this state of progression is by no means due to any real superiority. Germany is comparatively poor in natural resources, having a corner on potash only. The proper conservation and able husbanding of such natural resources as Germany possessed, has contributed most to their advantage, while the perseverance, patience, industry and economy, which are racial traits, deserve their full amount of credit. There is no corner on brains or inventive genius, but there is in Germany an appreciation of education, concerted effort and research, which to my mind have been the cardinal points in such successful conquests as have been waged.

There is a smaller percentage of illiterates in Germany than in any other country on earth. Of the population in the various countries the following is the percentage of illiterates:

Roumania	88.4	U. S. A. whites	6.2
Servia	79.3	France	4.7
Portugal	79.2	England	3.0
Spain	68.1	Scotland	2.8
Russia	61.7	Holland	2.3
Hungary	47.8	Finland	0.8
Austria	35.6	Denmark	0.2
Italy	33.0	Switzerland	0.13
Greece	30.0	Sweden and Norway	0.08
Belgium	10.0	Germany	0.05
Ireland	7.9		

In some German provinces, such as Saxony, one is said to rarely meet a person who cannot read or write.

In considering the percentage in the United States, it must be remembered that the population is a mixed one and contains large numbers of whites from those countries which have a large percentage of illiterates.

In the armies there are said to be the following number of illiterates per thousand:

Russian	700	Austrian	250
French	50	German	3

It must be remembered that the British army is a voluntary one and of such recent growth that no reliable figures are obtainable. Since the best men usually volunteer first, the percentage of illiterates may be expected to increase as the volunteer army grows large.

I regret that no figures were obtainable on the Turkish, Belgian, Serbian or other minor armies. While I believe that much of the German education must have been faulty to have permitted the present state of affairs, yet it is worth noting to what extent education has been appreciated.

The German accomplishments through research are already so well known to you that I need take no time in emphasizing what has been done.

ACTIVITIES ON OPENING OF WAR

To this state of affairs came August, 1914, and we find an entirely new order of things. As soon as Germany is blockaded and her merchant fleet swept from the seas, countries have awakened, as if by an alarm clock, to the extent of their dependence upon German products. A careful study of the causes leading to German predominance in various fields has led others to offer sincere compliment by imitation, and by taking a leaf from the German book. Research is evidently one of the things upon which German progress has been based, coöperation is

another, and the war has awakened the rest of the world to the desirability of employing the same methods.

A committee of the Privy Council of Great Britain, to consider scientific and industrial research, was appointed, and their report for the year 1915-16 is of great interest. A series of pamphlets are to be issued on various subjects pertaining to research, and one of these is to be written by your own Dr. Mees.

The National Physical Laboratory of Great Britain, encouraged by the Government, has undertaken an exhaustive study of optical glass manufacture, and Dr. Rosenhain's Cantor lectures on this subject indicate that real progress is being made.

The effort toward the establishment of a British dye industry is well known to you, while the progress which has been made in perfecting mechanical operations is little short of marvelous. Improvements in grinding and polishing machinery, which are said to have been made in the works of Adam Hilger, are sure to put that firm in a better position to compete for world markets than ever before, and many machine shops, heretofore accustomed to do only rough work, will emerge from the war with a staff of men trained to work to the fraction of an inch, from ten to one hundred times smaller than had been their custom previously.

Conditions have also tended to break down some of the strict rules of the trade organizations, and this will naturally have its effect in the commercial competition which is to follow.

All over the world there is being pointed out to manufacturers and business men, that, as united effort is necessary in things military, it is also necessary in things industrial and commercial. In Japan an imperial edict is said to have been promulgated, calling upon the smaller companies in Japan to combine, in fact the benefits of properly controlled combinations seem to be recognized the world over excepting in the United States, where efforts are constantly being made to dissolve large corporations. It would seem much better to control them properly, since in many cases we would be much worse off without the improvements and advances which could be accomplished only by such organizations. To my mind German industry will meet, after the war, to a competition which she herself has been instrumental in awakening, a competition organized, alert and progressive to an even greater degree than that which she attained previous to August, 1914.

I would call your attention to the economic conference of the Allies, held in Paris, during June of this year, where recommendations were made to render the allied countries independent of enemy countries in raw materials and manufactured articles, essential to the normal development of their economic activities, to facilitate and improve the interchange of their products, to assimilate the laws governing patents and indications of origin and trade marks, and for the adoption of an identical procedure in regard to patents, trade marks, literary and artistic copyright, which have come into existence in enemy countries during the war. There was also adopted at this conference a series of recommendations intended to offset entirely much of the advantage which the Teutonic power had obtained through methods now about to be adopted by most of the world.

In Australia there has been much accomplished toward breaking the hold which foreigners had upon the mineral resources. Where necessary parliamentary laws have been passed, and the work of constructing the whole industry on purely Australian and British foundations has been entered upon constitutionally and systematically. New companies have been formed, research men brought in, including Mr. Price, formerly with the New Jersey Zinc Company, and a comprehensive scheme covering the whole output of Australia has been adopted.

The awakening has not been confined to nations across the sea, for we find Canada more alert today than ever before. A Call to Service has been issued by the Department of Trade

and Commerce, in an effort to bring about cooperation among the business men to an extent heretofore thought impossible. Among many committees to be appointed for real service, is one whose duty it shall be to consider industrial research and to encourage the application of science throughout the Dominion, in an effort better to utilize Canadian natural resources.

SCIENTIFIC RESEARCH

The Royal Canadian Institute is taking steps to provide facilities for research work as applied to industry. The Canadian Manufacturers' Association, a very live organization, has an active committee which is constantly bringing before the members of the Association the desirability of employing research and the various methods by which results may be obtained.

Various Chambers of Commerce are bringing research to the attention of their communities, and the Union of Canadian Municipalities, through their official journal, will emphasize research as a part of their campaign of municipal preparedness for conditions after the war.

The Canadian Mining Institute, with which the Society of Chemical Industry is cooperating, is engaged upon a study of the mineral resources of Canada, and endeavoring to determine what can be made from raw materials within the Dominion. Lists of articles and materials produced from mineral wealth are being compared with data on the existence of raw materials in Canada, their probable market and the export possibilities, with the hope that many manufactured articles need no longer be imported.

Another evidence of the awakening is to be found in a collection of between 8,000 and 10,000 German- and Austrian-made articles now being shown in the industrial centers to indicate the sort of things which Canadian manufacturers are not making, but could and should make.

There is also a plan being considered by the Royal Society of Canada in cooperation with the Government, whereby it is proposed to form a commission which will consider the research problems that can be worked out in educational centers, and assign them to the laboratorians best qualified to work upon them together with an appropriation for carrying out the work contemplated.

An effort is also being made by the Canadian Pacific Railway to assist in research and development work, through Arthur D. Little, Limited, this Company having been formed in Canada under the auspices of the railway and at the suggestion of Lord Shalginess, the president of the railroad. It is the purpose of this company to do what it can to assist in a better and more economic utilization of the natural resources of Canada through the application of industrial research, and science to find economic uses for existing wastes, to generate and prevent wastes, to utilize by-product and serve existing industries. This applies to the whole of the Dominion and not to the territory served by the railroad alone.

Arthur D. Little, Limited, upon the authorization of the railroad, is about to begin a survey of the natural resources of Canada for the purpose of having together in one place, and in a form readily at hand, trustworthy scientific data on all forms of the Dominion's natural resources possible.

Let us consider for a moment what the history of Canada by the Commerce Department shows. There has been a steady increase in the number of patents granted to inventors in Canada, and the British Empire is the same condition. A great deal of the knowledge is now being put in the world's repository, and it is a great convenience, with access to various parts of the world, is being brought to the notice of Canadian scientists. It has been said and said the only country industrial in the United States but the only country where the scientific and engineering in the natural resources of Canada, would increase that very much, very much, for the same.

CANADIAN RESOURCES

The most important natural resources of Canada are agriculture, timber, minerals, fisheries, fur-bearing animals, and water power. Canada has an area of 3,730,000 square miles, which is greater than that of the United States, including Alaska, and but a little less than that of Europe.

It is a country of great resources, in a position to benefit by the errors which have been made in older countries, and well situated between populous countries in the east, the west and the south. So far as construction is concerned, Canada is to-day in about the same position as was the United States a generation or two ago.

Agriculture must always be the greatest natural resource, and in 1913 the products produced were worth nearly \$700,000,000. To some of you chemists the idea of agriculture brings to mind a tall figure, straw hat, top boots and long whiskers, but you may be interested to know that many of the Western Canadian farmers can afford to spend their winters in California and Florida; that this year one field of 115 acres, in Alberta, brought in over \$10,000,000 to its owner, through the sale of wheat, and that in 1915 a single farm of 1,356 acres averaged nearly 52 bushels of wheat per acre.

Not long ago the Canadian Pacific Railway constructed a branch line of some 70 miles, and in early winter an agent visited the territory in order to pay the farmers for the right-of-way—80 per cent of those whom he sought were spending the winter in Florida or California.

While the forests of Canada are by no means as extensive as is generally supposed, nevertheless, in 1912, the last figures available, they yielded \$182,300,000 worth of products, including 1,109,034 cords of wood for pulp. There are millions of acres of wonderful woods still standing, and by adopting conservative forestation methods, the remaining timber can be made to yield millions of dollars annually, and still leave the forest, or the principal, in better condition for posterity.

The minerals of Canada yielded over \$144,000,000 in 1913, and have little more than been touched. There are vast areas in the north of Canada undoubtedly containing much mineral wealth which has never been explored or prospected.

Four-fifths of the world's supply of asbestos comes from Canada, and sells at from 75 cents to \$400 per ton, depending upon the length and quality of the fiber.

More than two-thirds of the world's supply of nickel has its origin in Ontario, and the greatest nickel mines in the world are located there.

Some of the other minerals include cobalt, gold, barytes, amber, mica, graphite, copper, corundum, feldspar, silver, antimony, iron, zinc, lead, molybdenite, pyrite, tungsten, titanium, palladium, and a little platinum. There are also extensive deposits of oil shales, one deposit consisting of nearly 100,000,000 tons. This shale is said to be richer than the Scotch shale, much easier mined, and consequently more profitable to distill.

In minerals, as in other resources, Canada sold the raw products prior to the war and but rarely considered the advantage to be derived from converting such material into finished products from which a greater profit can be realized. With the awakening has come a demand for concentrators and refineries. Whereas all zinc was imported in 1914 we now find a considerable quantity being refined at Trail, along with other minerals. In Ontario a large nickel refinery is being built and there has also been established a refinery to handle molybdenite.

FUEL RESOURCES OF CANADA

It is also worthy of note that the fuel resources of Canada are second only to those of the United States, so far as surveys have been carried out. There may later prove to be larger bodies on some of the other continents. However, Canada possesses large areas of peat, lignite, bituminous and anthracite coal

There is also considerable natural gas and some oil. It should be noted, however, that the best of the coal is to be found on the Atlantic and Pacific slopes.

The fisheries of Canada are widely known, and in 1913 yielded nearly \$34,000,000 worth of fish and other marine animals. Fishing reaches such proportions during the cod season that the government maintains a daily telegraphic bait report. This is very useful, indicating as it does where bait may best be obtained on a given day.

The fur-bearing animals yielded an export trade in 1913 amounting to \$5,500,000, while there are no returns to indicate the value of the furs used for the home trade. You no doubt know of the fox farms in Prince Edward Island and the steps likely to be taken to raise other fur-bearing animals in captivity, especially since the fur from such animals brings a higher price than from the same species trapped wild. It is interesting to note that the caribou are so numerous in some parts of Canada that they must be reckoned by acres and square miles rather than by numbers.

CANADIAN WATER POWER

As other fuel supplies decrease, and before, for that matter, water power becomes increasingly important, and the water powers of Canada are more abundant than in any other country. There are 969 waterfalls known to be suitable for the generation of electric power, and already 1,712,193 twenty-four-hour H. P. has been developed, approximately 18,000,000 twenty-four-hour H. P. is in sight, and 8,000,000 of this is within the reach of present markets. The Province of Ontario has the most extensive developments of any province. The great importance of this becomes more apparent when we remember that improved methods of transmission are constantly coming into use, and in Ontario power is now transmitted 242 miles. Such a radius enables this power to be used over an area of 180,000 square miles.

In the central portion of Canada is 2,000,000 square miles, with an average elevation of 1500 feet. All the drainage from this area is to rivers flowing into the St. Lawrence or the sea, and making possible water power so great as to be difficult to compute. It has already been estimated that Ontario and Quebec have available water power equivalent to 8,403,899 H. P. When the total potential H. P. is considered with respect to the area, or population, Canada finds herself as favorably situated as other nations, and when we consider the H. P. per square mile, is well up in the list with other large countries. When we remember that it takes on an average 4 lbs. of coal to develop 1 H. P. hour under favorable conditions, we calculate an amount for the coal which must be burned to make equivalent power, that is startling and beyond our comprehension.

The prices at which hydro-electric power is sold, of course, varies with the amount of power taken and is usually reckoned at the power house, leaving the cost of transmission to the user. Fairly large quantities may be obtained at \$15.00 per H. P. year, larger quantities at a lower price, and there are some old contracts still in operation upon which power is supplied as low as \$4.50 per H. P. year. This figure compares very favorably with the prices in Norway where the fixation of atmospheric nitrogen has found a home, due to low cost of power. You will remember that Dr. Eyde said in 1912 that when their power cost reached \$6.00 per H. P. year they would not be able to compete successfully with other sources of nitrates.

To have awakened such an empire to its possibilities through the employment of methods which have been tried and found satisfactory, is something to be gravely considered.

In conclusion, I will point to a few accomplishments of research work since the war began. One of these is the production of acetone and acetic acid in its various forms, using calcium carbide made electrolytically as the starting point. It is expected that this process, which has just commenced on a com-

mercial scale, will have wonderful advantages in the production of these materials.

Another example is from our laboratories, where we have succeeded in producing a high-grade half stuff for paper, using the waste flax straw as our raw materials. When we consider that more than 1,000,000 acres are put to flax for seed each year, you realize the economic importance of conserving that portion of the product—the straw—which has heretofore been burned.

The particular difficulty to be overcome was the elimination of the shive without detriment to the fiber, and the solution of the problem has naturally given us much gratification. We have also undertaken a very extensive study of straw utilization, and within a year hope to announce important results based on this work. Extensive experiments have also been conducted having for their object the better utilization of natural gas, and the present indications are that successful results have been obtained.

May I conclude by quoting this phrase, "By the study of

natural conditions and development of neglected lines of production, an invaluable degree of general prosperity may be expected"—for Canada. I attribute much of the study now taking place, and about to begin, to the German alarm clock which has gone off with a bang sufficient to startle the world. There are many instances of awakening in the United States, where we are also happy to have a part in the work of progress. We feel especially gratified in being given some part in the development work of a country whose resources I have but mentioned, and whose future certainly seems rosy.

With the world so thoroughly awakened by the German alarm clock, and the near neighbors of the United States fully aware of the advantage which lies in their natural resources, does it not devolve upon the United States to be alert, better organized, and still more appreciative of science than she is to-day?

A. D. LITTLE, LIMITED
137 MCGILL ST. MONTREAL, CANADA

PUBLIC SERVICE SYMPOSIUM

Papers presented before the NEW YORK SECTION OF THE AMERICAN CHEMICAL SOCIETY, CHEMISTS' CLUB, NEW YORK CITY, NOVEMBER 10, 1916.

PUBLIC SERVICE IN THE UNITED STATES

By CHARLES A. BEARD

Supervisor Training School for Public Service

The most striking feature of modern politics is the steady increase in the number and variety of governmental activities. It makes no difference what party is in authority. It may be the party of Hamilton and nationalism which was early committed to the doctrine that the powers of the general government should be used freely and generously to protect, assist, and encourage private enterprises; or it may be the party of Jefferson and the New Freedom which, traditionally at least, is committed to the principle that the government which governs least is best. Each party cries out at the type of interference devised by the other and proceeds to propose its own lines of intervention. Democrats solemnly inform us that a protective tariff is unconstitutional and proceed to create a commission of experts presumably for the purpose of discovering what kind of protection is good for the country. Leading Republicans disinter Herbert Spencer's Mid-Victorian doctrines of individualism and publish them to mankind as the latest word on sound politics and then solemnly warn us that unless we have government intervention in the form of a protective tariff, labor and capital will perish from the United States. Democrats defend the government's use of power to establish an 8 hour day or higher wages for chosen workmen and then decry as outrageous the government's interference in the form of a tariff, theoretically favoring the maintenance of a high wage standard in American industries. New York property owners protest in the name of liberty and humanity against orders requiring them to install fire prevention apparatus, and then turn around and demand in the name of good city planning the protection of their property rights against encroachment. Apostles of American individualism are clamoring for the extreme form of subjection to the state, which is known to mankind, namely universal military service. We are told in the same breath that we must retain our traditional rights of person and property and yet be so organized for industry and for war that we can whip the earth on ten minutes' notice.

To speak more concretely of recent developments, the Congress of the United States has established an eight work day for certain railway employees and created a commission to supervise its operation; presumably a commission of men charged with the slight duty of monitoring the maintenance of railroad operation within a period of a few months. It has created a shipping board with extraordinary powers in the matter of building up a national merchant marine. It has passed a Federal

Employees Compensation Law and authorized a commission to administer its provisions. It has founded a Farm Loan Board which will engage in rural banking and be responsible among other things for learning the technicalities of agricultural economics. It has appointed a committee to study the whole problem of government ownership of railways. It has enacted a cotton futures law, a grain standards law, and a warehouse law, all calling for expert knowledge of broad domains of private economy. I shall say nothing of such light matters as the Interstate Commerce Commission, which has had control over all the intricate processes of common carriers, of the Federal Trade Commission, of the work of valuating railways, of pure food laws calling for experts in chemistry and bacteriology, or of state and municipal enterprises demanding the highest talent in every branch of science and economics.

We may differ among ourselves as to the wisdom of this or that act or this or that type of intervention and undertaking, but we know that most of this new governmental functioning is not the product of Democratic perversity, Republican paternalism, or Socialist vengeance; it is the product of our industrial civilization. It may be diminished here or altered there, but it cannot disappear unless we return to the hand loom, the stage coach and the tallow dip, and at the same time, declare ourselves to be pacifists with the courage of our convictions. I may be wrong, but I believe the day is past when free organization of capital or labor will be permitted without government intervention to preserve order in the land. Capitalism and socialism, the great industrial processes upon which the life of the people depends. If this is true, then the government has about it more stupor, inertia, and stupidity than any other body yet created.

The number of all government functioning is a great measure of the number of government employees, national, state and municipal. A very complete compiling began May 1, 1916. [Journal of Commerce, the monthly journal of the nation's great business employers by all governmental divisions in the United States is a figure between 1,000,000 and 1,500,000.] In a short time we shall have, and perhaps government will require, a number equal to almost one-fifth the entire white population of the United States when the Shanghai and combined Atlantic and Gulf, All-India and Far-east governments and their armies are fully members of the American family at world meetings now organized on peace-making projects and more than one hundred fire railway corporations are by railway home, Scotland and transporting companies.

It is not the mere number of men around a ship, plane, the gate

—The New York Times, 24 June 1916.

serious problems of the hour. It is rather the gigantic task that we have committed to them that should give us pause. It is the variety and complexity of the burdens we have thrown upon them. They must be proficient in all of the known sciences. They must master all of the intricacies of private business. They go down into the bowels of the earth to safeguard the lives of miners and to establish mining processes conducive to safety and health. Perhaps in the future there will be an aeroplane inspection corps to prevent unjust discrimination in the interplanetary service. Laying all levity aside, our government cannot discharge adequately the duties now imposed upon it unless it is as wise as science, as astute as the cleverest business man, as efficient as the best equipped corporation, as strong as a great military machine.

And this extraordinary necessity has fallen upon us within recent times. A few generations ago a President of the United States, Andrew Jackson, could say in all seriousness: "The duties of all public officers are, or at least admit of being made, so plain and simple that men of intelligence may readily qualify themselves for their performance." Contrast this genial and comforting assumption with the following qualifications demanded of a mere assistant engineer by the Civil Service Commission of the United States according to specifications announced for an examination to be held on November 22 and 23, 1916.

(1) Mathematics and applied mechanics (covering algebra to and including problems involving quadratics; geometry, plane and solid; plane trigonometry and use of tables of logarithms or a slide rule; elements of calculus; and elementary questions involving principles of mechanics and hydraulics as set forth in college textbooks).

(2) Theory and practice of construction on land and in water (involving elementary knowledge of designing and constructing highways, railroad dams, retaining walls, foundation work, trusses, etc.).

(3) Theory and practice of topographic and hydrographic surveying, as covered in first-class surveying textbooks.

(4) Training and experience.

(5) Applicants must have had at least four years' practical experience in engineering. Graduation from a technical course in a college or university of recognized standing will be accepted in lieu of two years of the required experience. The rating in training and experience will be based upon general experience in civil engineering, and upon technical description in detail of some important work upon which the competitor has been engaged. This description must be handed to the examiner on the day of the examination.

Here, then, is the general problem as I see it:

I—How can we educate the public up to an appreciation of the necessity for trained and expert service in every branch of the government?

II—How can we so order our public service that it will attract the ablest men and women and guarantee progressive careers to those who prove loyal and efficient?

III—How can we develop a science of public administration in all of its branches, which will take the place of that pseudo-science of administrative law which is in the main a guide to the art of administrative nihilism?

IV—How can we best train our prospective civil servants in all of the various arts, sciences and crafts called for by the exigencies of modern government and adjust our curricula and educational methods to the requirements of government recruiting? In other words, how can we best gear up our educational ideals and institutions with the demands of efficient government?

V—How can we continue the training of those admitted to the lower ranges of the public service, while they are in service, thus preparing them for progressive advancement according to talents and aptitudes?

VI—How can we develop our civil service commissions into genuine recruiting agencies capable of supplying the government with exactly the type of service needed at any given moment and maintaining a loyal and efficient personnel? And this is said in no disparagement of the splendid work done by many

commissions under the handicaps now imposed by law, custom, and public opinion.

In brief, how can we make our science of government a true science of management rather than a device for distributing party spoils, and at the same time retain and develop those democratic ideals which we have thought worthy of this great nation? It may be that in your opinion I have laid before you not a problem but a paradox. If so, my retort in the true spirit of modern research is that only the impossible is worthy of the true scientific imagination.

BUREAU OF MUNICIPAL RESEARCH
361 BROADWAY, NEW YORK CITY

THE STATUS AND COMPENSATION OF THE CHEMIST IN PUBLIC SERVICE

By FREDERICK E. BREITHEIT¹

Technicians, of all men, are supposed to be concrete and specific. They are—in the actual every-day practice of their professions. As soon as they begin to discuss the more general aspects of their work, however, they seem to lose their usual balance and their ability to stick to facts. Under these circumstances, they frequently indulge in a mellifluous eloquence which would make the average clergyman or politician turn green with envy.

Let me illustrate this point with a few examples from the field of engineering. Mr. Ernest McCollough, for instance, has written a book entitled "Engineering as a Vocation." On the whole, the work is an excellent one, evidently written by a man of wide experience who endeavors throughout to keep his feet on the ground and to avoid the oratorical flights of many of his colleagues. The book is supposed to be one which is to be placed in the hands of young engineering graduates for their advice and guidance. But in the chapter entitled "The Education of the Engineer" we read:

"The engineer changes the very face of nature. He makes millions of blades of grass grow where none grew before. He builds railroads which people the deserts. He erects factories and equips them. Thousands of people are employed through him * * * *"

In a more recent volume "Engineering as a Career—a Series of Papers by Eminent Engineers," we find the same tendency toward rhetorical fervor. Thus we have in the first paper a passage which reads:

"In the past the poets have sung of love and war. It has remained for the engineer to secure for the arts of peace the dominant position in civilization. The triumphs of transportation, of electric transmission and of power development have revolutionized the life of the race and caused during the last century a greater advance toward the millenium than has occurred in any preceding thousand years * * * *"

(Then follows a quotation from Kipling.)

The second paper in this highly interesting volume is entitled "Shall My Boy Become an Engineer?" It begins by telling us that:

"Forty years ago there were no triple or quadruple expansion steam engines, no commercial oil or gas engines, no steam turbines, no dynamos—the compound steam engine was the highest developed form of motive power, and the world had been waiting thousands of years for that. Forty years ago the Atlantic cable was not yet prepared for continuous service, and there were no telephones, no phonographs, no electric lamps, no trolley cars, no automobiles, no aeroplanes, no wireless telegraphy."

Then follows a brief historical account of the achievements of the last forty years, something about the value of new ideas, a few paragraphs on the misunderstandings which frequently arise between the technically trained engineer and his less enlightened brother, a few additional paragraphs on the need

¹ For the opportunity to collect and compile the data presented in this paper, the author is indebted to the Training School for Public Service, 261 Broadway, New York City.

of engineers in manufacturing in which we are assured that "the land, the sea and the air have been conquered, and the world has probably seen in these last forty years more diverse and remarkable inventions and discoveries than will ever again be seen in any future forty-year period in the world's history."

The final paragraph contains the only reference to the title of the article. It reads:

"The mechanical engineering profession is still in the very early morning of its life and it opens up to young men, who have a liking for mathematics and mechanics and at the same time a cultivated and balanced mind, an assurance of a high and respected position in life."

This last assurance must console the anxious parent seeking advice on "Shall My Boy Become an Engineer?"

It would be futile to continue an analysis of the remainder of the book. Much of it is excellent and to the point but, on the whole, it is not of sufficient definiteness or concreteness to aid either the young man about to decide whether he wants to study engineering or not, or the young engineering graduate.

Is it not a fact that chemists are as prone to this sort of thing as engineers and other technical men?

Picture the state of mind of the young graduate in chemistry. In many instances he does not know why he undertook a course in chemistry at all. Sometimes he has been led to this action by the glowing accounts of newspapers and magazines, by the well-meaning advice of vague enthusiasts and the fiery imaginations of commencement orators. Occasionally, the young man has actually taken an account of himself, of his natural aptitude and ability. Having convinced himself of the correctness of his choice of a life career, he has proceeded to acquire the necessary fundamentals of knowledge and technique.

In any case, as the young graduate emerges from the static, receptive status of the student to enter the dynamic, active condition of the worker he usually faces the world in a state of considerable bewilderment. All too frequently he has but little idea of the actualities of life. Having been stuffed with highly inflated notions of his future and coming face to face with the hard knocks of an indifferent world, he is apt to grow discouraged, to question his own ability, to lose faith in the idealistic elements of his vocation (and surely chemistry has enough of these without the necessity of exaggerating them), to look upon himself as a failure, when as a matter of fact, he is doing fairly well.

The young graduate certainly asks himself, and probably others, questions such as the following:

What are the usual prospects in my profession?

How do the compensations and rewards compare with those in other professions?

What is the usual rate of advancement?

What can a man normally expect to be earning by the time he reaches the age of thirty-five, let us say?

Strange as it may seem, but few attempts to answer these questions have been made and most of these are of general in nature that they are of little value. The instance offered above are as typical of chemistry as they are of engineering.

The engineering profession, however, has the advantage of the profession of the chemist in that several studies, based on definite, concrete information have been made from the standpoint of financial return. Financial return, of course, is not everything, though it is the *sine qua non* of much else.

The American Society of Civil Engineers, for example, has a special committee "to investigate the condition of employment of and compensation of civil engineers." The committee has made two reports and a third is promised.¹ In these two reports are presented which show (1) the average yearly compensations, the maximum, the minimum and that of the middle man, plotted against the years of experience, (2) the variation

of compensation with the character of employment, indicating the average compensation paid by the National Government, States, Municipalities, Technical Schools, Railroads, and Private Corporations and Companies, as well as the incomes of consulting engineers and engineering contractors; (3) the general averages of compensation arranged according to geographical distribution; (4) the relative compensations received by engineers who are graduates of technical schools and those who are not.

So far as I am aware, no studies of this nature have been made of the chemical profession.

The American Chemical Society now has a membership of over 8,200. Is not the time ripe for a survey of the field of the chemist? I want to offer as my first practical suggestion, a recommendation that a Committee on Status and Compensation of the American Chemical Society be appointed. If the New York Section takes the initiative and such a committee, representing this section, is appointed to-night they will be able to bring in their report at our December meeting. The action of the Section can then be brought before the Council and Directors at the general meeting to be held in conjunction with the American Association for the Advancement of Science in this city during the Christmas week.

Returning now to the specific subject of this paper and also to our young graduate in chemistry, let us ask a few questions:

Is there a career in chemistry in the public service?

What are the relative advantages and disadvantages of public service as compared with private?

Is public service in chemistry a useful stepping-stone, giving valuable experience, no matter what field the chemist eventually enters?

The time has come when these and related questions can be answered. In fact, they *must* be answered, and answered, too, in a manner other than the vague, general one which has sufficed heretofore.

To answer these questions we must know:

- (1) The numbers and salaries of each class of chemists in the service of our governments—national, state and municipal.
- (2) The nature of the work they are called upon to do.
- (3) The qualifications usually called for.
- (4) The training best adapted to fit men for public service, and the best manner of giving such training.¹
- (5) The likely number of appointments.
- (6) The rate of advancement and maximum return of the public servant.
- (7) The proposed scheme, if any, of improvement and standardization of positions in chemistry in the public service.

It is the purpose of this paper to give the information by presenting the facts as they exist in the United States Government service, the service of New York State and the service of New York City.

1. THE CHEMIST IN THE SERVICE OF THE U. S. GOVERNMENT

One of the difficulties of making a survey of the chemical service of the Federal Government is the great confusion which exists with regard to titles. Different titles sometimes mean the same thing and the same title may mean different things. Not only that, but sometimes a title is identical in a work or position which is entirely different from that of a chemical service. On the other hand, two titles have been found in chemical service which are identical in service. In this paper an attempt is made to clear up these difficulties by listing the names of all chemists in the Federal Government service, as far as is practicable, in the same order as they are in the official records of the Government Department.

It is to be frankly admitted that the material service of the Federal Government is limited in public duty, being, practically

¹ See *Proceedings of the American Society of Civil Engineers*, Vol. 43, No. 10 (December, 1914).

² See *Transactions of the Public Service Commission*, Boston, April, 1911, Vol. 68, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100.

TABLE 1

DEPARTMENTS

CHEMISTS IN THE SERVICE OF THE UNITED STATES GOVERNMENT SEPTEMBER 1, 1916	DEPARTMENTS						
	Treasury	Navy	Interior	Agriculture	Commerce	Civil Service Commission	Public Printer
TITLE							TOTAL
Alloy Chemist	1						1
Analyst	1						1
Assistant Alloy Chemist	1						1
Assistant Biochemist	1						1
Assistant in Biochemistry			1				1
Assistant Biochemist (Soil Fertility Investigations)				1			1
Assistant Chemist	47	10	4	3			62
Assistant Chemist in Forest Products			4				4
Assistant Chemist (Mining)	1						1
Assistant Explosives Chemist	1						1
Assistant Metallurgist	2						2
Assistant Organic Chemist	1						1
Assistant Physical Chemist	3						3
Assistant Technologist	1						1
Biochemist	1		2				3
Biochemist in charge of Soil Fertility Investigations			1				1
Biochemist (conducting biochemical investigations) in connection with plant diseases			1				1
Biochemist (Soil Fertility Investigations)			4				4
Cement Chemist	1						1
Cement Expert	1						1
Cement Tester	4						4
Chemical Biologist			4				4
Chemical Engineer	70	18	15	4	327	49	1,485
Chemist	4			5			9
Chemist (Fuel)	3						3
Chemist (Physical)	1						1
Chemist in Radioactivity	2						2
Chemist (Technical Assistant)	1						1
Chief Chemist (Mineral)	1						1
Chief Metallurgist	1						1
Chief Petroleum Technologist	1						1
Consulting Chemist (Fuel)	1						1
Consulting Chemist (Mineral)	1						1
Consulting Explosives Chemist	1						1
Consulting Metallurgical Chemist	2						2
Consulting Metallurgist	2						2
Consulting Quarry Technologist	1						1
Explosives Chemist	1						1
Inspector and Chemist	1						1
Junior Ceramic Chemist	1						1
Junior Chemist	18						18
Junior Chemist in Radioactivity	4						4
Junior Chemist (Table Syrup Investigations)	1						1
Junior Explosives Chemist	1						1
Junior Laboratory Inspector	3						3
Junior Physical Chemist	5						5
Junior Organic Chemist	1						1
Laboratorian	10						10
Laboratory Aid and Engineer	9						9
Laboratory Assistant	2						2
Laboratory Assistant (Conducting chemical phases of investigations of malnutrition of citrus trees)	1						1
Laboratory Helper	1						1
Laboratory Inspector	4						4
Metallographer	1						1
Metallurgist	2						2
Mineral Technologist	1						1
Organic Chemist	2						2
Paper Plant Chemist	1						1
Physical Chemist	1						1
Physiological Chemist	1						1
Powder Expert	1						1
Quarantine Inspector	1						1
Sanitary Chemist	5						5
Scientific Assistant in Chemistry	1						1
Scientific Assistant in Soil Chemistry	1						1
Scientific Assistant in Tobacco Investigations, conducting chemical phases of Tobacco Work	1						1
Second Assistant Chemist	1						1
Senior Biochemist	3						3
Senior Laboratory Inspector	7						7
Under Laboratory Inspector	2						2
TOTAL	81	20	73	94	397	49	1,716

TABLE 1 shows the number of chemists (and allied workers¹) under each title and in each department and the total number for each title and each department. There are 71 distinctive titles in the list. In compiling this table, the following departments were considered:

EXECUTIVE DEPARTMENTS	OTHER GOVERNMENT ESTABLISHMENTS
State	Interior
Treasury	Interior
War	Interior
Justice	Commerce
Post Office	Labor
	Intermediate Commerce Commission
	Civil Service Commission
	Federal Reserve Board
	Federal Trade Commission
	Smithsonian Institution
	Government Printing Office
	The Public Printer

¹ Chemists and laboratory assistants have been combined in the Federal Service. The titles and compensations are not distinctive.

Of these the Departments printed in *italics* employ no chemists in the sense in which the term is used in this paper.

TABLE 2 gives the number of chemists employed in each federal department, arranged by bureaus. TABLE 3 contains a summary giving the numbers of chemists in the Federal service at each rate of pay and the total salaries at each rate. This table shows that the United States Government is paying \$1,447,305 per annum in salaries for its chemistry service. Summarizing the data

TABLE 2 NUMBER OF CHEMISTS IN EACH FEDERAL DEPARTMENT
ARRANGED BY BUREAUS (See Table 4)

	No. TOTAL
TREASURY DEPARTMENT	81
Treasury Department	38
Customs Service	32
Division of Scientific Research	11
WAR DEPARTMENT	20
Ordinance Department at Large	13
Quartermaster Corps of the Army	4
Engineer Department at Large in connection with Filtration Plant, Washington, D. C.	2
Military Department at Large	1
NAVY DEPARTMENT	73
Navy Yard	
Portsmouth, N. H., Industrial Department	1
Boston, Mass., Supply Department	4
New York, N. Y., Hull Division	9
Supply Department	15
Philadelphia, Pa., Supply Department	4
Washington, D. C., Ordnance Department	5
Norfolk, Va., Supply Department	4
Mare Island, Cal., Machinery Division	2
Supply Department	3
Naval Magazine	1
Puget Sound, Washington, Manufacturing Department	1
Supply Department	1
Naval Torpedo Station, Newport, R. I.	1
Naval Academy, Annapolis, Md., Engineering Station	3
Naval Proving Ground, Indianhead, Md.	15
Naval Station, Olongapo, P. I.; Naval Magazine and Chemical Laboratory	1
Office of Inspector of Engineering Material, Munhall, Pa.	1
Pittsburgh, Pa.	1
Inspector of Hull Material, Philadelphia, Pa.	1
DEPARTMENT OF THE INTERIOR	94
U. S. Geological Survey	9
U. S. Reclamation Service	6
Bureau of Mines	79
DEPARTMENT OF AGRICULTURE	397
Bureau of Plant Industry—Designation	20
Forest Service—Designation	18
Bureau of Chemistry	308
Office of Public Roads and Rural Engineering—Designation	5
Bureau of Animal Industry	28
Bureau of Soils—Designation	18
DEPARTMENT OF COMMERCE	49
U. S. Civil Service Commission	1
THE PUBLIC PRINTER	1
GRAND TOTAL	716

TABLE 3—NUMBERS OF CHEMISTS, ETC., IN THE FEDERAL SERVICE AT EACH RATE OF PAY (See Table 4)

No.	Annual Salaries	Total Salaries	No.	Annual Salaries	Total Salaries
1	\$ 500	\$ 500	10	\$2,280	\$43,430
1	800	800	3	2,900	6,900
10	900	9,000	1	2,340	2,340
1	960	960	11	2,400	26,400
2	1,000	2,000	14	2,500	35,000
4	1,020	4,080	21	2,520	52,920
3	1,080	3,240	11	2,580	11,152
60	1,100	72,000	5	2,640	13,200
1	1,260	1,260	7	2,700	18,900
4	1,320	5,280	2	2,750	5,500
6	1,380	8,280	3	2,760	8,280
11	1,400	15,400	2	2,820	5,640
28	1,440	40,320	28	3,000	84,000
1	1,500	1,500	3	3,240	1,368
4	1,560	6,240	4	3,250	13,000
9	1,600	14,400	1	3,420	3,420
46	1,620	74,520	5	3,500	17,500
3	1,680	5,040	5	3,600	18,000
5	1,740	8,700	1	3,750	3,750
89	1,800	160,200	1	3,800	3,800
1	1,860	1,860	8	4,000	32,000
1	1,900	1,900	4	4,200	16,800
3	1,920	5,760	5	4,800	24,000
7	1,980	13,860	2	5,000	10,000
28	2,000	56,000	1	1,000(a)	1,000
27	2,040	55,080	7	1,340	9,380
2	2,100	4,200	1	1,900	1,900
2	2,160	4,320	2	1,800(a)	3,600
9	2,200	19,800	5	2,000(a)	10,000
3	2,220	6,660	10	2,500(a)	25,000
1	2,250	2,250	1	3,000(a)	3,000
					716
					\$1,407,305

(a) Salaries paid on monthly basis.

(b) Salaries paid on per diem basis, figures given on 300 working days to the year.

TABLE 4—TITLES, NUMBERS AND SALARIES OF CHEMISTS IN THE EMPLOY OF THE U. S. GOVERNMENT, SEPTEMBER 1, 1916

[illegible]

given in TABLE 3, and rearranging in groups at intervals of \$500 it will be seen that 92.2 per cent of these salaries lie in the region between \$1001 and \$3000.

ANNUAL SALARIES (or Equivalents)	No.	Per Cent of Total No.
\$ 500 to 1000	23	3.2
1001 to 1500	189	26.4
1501 to 2000	219	30.6
2001 to 2500	189	22.2
2501 to 3000	93	13.0
3001 to 3500	13	1.9
3501 to 4000	12	1.7
4001 to 4500	7	0.1
4501 to 5000	7	0.9
	716	100.0

In the discussion of the report of the Committee on Status and Compensation of the American Society of Civil Engineers which we have mentioned, it was brought out that, taking it all in all, the engineer who clears \$3000 per annum, year after year, is considered a success by his co-laborers. Of course,

there are many who earn very much more than this. On the other hand, there are a great many more who earn decidedly less. The same statements are true, we believe, with regard to the chemical profession. Ask any ordinary, every-day practicing chemist of good ability, who is thought to be doing fairly well by his colleagues, what he regards as a successful chemist from the standpoint of compensation and he will probably agree that the chemist who clears \$3000 per annum, year in and year out, is above the average.

Adopting this standard as a fair measure of the successful chemist, and rearranging the data covering the Federal service, we find the following:

	Below \$3000	\$3000 or over	TOTAL
Number.....	639	77	716
Per cent.....	89.2	10.8	100

The implications of this result are so glaringly obvious that they call for no comment.

TABLE 5—QUALIFICATIONS FOR APPOINTMENT AS CHEMISTS IN FEDERAL CIVIL SERVICE

TITLE OF POSITION	AGE, SEX, ETC.	(a)	EDUCATION, TRAINING AND EXPERIENCE	CONTENT OF EXAMINATION AND RELATIVE WEIGHTS	SALARY
Aid, qualified in Chemistry	Male 18 to 22 No Med. Cert.	N & A	<i>Relative weight, 10.</i> Special consideration given to graduates of mechanical training, technical or scientific schools, or for training in scientific or technical laboratories.	Elementary algebra, geometry and trigonometry, 25; general physics, 25; elementary chemistry, 30; training and experience, 20.	\$ 600 to \$ 840
Alloy Chemist	Male 25 to 40	A	<i>Relative weight, 80. Required:</i> Education equivalent to degree of Ph.D. in chemistry, and knowledge of physical chemistry, with special reference to the phase rule, and its application to alloys, a knowledge of microchemistry and metallography, and a reading knowledge of French and German. Also must have experience in foundry practice for nonferrous alloys, in the construction and manipulation of electrical furnaces, and in accurate high temperature measurements.	General education in scientific training, 40; practical experience and fitness, 40; publications or thesis, 20.	\$2400 to \$3000
Alloy Chemist Assistant	Male 21 to 35 No Med. Cert.	N	<i>Relative weight, 20. Required:</i> Graduation from college or university and in addition, 2 years' post-graduate work or 3 years' experience in nonferrous alloy industries.	Physical and electrochemistry, 35; French and German, 10; microchemistry and metallography, 25; thesis, 10; education, training and experience, 20.	\$1620
Alloy Chemist Junior	Male 21 to 35		<i>Relative weight, 20. Required:</i> Education equivalent to degree of Ph.D., knowledge of physical chemistry, with special reference to the phase rule and its application to commercial and scientific problems, and a reading knowledge of French and German.	Same as assistant alloy chemist.	\$1500 to \$1800
Analyst	Male 18 to 40	N & A	<i>Relative weight, 25. Required:</i> Graduation from high school; 2 years' college work in science, including physics, chemistry, laboratory work in inorganic analytical chemistry, and 1 year college mathematics.	General chemistry, 30; inorganic analytical chemistry, 30; physics, 15; training and experience, 25.	\$ 800 to \$1020
Assayer, Assistant	Male Over 18 No Med. Cert.	N	<i>Relative weight, 40. Required:</i> Education including a course in inorganic chemistry, both qualitative and quantitative; also 1 year's experience in positions requiring the making of quantitative chemical analyses for the various metals and assays for lead, silver and gold.	Practical questions, 60; training and experience, 40. Duties require determination of zinc, lead, copper, tin, antimony, iron, calcium, silver and gold, and general laboratory work.	\$1200
Assistant in Metabolism Investigations	Male Under 45 No Med. Cert.	N	<i>Relative weight, 35. Required:</i> Graduation in medicine, and 6 months' practical experience in work with the respiration apparatus, and the calorimeter.	General chemistry, 25; calorimetric, and respiration determinations, 40; education and experience, 35.	\$1500
Biochemist, Assistant	Male 25 to 45 No Med. Cert.	N	<i>Relative weight, 80. Required:</i> Ph.D. degree for graduation from college, and 3 years' post-graduate work in biochemistry.	General education, 40; laboratory experience, 40; publications or thesis, 20.	\$2000
Ceramic Chemist Associate (qualified in Glass Technology)	Male Under 45 No Med. Cert.	N & A	<i>Relative weight, 80. Required:</i> Degree in ceramic engineering or equivalent courses, and 3 years' experience in operating ceramic plants, of which 2 years must have been in the technical study of glass or in teaching glass technology; also a thorough knowledge of refractory clays is necessary.	General education and scientific training, 40; practical experience and fitness, 40; publications or thesis, 20.	\$2000 to \$2500
Ceramic Chemist, Junior	Male Under 35 No Med. Cert.	A	<i>Relative weight, 30. Required:</i> Graduation from 4 years' course in college or university, additional credit given for specialized training in ceramics and for experience in the pottery industry.	Inorganic chemistry, including mineral analysis, 15; mineralogy and blowpipe analysis, 10; French or German, 10; ceramics, 35; education and experience, 30.	\$1200 to \$1500
Chemical Engineer	Male 25 to 40	N & A	<i>Relative weight, 75. Required:</i> Ph.D. degree, training including special courses in physical chemistry, and 1 year's experience in a chemical or metallurgical industry.	General education and scientific training, 40; professional experience and fitness, 35; published or manuscript reports, 25.	\$1800 to \$3000
Chemical Engineer, Explosives	Male Under 40 No Med. Cert.	N	<i>Relative weight, 80. Required:</i> Ph.D. degree, and 5 years' experience, since receiving bachelor's degree, in chemical and physical investigation of explosives.	Education, 40; experience, 40; publications or manuscript reports, 20.	\$1800 to \$2400
Chemist, Ordnance Department	Male Under 35 No Med. Cert.	N	<i>Relative weight, 40. Required:</i> Graduation with bachelor's degree from 4 years' course in chemistry and 2 years' experience in analysis of iron and steel or melting and mixing of steel.	Physics, 10; general chemistry, 20; iron and steel analysis, 30; education and experience, 40.	\$1200
Chemist, Ordnance Department	Male Under 35 No Med. Cert.	N	<i>Relative weight 40. Required:</i> 5 years' practical laboratory experience, 1 year in an iron works. Each year of college work in a chemical course is equivalent to 1 year's experience.	Iron, steel, and nonferrous alloy analysis, 35; general analytical chemistry, 25; education and experience, 40.	\$3.84 per day

TABLE 5—QUALIFICATIONS FOR APPOINTMENT AS CHEMISTS IN FEDERAL CIVIL SERVICE

TABLE 5—QUALIFICATIONS FOR APPOINTMENT AS CHEMISTS IN FEDERAL CIVIL SERVICE			EDUCATION, TRAINING, AND EXPERIENCE	EXAMINATION, WEIGHTS, ETC.	SALARY
TITLE OF POSITION	AGE, SEX, ETC.	(a)			
Chemist, Government Printing Office	Male 20 to 40	A	Relative weight, 40. Required: Bachelor's degree or equivalent, and practical experience in analysis of paper.	General chemistry, 30; analytical chemistry, 10; education, training, experience and fitness, 40.	\$1000
Chemist, Bureau of Chemistry	Male 30 to 45 No Med. Cert.	A	Relative weight, 40. Required: Bachelor's degree or equivalent, and practical experience in analysis of paper.	Education, practical experience and fitness, 100.	\$1000
Chemist, qualified in Physical Chemistry			Relative weight, 100. Required: High order of scientific training equivalent to that required by leading American universities for a professorship in physical chemistry.	Education, training, technical and professional achievements as shown by publications and results accomplished.	\$1500
Chemist, Assistant Engineer, Department at Large	Male Over 20	A	Relative weight, 25. Required: Educational training equivalent to B. S. degree.	Chemical arithmetic, 15; chemistry of water, 25; bacteriology of water, 25; microscopy of water, 10; education, training, experience and fitness, 25.	\$1000
Chemist, Assistant Custom-House Service	Male Over 18	N	Relative weight, 15. Duties of position include making laboratory tests of sugar, chemical examination of the contents of drugs, chemicals, oils, acids, etc., the assay of gold, silver and lead, the examination of starches, flours, fibers, and dyes, and general analytical work.	General physics, 20; general and analytical chemistry, 35; education, training, experience and fitness, 45.	\$1200
Chemist, Assistant Geological Surveying	Male Over 20	A	Relative weight, 30. Required: Education equivalent to B. S. degree.	Analytical chemistry, 30; general chemistry, 20; French, 10; German, 10; education, training, experience and fitness, 30.	\$1200
Chemist, Assistant Navy Yard	Male Over 20		Relative weight, 25. Required: Educational training equivalent to B. S. degree.	Quantitative analysis, 25; general chemistry, 25; education, training, experience and fitness, 25.	\$4.00 per day
Chemist, Assistant Bureau of Standards	Male 20 to 30	A	Relative weight, 25. Required: Graduation from 4 years' course in chemistry.	General physics, 25; general chemistry, 25; education, training, experience and fitness, 25.	\$1400
Chemist, Assistant Bureau of Chemistry, Department of Agriculture	Men & Women Over 20	N & A	Relative weight, 40. Required: Educational training equivalent to B. S. degree with 3 years' course in chemistry.	Practical questions on theoretical and applied chemistry, consisting of general, inorganic and organic chemistry, physical chemistry, and analytical chemistry, 50; translation into English from French or German technical literature, 10; education, training, experience and fitness, 40.	\$1400
Chemist, Assistant Ordnance Department	Male Over 20 No Med. Cert.	N	Relative weight, 50. Required: B. S. degree from 4 years' course in chemistry or chemical engineering, including 1 year in organic chemistry. Experience in testing analysis or manufacture of explosives is desirable.	Chemistry (manufacture and testing of explosives), 50; education, training, experience and fitness, 50.	\$1400
Chemist, Assistant Office of Public Roads, Department of Agriculture	Male 25 to 50	A	Relative weight, 90. Required: Educational training equivalent to graduation from chemical or chemical engineering course.	General education and technical training, 25; practical laboratory experience, particularly in bituminous materials, 40; practical field experience in use of bituminous materials, 25; education, training, experience and fitness, 10.	\$1400
Chemist, Assistant Bureau of Mines	Male Under 40 No Med. Cert.	N	Relative weight, 80. Required: Educational training equivalent to graduation from chemical or chemical engineering course, and 2 years' practical work or 2 years' experience in electrochemistry or chemical engineering.	Undergraduate chemistry, 40; experience and fitness, 40; publications, 20.	\$1400
Chemist, Associate (qualified in Chemistry of Metals) Bureau of Standards	Male 25 to 45 No Med. Cert.	A	Relative weight, 30. Required: Graduation with bachelor's degree in chemistry from full 4 years' course and 3 years' subsequent research work in chemistry of metals and alloys.	Education, training, experience and fitness, 40; publications, 20.	\$1400
Chemist, Junior	Men & Women Over 20 No Med. Cert.	N & A	Relative weight, 30. Required: Graduation from full 4 years' course in chemistry or chemical engineering.	Education, training, experience and fitness, 40; publications, 20.	\$1400
Chemist, Junior Bureau of Mines	Male 21 to 40 Med. Cert.	N & A	Relative weight, 30. Required: Graduation from full 4 years' course in technical college, and 2 years' practical work or 2 years' experience in electrochemistry or chemical engineering.	Education, training, experience and fitness, 40; publications, 20.	\$1400
Chemist, Junior Geological Surveying	Male 20 to 45	A	Relative weight, 30. Required: Graduation from full 4 years' course in chemistry or chemical engineering.	Education, training, experience and fitness, 40; publications, 20.	\$1400
Chemist, Junior (qualified in Fuels)	Male Over 20 No Med. Cert.	N & A	Relative weight, 30. Required: Graduation from full 4 years' course in technical college, and 2 years' practical work or 2 years' experience in electrochemistry or chemical engineering.	Education, training, experience and fitness, 40; publications, 20.	\$1400
Chemist in Chemical Metallurgy, Assistant	Male Under 40 No Med. Cert.	A	Relative weight, 30. Required: Graduation from full 4 years' course in technical college, and 2 years' practical work or 2 years' experience in electrochemistry or chemical engineering.	Education, training, experience and fitness, 40; publications, 20.	\$1400

TABLE 5—QUALIFICATIONS FOR APPOINTMENT AS CHEMISTS IN FEDERAL CIVIL SERVICE—(Continued)

TITLE OF POSITION	AGE, SEX, ETC.	(G)	EDUCATION, TRAINING AND EXPERIENCE	EXAMINATION, WEIGHTS, ETC.	SALARY
Chemist's Aid	Men & Women 18 to 30 No Med. Cert.	N & A	<i>Relative weight, 30. Required:</i> 1 year college chemistry or 3 years' experience in chemical laboratory, or 1 year's experience in chemical laboratory and graduation from manual training school.	Elementary chemistry, including simple problems in qualitative and quantitative analysis, chemical calculations, and practical laboratory manipulations, or simple elementary physics, 70; education and experience, 30.	\$ 720 to \$1200
Chief, Bureau of Chemistry, Assistant	Male 30 to 45	A	<i>Relative weight, 100. Required:</i> Educational training, including M.D. degree, and special training in analytical and physiological chemistry, and 3 years' experience as a medico-legal expert and some experience as an administrative officer.	Education training, practical experience, fitness and publications, 100	\$4000
Dairy Chemist	Male	N & A	<i>Relative weight, 70. Required:</i> Education equivalent to Ph.D. degree, and thorough training in biochemistry.	General education, 20; college education in chemistry, 30; practical experience and fitness for conducting investigations along the lines related to chemistry, including experience in teaching, research work and commercial work, 20; plans for an investigation, 15; thesis on some subject relating to chemistry, 15.	\$1800
Electrochemical Engineer	Male Under 40 No Med. Cert.	A	<i>Relative weight, 30. Required:</i> Graduation from 4 years' course in chemistry, and 2 years' experience in construction and operation of electric furnaces.	Chemistry, 25; physics, 15; construction and operation of electric furnaces, 30; education and experience, 30.	\$1500 to \$1800
Electrometallurgist	Male 25 to 40	N & A	<i>Relative weight, 80. Required:</i> Educational training equivalent to graduation from college, including courses in geology, chemistry, physics and metallurgy, and 3 years' experience in electric furnaces.	General education and scientific training, 40; practical experience and fitness, 40; publications or thesis, 20.	\$1800 to \$3000
Explosives Chemist, Bureau of Mines	Male Under 40 No Med. Cert.	N	<i>Relative weight, 75. Required:</i> Graduation from 4 years' course in chemistry, and 5 years' experience, including research work in explosives. Graduate work in chemistry accepted in lieu of experience.	Education, 25, experience, 50; publications, 25.	\$2100 to \$2700
Forest Products Chemist	Male 20 to 30	N & A	<i>Relative weight, 40. Required:</i> Educational training equivalent to bachelor's degree or chemical engineer's degree, and 3 years' experience in research or industrial chemical work. Desired a knowledge of the chemistry of wood distillation, pulp manufacture, tannins and gums derived from wood, and wood preservation.	Organic chemistry, 15; chemistry in industries utilizing forest products, 25; thesis or publications, 20; education, training and experience, 40	\$1600 to \$2900
Forest Products Chemist, Assistant	Male Under 30	N & A	<i>Relative weight, 25. Required:</i> Graduation with degree of B.S. or chemical engineer.	Chemical arithmetic, 20; general chemistry (including qualitative and quantitative analysis, physical chemistry, and general organic chemistry), 35; chemistry and technology of wood, and wood-using industries, 20; education, training and experience, 25.	\$ 900 to \$1200
Fuels Chemist, Junior	Male Over 20 No Med. Cert.	N	<i>Relative weight, 25. Required:</i> Graduation from 4 years' course in physical and organic chemistry in technical college.	General and physical chemistry, 25; organic chemistry, 25; elementary physics, 15; translation from French and German technical works, 10; training and experience, 25.	\$1200 to \$1500
Inorganic Chemist, Philippine Service	Male Under 40 Med. Cert.	N	<i>Relative weight, 80.* Required:</i> Graduation from 4 years' course in chemistry.	Education, 40, experience, 40; publications or thesis, 20.	\$1600 to \$2250
Laboratory Aid in Chemistry and Physics	Men & Women 18 to 25 No Med. Cert.	N & A	<i>Relative weight, 20. Required:</i> 2 years' college work or 2 years' experience in chemical or physical laboratory.	Elementary algebra, geometry and trigonometry, 15; general chemistry, 25; general physics, 25; free-hand and elementary mechanical drawing, 15; education and experience, 20.	\$ 600 to \$ 900
Laboratory Assistant in Chemistry, Bureau of Standards	Male 20 to 30	A	<i>Relative weight, 25. Required:</i> Graduation from 4 years' course in chemistry or equivalent. Special consideration given for reading knowledge of French and German.	General physics, 25; general chemistry, 50; education and experience, 25.	\$1000 to \$1440
Leather Chemist	Male Under 40 Med. Cert.	N	<i>Relative weight, 40. Required:</i> Graduation in science, and 2 years' practical course in tannery.	Practical questions in chemistry and tannery, 40; thesis, 20; education, experience, 40.	\$1600
Master Steel Maker	Male 25 to 45 No Med. Cert.	N	<i>Relative weight, 90. Required:</i> Bachelor's degree in chemistry or metallurgy, and 3 years' subsequent experience in physical metallurgy in research or industrial plant laboratories, or as foreman of a steel casting plant.	Education, 30; professional experience, 80; publications, official reports or thesis, 10. Should have expert knowledge of molding, the treatment of steel molding sand, the making of molds and cores for steel castings, the maintenance and operation of the Tropenas converter and small open-hearth furnaces, the operation of iron cupolas, and the making up of charges to meet specific requirements. In addition, he must be able to make qualitative and quantitative analyses of wrought iron, pig iron, ferromanganese, ferrosilicon, ferrochrome, ferroaluminum, ferrotungsten, ferrovanadium, gunite, limestone, dolomite, slags, and silica sand, also silica brick, common fire brick, and clays. He must know the effect of the different elements in steel and have a full knowledge of the best treatment of steels.	\$8.00 per day
Metallographist, War Department	Male Under 40 No Med. Cert.	N	<i>Relative weight, 80. Required:</i> Bachelor's degree from 4 years' chemical course and 3 years' experience in metallurgical work, including the use of the microscope in examination of metals, and the making and interpretation of photomicrographs and metals.	Education, 40; experience, 40; publications or reports, 20.	\$2000

TABLE 5—QUALIFICATIONS FOR APPOINTMENT AS CHEMISTS IN FEDERAL CIVIL SERVICE—(Continued)

TITLE OF POSITION	AGE, SEX, ETC.	(a)	EDUCATION, TRAINING, AND EXPERIENCE	EXAMINATION, WEIGHTS, ETC.	SALARY
Metallurgical Chemist, Ordnance Department	Male Under 45 No Med. Cert.	N	Relative weight, 80. Required: Bachelor's degree from four years' course in chemistry, and 1 year's subsequent experience in metallurgical chemistry, either in graduate work or in a laboratory.	Education, 40; experience, 40; publications or reports, 20.	\$1800
Metallurgical Chemist, Ordnance Department	Male Under 50 No Med. Cert.	N	Relative weight, 80. Required: 5 years' experience in chemical laboratory, including metallurgical work. Bachelor's degree in chemistry accepted in lieu of 3 years' experience.	Education, 20; experience, 60; publications or thesis, 20.	\$1500
Metallurgist, qualified in Metallography, Ordnance Department	Male 20 to 45	N	Relative weight, 70. Required: Education equivalent to graduation from technical school or college. Desired, experience in manufacture and heat treatment of iron, steel, bronze, and other alloys, and also experience in examining such metals under the microscope.	General education and technical training, 40; practical experience and fitness, 30; publications or thesis, 20.	\$2000
Metallurgist, for Work with Smelter Fumes, Bureau of Mines	Male 25 to 40	N & A	Relative weight, 80. Required: Education equivalent to bachelor's degree, including courses in chemistry, physics, metallurgy, and mineralogy, and in addition, 3 years' experience in chemical and metallurgical phases of smelter operations in both copper and lead, and in the examination of smelter fumes. Also ability as a writer of reports.	General education and technical training, 40; practical experience and fitness, 30; publications or reports, 20.	\$2700 to \$3000
Metallurgist, for Work in Low Grade Ores, Bureau of Mines	Male 30 to 45	N & A	Relative weight, 70. Required: Education equivalent to bachelor's degree, including courses in chemistry, metallurgy, and geology, and in addition, 5 years' experience in metal mining or metallurgical operations, also ability as a writer of reports.	General education and technical training, 40; professional experience and fitness, 35; publications or reports, 20.	\$2000 to \$3000
Metallurgist, Assistant Bureau of Mines (Work in Low Grade & Complex Ores)	Male 25 to 45 No Med. Cert.	N	Relative weight, 90. Required: College university course in chemistry, metallurgy and geology, and 5 years' experience in ore-dressing and metallurgical operations.	Education, 30; professional experience, 60; publications, official reports, or thesis, 10.	\$2000 to \$3000
Mineral Technologist, Bureau of Mines	Male 25 to 45 No Med. Cert.	N	Relative weight, 70. Required: Graduation from technical or mining school, and 3 years' experience in mineral technology.	General education and technical training, 30; experience in connection with rarer minerals and fitness, 40; publications, or technical or professional reports, 30.	\$2400 to \$3600
Organic Chemist, Philippine Service	Male Under 40 Med. Cert.	N	Relative weight, 80. Required: Graduation from four years' course in chemistry.	Education, 30; scientific papers, publications, or thesis, 20.	\$2000 to \$2400
Organic Chemist, Bureau of Chemistry, Hygienic Laboratory, Public Health Service	Male 21 to 40 No Med. Cert.	N & A	Relative weight, 60. Required: Degree of Ph.D. in chemistry.	General education and scientific training, 30; technical and professional experience, 30; publications and other evidence indicating ability to do research work, 40.	\$2800 to \$3000
Petroleum Chemist, Assistant, Bureau of Mines	Male 25 to 35	N & A	Relative weight, 80. Required: Graduation from college or university. Desired, Ph.D. degree in chemistry and physics, and 1 year's experience in chemical and physical researches in petroleum.	General education and technical training, 30; professional experience and fitness, 30; publications or reports, 20.	\$2800 to \$3000
Pharmaceutical Chemist, Bureau of Chemistry	Men & Women No Med. Cert.	A	Relative weight, 70. Required: Ph.D. degree in chemistry and at least 3 years' experience in research in pharmaceutical chemistry or in manufacturing of pharmaceutical products.	Education, 30; experience, 40; publications or scientific literature, 30.	\$1800 to \$2500
Pharmaceutical Research Chemist, Bureau of Chemistry	Male No Med. Cert.	A	Relative weight, 80. Required: Graduation in pharmacy, degree of Ph.D. in chemistry or pharmacy, and 3 years' experience in research laboratories in chemical pharmaceutical investigations.	Education, 20; experience, 40; publications or thesis, 20.	\$2000
Pharmacological Aid, Bureau of Chemistry	Men & Women 20 to 35 No Med. Cert.	A	Relative weight, 25. Required: 2 years' attendance at college or university.	Pharmaceutical education, 20; experience, 20; publications or thesis, 20.	\$1000 to \$1200
Pharmacologist, Junior Bureau of Chemistry	Male 21 to 35 No Med. Cert.	A	Relative weight, 30. Required: Graduation from college or university.	Pharmaceutical education, 20; experience, 20; publications or thesis, 20.	\$1200 to \$1400
Physical Chemist, Philippine Service	Male 18 to 40 Med. Cert.	N	Relative weight, 70. Required: Graduation from college or university, and 1 year's experience in chemistry.	Education, 30; scientific papers, publications, or thesis, 20.	\$2000 to \$2400
Physical Chemist, Junior, Bureau of Chemistry	Male 25 to 40 No Med. Cert.	A	Relative weight, 30. Required: Graduation from college or university, and 1 year's experience in chemistry.	Education, 30; scientific papers, publications, or thesis, 20.	\$2000 to \$2400
Physical Chemist, Junior, Bureau of Mines	Male 20 to 30	N & A	Relative weight, 30. Required: Graduation from college or university, and 1 year's experience in chemistry.	Education, 30; scientific papers, publications, or thesis, 20.	\$2000 to \$2400
Physical Metallurgist, Navy Yard	Male 25 to 45 No Med. Cert.	N & A	Relative weight, 30. Required: Graduation from college or university, and 1 year's experience in chemistry.	Education, 30; scientific papers, publications, or thesis, 20.	\$2000 to \$2400
Physiological Chemist, Bureau of Animal Industry, Department of Agriculture	Male Under 45 No Med. Cert.	N	Relative weight, 30. Required: Graduation from college or university, and 1 year's experience in chemistry.	Education, 30; scientific papers, publications, or thesis, 20.	\$2000 to \$2400
Professor of Chemistry, Hygienic Laboratory, Public Health Service	Male Under 40	A	Relative weight, 30. Required: Graduation from college or university, and 1 year's experience in chemistry.	Education, 30; scientific papers, publications, or thesis, 20.	\$2000 to \$2400

TABLE 5—QUALIFICATIONS FOR APPOINTMENT AS CHEMISTS IN FEDERAL CIVIL SERVICE—(Continued)

TITLE OF POSITION	AGE, SEX, ETC.	(4)	EDUCATION, TRAINING AND EXPERIENCE	EXAMINATION, WEIGHTS, ETC.	SALARY
Radioactivity Chemist, Bureau of Mines	Male 22 to 45	N & A	Relative weight, 70. Required: Education equivalent to Ph.D. degree and practical experience in radioactivity and the rarer metals.	General education and scientific training, 30; practical experience and fitness, 40; publications or thesis, 30.	\$1800 to \$2160
Radioactivity Chemist, Bureau of Mines	Male Under 35 No Med. Cert.	N	Relative weight, 60. Required: Graduation from 4 years' course in chemistry.	Inorganic and physical chemistry with special reference to the rarer metals and radioactivity, 30; mineralogy and blowpipe analysis, 10; French and German, 10; thesis, 10; education and experience, 10.	\$1200 to \$1500
Research Chemist, Bureau of Animal Industry, Depart- ment of Agriculture	Male 24 to 45	A	Relative weight, 80. Required: Degree of Ph.D. in chemistry.	General education and scientific training, 40; practical or professional experience and fitness, 40; publications, 20.	\$1800
Sanitary Chemist, Hygienic Laboratory, Public Health Service	Male 25 to 35		Relative weight, 80. Required: Bachelor's degree from scientific course, including sanitary chemistry, bacteriology, and public health work, and 3 years' experience in laboratory and field work in water purification, sewage purification, stream pollution, and chemistry and bacteriology of milk. Knowledge of French and German and of elementary engineering is desirable.	General education and technical training, 40; technical or professional experience and fitness, 40; publications or thesis, 20.	\$1800 to \$2500
Soil Laboratory Assistant, Bureau of Soils, Department of Agriculture	Male 21 to 30	A	Relative weight, 30. Required: 3 years' college work in science, including courses in general and analytical chemistry.	General chemistry, 15; analytical chemistry, 15; soil chemistry, 30; German or French, 10; education, training, experience and fitness, 30.	\$1000 to \$1500
Soil Chemistry Assistant, Bureau of Soils, Department of Agriculture	Male 22 to 40	A	Relative weight, 15. Required: Education equivalent to B.S. degree.	Inorganic and analytical chemistry, 20; organic chemistry, 10; physical chemistry, 20; soil chemistry, 20; French or German, 15; education, training, experience and fitness, 15.	\$1500 to \$1800
Specialist in Agricultural, Biological and Physiological Chemistry, Office of Experiment Stations, Department of Agriculture	Male 21 to 40 No Med. Cert.	A	Relative weight, 35. Required: Graduation from college or university, with specialization in chemistry, including laboratory investigation in agricultural, biological, or physiological chemistry. SPECIAL consideration given to experience in preparing bibliographies or reviews of literature in agricultural, biological or physiological chemistry, and for familiarity with the methods of agricultural analysis, and with immunochemistry and serum therapy.	Biological and physiological chemistry, 25; preparation and abstract of English, French and German articles, 40; education and experience, 35.	\$1500 to \$1800
Superintendent of Acid Plants	Male Over 20 No Med. Cert.	N	Relative weight, 40. Required: 1 year of college chemistry, including course in qualitative analysis, and 2 years' practical experience, part of which was in actual supervision in the manufacture of nitric acid, and contact sulfuric acid.	General chemistry, 20; practical questions in acid manufacture, 40; education and experience, 40.	\$6.00 per day
Technical Assistant, Customs Service	Male 21 to 15 No Med. Cert.	N	Relative weight, 35. Required: Bachelor's degree, including courses in chemistry, or 2 years' specialization in chemistry.	Arithmetic, 10; report-writing, 10; chemistry, 30; thesis, 15; education and experience, 35. Duties include assisting in tea examination and keeping records and reports.	\$1200

Having completed the picture of the present constitution of the Federal service in chemistry, the next questions before us are those of the qualifications usually called for in filling these positions and the probable number of vacancies.

TABLE 5 contains a summary of the examinations in chemistry in the Federal service of the last five years, giving the titles, qualifications, relative weights, content of examinations and weights of subjects, and salaries. TABLE 6 gives the number of appointments made to positions in chemistry in the Federal service during the fiscal years 1911-1915.

TABLES 1 to 4 are based on replies to a circular letter (7/28/16) to the departments of the Federal Government enumerated above by the Hon. Jos. V. Flynn, member of Congress from the Third District of New York. These replies were signed in the case of the Executive Departments either by the Secretary of the Department or some one directly designated by him. In the other Government establishments the answers were signed by the properly constituted authorities. It can therefore be stated that the information is up-to-date, reliable and authoritative. It is a pleasure to acknowledge our indebted-

TABLE 6—APPOINTMENTS OF CHEMISTS MADE TO FEDERAL CIVIL SERVICE FROM COMPETITIVE ELIGIBLE LISTS FOR FISCAL YEARS 1911-1915

Number Appointed						Number Appointed							
POSITION	1911	12	13	14	15	TOTAL	POSITION	1911	12	13	14	15	TOTAL
Aid qualified in Chemistry.....	1	1	2	4	Medico-Chemical Analyst.....	..	1	1	2
Alloy Chemist.....	1	1	Metallurgical Chemist.....	..	1	1	2
Alloy Chemist, Junior.....	1	1	Metallurgical Chemist and Assayer.....	1	1	2
Analyst.....	2	2	Metallurgist.....	1	1	2
Analytical Chemist.....	1	1	Metallurgist, Assistant.....	1	1	1	3
Assayer's Assistant.....	2	2	4	Metallurgist, Chief.....	1	1	1	3
Bacteriological Chemist.....	1	2	3	Mineral Examiner.....	..	1	5	..	6	11
Biochemist, Assistant.....	1	1	2	Mineral Technologist.....	1	..	1	2
Ceramic Chemist, Junior.....	1	1	Organic Chemist.....	..	2	..	10	12	24
Chemical Metallurgy, Assistant.....	1	1	2	Pharmaceutical Chemist.....	3	..	1	..	4	8
Chemist.....	2	2	4	Pharmacologist, Assistant.....	1	..	1	2
Chemist, Ordnance Department.....	..	1	1	Pharmacologist, Junior.....	2	2	4
Chemist, Assistant.....	..	14	14	2	6	36	Pharmacology, Technical Assistant in.....	2	..	1	3
Chemist, Assistant, Bureau of Standards.....	..	4	4	Pharmacology, Scientific Assistant in.....	1	1	2
Department of Agriculture.....	..	18	25	43	Professor of Pharmacology.....	1	..	1	2
Ordnance Department.....	18	18	Physical Chemist, Assistant.....	2	2	1	..	5	10
In Sugar Plant Investigations.....	..	1	2	..	5	8	Physical Chemist, Chief.....	3	1	4
Chemist's Aid.....	3	2	5	10	Physical Chemist, Junior.....	..	2	2	4
Dairy Chemist.....	Public Roads Chemist, Assistant.....	1	..	1	2
Dairy Chemist, Assistant.....	2	2	Professor of Chemistry.....	1	1	2	4
Dairy Chemist, Assistant in.....	..	3	2	5	Radioactivity Chemist, Assistant.....	1	1	2	4
Expert Chemist.....	Radioactivity Chemist, Junior.....	1	1	3	5
Forest Products Chemist.....	1	2	1	4	Sanitary Chemist.....	5	1	6	12
Forest Products Chemist, Assistant.....	2	2	4	1	9	18	Scientist in Soil Chemistry.....	3	2	5	10
Junior Chemist.....	5	15	6	13	90	129	Soil Biochemist.....	3	2	5	10
Laboratory Assistant in Chemistry.....	1	1	2	Soil Chemistry, Assistant in.....	..	1	1	2

ness to Mr. Flynn and to express our sincere thanks to him. We wish to express our thanks also to Mr. John T. Doyle, Secretary of the United States Civil Service Commission, for valuable aid generously given.

TABLE 5 was compiled from the examination announcements of the United States Civil Service Commission for the last five years; TABLE 6, from the annual reports of the United States Civil Service Commission for the fiscal years 1911-1915.

II—THE CHEMIST IN THE SERVICE OF NEW YORK STATE

The same confusion with regard to titles which was noted in the Federal service exists in the service of New York State. It may be, therefore, that some titles which should have been included in the data which follow, have been omitted.¹ Possibly some which have been included should have been left out. The only way to settle the question would be to appraise each position individually. This would involve an expenditure of energy incommensurate with the end to be attained. The picture of the chemical service of New York State, as here presented, is believed to be sufficiently correct for all practical purposes. It is accurate as far as it goes.

As with the Federal service, only recognized chemical positions are considered. In what follows, we have proceeded in exactly the same manner as in the Federal service except that the laboratory assistant group is treated separately from the chemist group. In this regard the titles and corresponding compensations in the New York State service are more distinctive than in the Federal service. In the general salary summaries, laboratory assistants have been omitted.

Positions in the Public Service Commission, 1st District, are under the jurisdiction of the State Civil Service Commission. On the other hand, the work of this Commission is confined to New York City as contrasted with that of the Public Service Commission, 2nd District, which includes the rest of New York State. The employees of the Public Service Commission, 1st District, are paid by the City of New York.² On the whole, therefore, it has seemed advisable to treat the Public Service Commission, 1st District, as a Department of the City of New York rather than of the State. If, for any reason, one wants to consider them along with the State service, it is necessary only to transfer the data given in Section III to Section II and to make the corresponding additions and subtractions.

TABLE 7

TITLE	CHEMISTS AND LABORATORY ASSISTANTS IN THE SERVICE OF NEW YORK STATE JANUARY 1, 1916									
	Agr. Expt. Sta., Geneva	School of Agr., Morrisville	Department of Agriculture	Department of Health	Highways Commission	Industrial Commission	Institute for Study of Malignant Diseases	Psychiatric Institute	Saratoga Reservation	TOTAL
Analytical Chemist.....	1	1								2
Assistant Chemist.....	8	1								9
Associate Chemist.....	3									3
Chemical Engineer.....	1									1
Chemist.....	1	8	2	1						12
Chief Chemist.....	1									1
Consulting Chemist.....	1									1
Director of Laboratories and Research.....		1								1
Physiological Chemist.....			1							1
Sanitary Chemist.....			1							1
Special Assistant in Chemistry.....							1			1
Water Analyst.....			2							2
TOTAL.....	12	11	5	2	1	1	1	1	1	34
LABORATORY ASSISTANTS										
Laboratory Apprentice.....			5							5
Laboratory Assistant.....	1	1	13							15
Laboratory Helper.....							4			4
TOTAL.....	1	1	18				4			24

¹ The inspectional service, especially, has certain positions which are for chemical qualifications.

² With the exception of the Commissioner, Council, and Secretary.

TABLE 7 shows the number of chemists and the laboratory assistants under each title in each State department and the total number for each title and for each department.

TABLE 8 gives the titles, numbers and individual salaries of chemists and laboratory assistants for the whole New York State service.

TABLE 8—CHEMISTS AND LABORATORY ASSISTANTS IN THE EMPLOY OF THE STATE OF NEW YORK, JANUARY 1, 1916

DEPARTMENT	TITLE	NO.	SALARIES
Agricultural Experiment Station, Geneva	Chemist	1	1 @ \$3000
	Associate Chemist	3	2 @ 1800 1 @ 2000
	Assistant Chemist	8	4 @ 1200 4 @ 1400
	Chief Chemist	1	1 @ 3000
	Chemist	8	1 @ 600 1 @ 1200 1 @ 1500 1 @ 1800 1 @ 1800 2 @ 2000 1 @ 3000 1 @ 800
Department of Agriculture	Assistant Chemist	1	1 @ 1500
	Consulting Chemist	1	1 @ 4000
	Director of Laboratories and Research	1	1 @ 4000
	Sanitary Chemist	1	1 @ 1500
	Physiological Chemist	2	1 @ 1600 1 @ 1800
Department of Health	Water Analyst	2	1 @ 2100 1 @ 2400
	Chemist	2	1 @ 600 1 @ 800
Highways Commission	Chemical Engineer	1	1 @ 3000
Industrial Commission	Chemist	1	1 @ 3000
Institute for Study of Malignant Diseases	Special Assistant in Chemistry	1	1 @ 1200
Psychiatric Institute	Analytical Chemist	1	1 @ 1800
Saratoga Reservation	Laboratory Assistant	1	1 @ 720
Agricultural Experiment Station, Geneva	Laboratory Assistant	13	6 @ 720 3 @ 900 1 @ 900 3 @ 1200
School of Agriculture, Morrisville	Laboratory Assistant	1	1 @ 540
Department of Health	Laboratory Assistant	5	4 @ 600 1 @ 720
Psychiatric Institute	Laboratory Assistant	4	1 @ 540 1 @ 600 1 @ 600 1 @ 720
	Laboratory Apprentice	5	4 @ 600 1 @ 720
	Laboratory Helper	4	1 @ 540 1 @ 600 1 @ 600 1 @ 720

TABLE 9 gives the number of chemists and laboratory assistants at each rate of pay in the service of New York State, January 1, 1916.

TABLE 9—NUMBER OF CHEMISTS AND LABORATORY ASSISTANTS AT EACH RATE OF PAY IN THE SERVICE OF NEW YORK STATE, JANUARY 1, 1916

CHEMISTS		LABORATORY ASSISTANTS	
NO.	ANNUAL SALARY	NO.	ANNUAL SALARY
1	\$ 600	2	\$540
1	800	1	720
6	1000	1	750
4	1400	9	600
2	1600	1	900
1	1800	1	900
1	1800	1	900
5	1800	1	1200
1	1800(a)		
3	2000		
1	2400		
1	2800		
4	3000		
1	3000		
1	4000		
1	4500(a)		
34	\$4348		

(a) Bonus three weeks' earnings for working day in the year.

These tables show that the State of New York (omitting Public Service Commission, 1st District) is paying \$44,980 per annum for its personnel service in chemistry.

Summarizing the data given for chemists in Table 9 and we group as follows of salary, number and percentages relative to the following:

SALARY	NUMBER	PER CENT
\$ 600-1000	2	5.9
1001-1500	12	35.3
1501-2000	11	32.3
2001-2500	1	3.0
2501-3000	5	14.7
3001-4500	3	8.8
Total, 34		100.0

If, following the same method used in Section I, we regard \$3000 or over per annum as a fair measure of the "successful" chemist, we obtain:

	Below \$3000	\$3000 or over	TOTAL
Number	27	7	34
Per cent	79.4	20.6	100

TABLE 10 contains a summary of examinations in chemistry

TABLE 10—QUALIFICATIONS FOR APPOINTMENT AS CHEMISTS, NEW YORK STATE SERVICE

TITLE OF POSITION	OPEN TO	EDUCATION, TRAINING AND EXPERIENCE	CONTENT OF EXAMINATION AND RELATIVE WEIGHTS	SALARY
ANALYTICAL CHEMIST State Reservation Commission Saratoga Springs	Required: Thorough technical training in chemistry and practical experience in chemistry. Must have ability to make water analyses, bacteriological determinations, analyses of rocks, earth, minerals and metals; radioactivity determinations; calculation of carbonic acid gas content in mineral waters, analyses of paints, oils, enamels, asphalt, tiling, and other materials for flooring.	Written examination pertaining to duties of position, 1. Experience, 1.	\$1200
CHEMIST Public Service Commission	Non-residents	Required: Thorough technical training in chemistry and 5 years' experience; 3 years' training in technical school is equivalent to 1 year experience; must have experience in analysis of asphalt, coal tar, pitches, and mixed paint; also experience in analysis of steel, cast iron, cement, draw pigments, water, etc., is helpful.	Written examination pertaining to duties of position, 1. Experience, 1.	\$1801 to \$2100
CHEMIST Department of Highways	Required: Thorough technical training in chemistry; duties involve making and reporting on laboratory tests of oils, asphalts, tars, cements sands, stone, etc., used for road building.	Elementary chemistry including physical chemistry, 10. Analytical chemistry, qualitative and quantitative analysis, 10. Chemistry of bitumens, 40. Chemistry of cements, 20. Training and experience, 20.	\$4 to \$6 per day
CHEMIST Department of Agriculture	Written examination with special reference to analysis of food and dairy products, 2. Education, experience and special qualifications, 1.	\$ 800 to \$1200
ASSISTANT CHEMIST Agricultural Experiment Station	Non-residents	Required: Graduation from college or university; special undergraduate training in agricultural chemistry and agricultural laboratory analysis; also post-graduate experience, either in chemical analysis of fertilizers and feeds or in agricultural chemical analysis of foods and dairy products.	Rated on training and experience.	\$ 960 to \$1200
ASSISTANT CHEMIST Public Service Commission	Non-residents	Must be graduate chemist with 2 years' practical experience.	Written examination including analyses of steel and cast iron, cement, asphalt, coal tar, pitches, mixed paints, dry pigments, water analyses, use of microscope and general chemistry, 1. Education and experience, 1.	\$1201 to \$1500
LABORATORY ASSISTANT State Department of Health	Men and women	Elementary chemistry, 1. Education and experience, 1.	\$720 to \$1200
PHYSIOLOGICAL CHEMIST State Department of Health	Men and women Non-residents Non-citizens	Required: Thorough knowledge of the principles of organic and physiological chemistry and 3 years' practical experience in physiological or biological chemistry.	Written examination on duties of position, 1. General and special training, practical experience and personal qualifications, 1.	\$1800 to \$2500
WATER ANALYST State Department of Health	Non-residents Non-citizens	Required: Thorough training in general chemistry with practical laboratory experience in water analysis.	General and sanitary chemistry and water analysis, 7; education and experience, 3.	\$720 to \$1200

of recent years, giving titles, qualifications, relative weights, content of examinations and weights of subjects, and salaries.

TABLE 11 shows the number of appointments to positions in chemistry, from competitive eligible lists, in New York State, during the years 1910-1915.

TABLE 11—APPOINTMENTS OF CHEMISTS, LABORATORY ASSISTANTS, ETC., FROM COMPETITIVE ELIGIBLE LISTS, NEW YORK STATE SERVICE 1910-1915

TITLE	1910	1911	1912	1913	1914	1915	Total
Chemist	2	2	5	0	9
Director of Laboratory	1	1	2
Laboratory Assistant	1	3	4	11
Technical Assistant	1	1	3
Water Analyst	1	1

TABLES 7, 8 and 9 were compiled from the Civil List of New York State of January 1, 1916; TABLE 10 from the examination announcements of recent years of the New York State Civil Service Commission; TABLE 11 from the Annual Reports of the same Commission.

III. THE CHEMIST IN THE SERVICE OF NEW YORK CITY

The statements which were made with regard to the Federal service and the service of New York State, apply also to the service of New York City; *viz.*, an employee's title is not always

a guarantee of the nature of his work and technical chemists only are here considered. We have included the Public Service Commission of the 1st District for the reasons stated in Section II.

TABLE 12 shows the number of chemists and laboratory assistants under each title in each City department and the total number for each title and for each department.

TABLE 13 gives the titles, numbers and individual salaries of chemists and laboratory assistants for the entire New York City service. TABLE 14 gives the number of chemists and laboratory assistants at each rate of pay in the service of New York City, June 30, 1916.

These tables show that the City of New York (including the Public Service Commission, 1st District) is paying \$200,786 per annum for its service in chemistry.

TABLE 12

	Department of Education	Board of Estimate and Apportionment	Board of Water Supply	President, Borough of Manhattan	President, Borough of Brooklyn	President, Borough of Queens	Public Service Commission	Department of Health	Department of Water Supply, Gas and Electricity	Fire Department	Bellevue and Allied Hospitals	Department of Public Charities	TOTALS
CHEMISTS AND LABORATORY ASSISTANTS IN THE EMPLOY OF THE CITY OF NEW YORK, JUNE 30, 1916													
Assistant Chemist	1	1	1	1	1	10	1	1	13
Chemist and Bacteriologist	1
Chemist	1	8	1	1	1	1	11	3	27
Chief Chemist	1	1
Consulting Chemist	1	1
Director of Laboratory	1	1
Engineering Chemist
Fuel Engineering Chemist	6
Junior Chemist	9	2	1	12
Pathological Chemist	1
TOTAL	1	16	11	5	2	10	11	4	1	1	2	65	115
Laboratory Assistant	11	..	3	2	..	81	4	..	4	10	115	..	115

TABLE 15—QUALIFICATIONS FOR APPOINTMENT AS CHEMISTS IN NEW YORK CITY SERVICE
Minimum Age 21, in Each Case

TITLE		EDUCATION, TRAINING AND EXPERIENCE	CONTENT OF EXAMINATION, AND RELATIVE WEIGHTS	SALARY
Chemist	Open to non-residents	Required: Knowledge gained by experience of general chemistry, principles of organic chemistry and quantitative analysis, including processes applicable to food examination; some credit given for ability to consult reference books in French and German, and for facility and accuracy in chemical computations.	Technical, 6; experience, 4.	\$1200
Chemist	Open to non-residents	Same as above, except qualitative analysis.	Technical, 6; experience, 4.	\$1200 to \$1350
Chemist	Open to non-residents	Must have degree of B.S. or its equivalent, or 2 years' course in a technical school. Some credit given for ability to consult scientific journals in French and German.	Technical, 6; experience, 4.	\$1200 to \$1800
Chemist and Bacteriologist		Required: General knowledge in chemistry and ability to make qualitative and quantitative chemical tests and bacteriological tests of sewage and sewage effluents.	Technical, 6; experience, 4.	\$1800
Engineering Chemist	Physical exam. required	Required: A degree granted on completion of a standard course of instruction with chemistry as the major subject, and in addition, 1 year of experience in the practice of chemistry or other training and experience recognized by the Municipal Civil Service Commission as equivalent. Some credit given for ability to consult scientific journals in French and German.	Technical, 6; experience, 4; technical paper divided into two parts; general chemistry and engineering chemistry.	\$1500 to \$2100
Chemist, Food and Drugs	Physical exam. required	Required: A degree granted on completion of a standard course of instruction with chemistry as the major subject, or proof of other training and experience recognized by the Municipal Civil Service Commission as equivalent. Some credit given for ability to consult scientific journals in French and German.	Experience, 4; technical, 6; technical paper divided into two parts, general chemistry and the chemistry of food and drugs.	\$1200 to \$1500
Fuel Engineering Chemist	Non-residents admitted	Must be graduates of technical college. Some credit given for ability to consult scientific journals in French and German.	Technical, 6; experience, 4.	\$1500 to \$1800
Junior Chemist (Asphalt)	Physical exam. required	Required: Training in qualitative and quantitative analysis, or practical experience in mixing asphalt with sufficient knowledge of qualitative and quantitative analysis to make the usual laboratory tests of asphalt.	Examination includes general chemistry and engineering chemistry.	\$1200
Pathological Chemist	Physical exam. required	Required: Degree of M.D. or Ph.D. or equivalent and in addition, at least 3 years' experience in original research work; consideration given to satisfactory evidence of successful management of a scientific laboratory or branch thereof.	Experience, 4; technical, 6.	\$2500

eligible lists to positions in chemistry in New York City during the years 1908-1915.

TABLE 16—APPOINTMENTS OF CHEMISTS, LABORATORY ASSISTANTS, ETC., FROM COMPETITIVE ELIGIBLE LISTS, NEW YORK CITY SERVICE, 1908-1915

TITLE	1908	09	10	11	12	13	14	15	TOTAL
Assistant Chemist.....					1				1
Chemists.....	2	2	5	1					10
Food and Drugs.....							6	6	
Asphalt, Jr., as Junior Chemist.....						5	3	8	
Chemist & Bacteriologist.....					2				2
As Assistant Chemist.....					1				1
Chemist, Fuel Engineering.....					4				5
Chemist, Engineering.....					1		9		10
As Assistant Chemist.....					1				1
As Chemist.....							1	1	2
Chemist, Health.....						1	1		2
Chemist, Junior.....									1
Chemist (Sewage Disposal Methods).....									1
Fuel Engineer and Engineering Chemist.....			3						3
Laboratory Assistant.....		11	19						30
Laboratory Assistants:									
Chemical.....					1	6			7
Chemical (Female).....						1			1
Chemical (Male).....							2	5	7
Diagnostic.....					8	11			19
Diagnosis (Female).....							1		1
Diagnostic (Male).....							3	2	5
(Female).....			2		5				7
(Male).....			10	27					37
Research.....									10
Research (Female).....						5	7		12
Research (Male).....							5	4	9
Vaccine.....						3	3		6
Vaccine (Female).....									1
Pathologist, as Pathological Chemist.....							1		1
Pathological Chemist.....							1	1	2

TABLES 12, 13 and 14 were compiled from the Civil List of New York City for June 30, 1916; TABLE 15 from recent examination announcements of the Municipal Civil Service Commission of New York City; TABLE 16 from the Annual Reports of the same Commission.

IV—THE STANDARDIZATION OF EMPLOYMENTS IN CHEMISTRY IN THE PUBLIC SERVICE

Until quite recently, the salaries of employees in the public service have been determined in a haphazard manner. In

many instances salaries have been fixed by accident, expediency or political preferment rather than by any consideration of the nature of the work performed or of the service rendered. This state of things has been unfortunate, to say the least. It has led to the squandering of money, to inefficiency of service, to the disgruntlement of many of the employees and, in some instances, to the disruption of that loyal *esprit de corps* so essential to the smooth running of a large organization.

Of late, there have been several attempts to improve these highly undesirable conditions, by an endeavor to standardize public employments. The standardization movement has as its primary objects:¹

- (1) The establishment of a basis for fixing salary rates in relation to work values.
- (2) The establishment of standard factors of education or experience for each class and grade of employment prescribing conditions which must be met by persons preliminary to appointment.
- (3) The establishment of standard titles and work requirements for each class and grade of employment prescribing conditions which must be met or conformed to after appointment.
- (4) The establishment of standards to govern promotions, transfers and other subjects of employment control.
- (5) The establishment of a formal procedure which shall currently inform the public and the official organization of conditions governing entrance to the public service and advancement therein.

As these matters are at present under discussion, and as they are likely to be acted upon in the near future, it has been deemed advisable to bring together such comparative data as bear on the problem in so far as chemists are concerned.

¹ Municipal Research No. 67, page 17.

TABLE 17—STANDARD SPECIFICATIONS FOR POSITIONS IN CHEMISTRY PROPOSED BY THE COMMITTEE ON CIVIL SERVICE OF THE SENATE OF THE STATE OF NEW YORK

PROPOSED CLASSIFICATION, BASED UPON DUTIES AND WORK REQUIREMENTS: STANDARD TITLES AND RATES			EXISTING AUTHORIZED POSITIONS ^(a)	
DEFINITION GROUP	GRADE	TITLE	TITLE	RATES
TECHNICAL ASSISTANT	I	The duties of the incumbents of these positions are to perform, under supervision the technical duties for which they have qualified, in the routine and research work of a pathological, bacteriological, serological or chemical laboratory.	Technical Assistant	\$ 540
			Technical Assistant	600
			Technical Assistant	660
			Technical Assistant	900
CHEMIST	I	The duties of incumbents of these positions are to make under supervision, routine chemical analyses or tests of an ordinary character, to perform definite details of difficult analyses or tests, and to conduct research work within this field.	Junior Chemist	1080
			Chemist	1200
			Chemist	1320
			Chemist	1800
			Chemist, part time	1200
	II	The duties of incumbents of these positions, which may involve supervision of employees in Grade I, are to assume responsibility for a division of chemical work in an important laboratory, and to make difficult chemical analyses and tests.	Assistant Chemist	600
			Chemist	1680
			Chemist	1800
			Chemist	2000
			Water Analyst	1600
	III	The duties of incumbents of these positions, which require the highest degree of skill and judgment in the practice of chemistry, are to direct and be responsible for the work of a small laboratory, or to initiate, conduct and supervise difficult chemical research work.	Water Analyst	1800
			Physiological Chemist	1500
			Chemist	2400
			Chemist	2800
			Chemist	3000
IV		The duties of the incumbent of this position which involves the application of advanced scientific technique and research methods, are to undertake the solution of biological-chemical problems in their relation to disease and to supervise and be entirely responsible for the work in a particular field of research of an important laboratory.	Chief Chemist	3000
			Sanitary Chemist	2800
			Water Analyst	1600
			Water Analyst	1800
			Physiological Chemist	2800
			Biological Chemist	3000
			Chemist	3600
			Chemist	4200
			Chemist	4500

(a) Existing titles and rates are shown opposite proposed grades in which they were classified after appraisal.

TABLE 17 contains the standard specifications¹ for chemists proposed by the Committee on Civil Service of the Senate of the State of New York transmitted to the Legislature, March 27, 1916.

TABLE 18 contains the standard specifications² for chemists

TABLE 18—STANDARD SPECIFICATIONS FOR CHEMISTS PROPOSED BY THE BUREAU OF STANDARDS OF NEW YORK CITY

GRADE	TITLE	SALARIES (DOLLARS)
I	Junior Chemist.....	900 1020 1140 1260 1380
II	Assistant Chemist (full time).....	1500 1620 1740 1920 2100
	Assistant Chemist (not less than 18 hrs. a wk.).....	1020 1140 1260 1380
III	Chemist.....	2280 2460 2700 2940 3180 3420 3660
IV	Director (Central Testing Laboratory).....	5100 5520 5940
	(No recommendation above \$5940)	
I	Laboratory Assistant.....	600 720 840 960 1080 1200

(With or without maintenance: no rate with maintenance above \$960)

TABLE 20 contains data of the salaries of chemists employed at present in typical American cities. This is inserted for purposes of comparison.

If the members of the American Chemical Society are to have any voice in the determination of the compensations of those of their number who are employed in the public service, now is the time for them to express themselves. These matters are under discussion at the present moment. If our profession is to let itself be heard in tones of no uncertain meaning, it is imperative that we adopt one of the most popular expressions of the day—"Do It Now." Here is a field of immediate usefulness for the Committee on Status and Compensation which has been proposed above.

In their negotiation with governmental authorities the members of this Committee should remember that standardization without representation is tyranny. Furthermore, faint chemist ne'er won fair salary and none but the brave deserve the fair.

proposed by the Bureau of Standards of the Board of Estimate and Apportionment of the City of New York, June, 1916.

TABLE 19—COMPARATIVE STANDARDIZATION DATA—CITIES OTHER THAN NEW YORK

TITLES—CHEMIST:	CHICAGO				PITTSBURGH				PORTLAND				ST. PAUL			
	RATES				RATES				RATES				RATES			
Junior Sanitary.....	1200	1320	1440	Junior Chemist	1070	1080	1110	1200	Asst. Milk Chemist	1020	1080	1140	1200	1260	1320
Boston.....	1620	1740	1860	Chemist.....	1350	1500	1650	1800	Milk Chemist.....	1680	1740	1800	1920	2040	2160
Senior Sanitary.....	1980	2100	2280	2520	Chief Chemist	2100	2400	2700	3000							
Principal Sanitary.....	1980	2100	2280	2520		780	840	900	960		780	840	900	960	1020	1080
LABORATORY ASSISTANT:	780	840	900	960												

TABLE 20—COMPARATIVE SALARY DATA FROM MUNICIPAL PAYROLLS—1916

SERVICE POSITION AND CITY	CHEMIST					LABORATORY ASSISTANT				
	MINIMUM	MOST FREQUENT	INTERMEDIATE	MAXIMUM	TOTAL	MINIMUM	MOST FREQUENT	INTERMEDIATE	MAXIMUM	TOTAL
Philadelphia.....	1 960	1 1300	1 1500	1 2000	7	1 600	1 680	1 750	1 800	41
Boston.....	1 1900	1 1900	1 1900	1 1900	1	1 600	1 600	1 600	1 600	1
Cleveland.....	1 1200	1 1500	1 1500	1 1500	6	1 600	1 600	1 600	1 600	1
Baltimore.....	1 720	1 800	1 800	1 800	1	1 600	1 600	1 600	1 600	1
Buffalo.....	2 1200	2 1500	1 1800	1 1800	1	1 600	1 600	1 600	1 600	1
Pittsburgh.....	1 1800	1 1800	1 1800	1 1800	1	1 600	1 600	1 600	1 600	1
San Francisco.....	2 1500	1 1500	1 1500	1 1500	1	1 600	1 600	1 600	1 600	1
Milwaukee.....	1 1000	1 1500	1 1500	1 1500	2	1 600	1 600	1 600	1 600	1
Cincinnati.....	1 1500	1 1500	1 1500	1 1500	1	1 600	1 600	1 600	1 600	1
Los Angeles.....	1 1500	1 1500	1 1500	1 1500	1	1 600	1 600	1 600	1 600	1
Minneapolis.....	2 1500	1 1500	1 1500	1 1500	1	1 600	1 600	1 600	1 600	1

(a) Two (2) others at rates not given.

TABLE 19 contains comparative standardization data compiled from the standards³ proposed in the cities of Chicago, Pittsburgh, St. Paul and Portland.

¹ First Report of the Committee on Civil Service of the Senate of the State of New York appointed to investigate the Civil Service of the State, with particular reference to salaries, grades and duties of officers and employees—transmitted to the legislature, March 27, 1916.

² Standard Specifications for Personal Service, prepared by the Bureau of Standards for the Board of Estimate and Apportionment of the City of New York, June, 1916.

³ See Comparative Salary Data—Philadelphia Bureau of Municipal Research, March 1, 1916.

Whether or not positions of high grade, involving initiative and responsibility, should be standardized at all is open to question, to say the least.

SUMMARY AND CONCLUSIONS

Having the facts before us, we are in a position to summarize and to draw conclusions.

If we compare the treatment of chemists employed by the United States Government, the Government of New York State and the Government of New York City, we find that we have no positions which may be regarded as attractive to the

graduate in chemistry. From the view-point of compensation, these are distributed as follows:

SALARIES	FEDERAL	NEW YORK State	City	TOTAL No.	Per Cent
\$500 to 1000	25	2	..	25	3.1
1001 to 1500	187	12	30	240	29.4
1501 to 2000	219	11	14	244	30.0
2001 to 2500	159	1	5	165	20.2
2501 to 3000	93	5	4	102	12.5
3001 to 3500	13	1	2	16	2.0
3501 to 4000	12	1	..	13	1.6
4001 to 4500	1	1	..	2	0.2
4501 to 5000	7	7	0.9
5001 to 6000	1	1	0.1
Total	716	34	65	815	100.0

If we adopt \$3000 or over per annum as a fair measure of the "successful" chemist, we find the following:

	Below \$3000	\$3000 or over	TOTAL
Number.....	727	88	815
Per cent	89.2	10.8	100

This bare statement of figures constitutes a revelation, the implications of which are so obvious that it would be an insult to the intelligence of this audience to repeat them.

Let us turn aside from compensations a moment, to focus our attention on the question of the numbers of chemists in governmental employ.

The total numbers of employees in the branches of the public service which we have considered in detail (*i. e.*, the United States Government, New York State and New York City) are in round numbers:

United States.....	480,000
New York State (excluding Public Service Commission, 1st District).....	18,000
New York City (including Public Service Commission, 1st District).....	85,000
Total.....	583,000

Of the total number of positions in these services, the chemists constitute 0.15 per cent for the United States, 0.19 per cent for New York State, and 0.08 per cent for New York City. Of the total number in the three services (583,000) the chemists (815 in number) constitute 0.14 per cent.

Mr. J. L. Jacobs¹ has recently estimated that the total number of civil employees in the United States (including the Federal Government, States and Cities) is 1,800,000 to 2,000,000. If the average just stated is roughly indicative of the general proportion of chemists in all these services, there are probably about 2800 chemists who are employed in public service. If we add to these, those who are dependent on them, we find that the part of our population involved in the social matter of this paper is about 11,200, counting 4 to a family.

Again, the conclusions are obvious. The insignificance of the proportion of chemists in public service is wholly at variance with the importance of their work of regulation, enforcement, conservation and creation.

In our introduction, we pictured the young chemistry graduate in a questioning mood with regard to the usual prospects of his profession, its compensations and rewards. To these questions others were added: *Is there a career in the public service? What are the relative advantages and disadvantages? Is public service in chemistry a useful stepping stone? And so on.* The facts before us should aid us in answering such questions.

In the first place, we may count security as one of the most obvious of the advantages. The average chemist, like the average engineer, is proverbially a job chaser. The special committee of the American Society of Civil Engineers "to investigate the conditions of employment of and compensation of civil engineers," by the way, has set as one of its tasks "to secure information indicating the proportion of time when engineers

are out of employment." Should a similar committee be created in the American Chemical Society, as suggested above, this line of activity is one of its legitimate functions.

As contrasted with the depressing picture of the average chemist, roving over the earth in search of a job, public service offers the one great advantage of *security*. Permanency of tenure is usually assured. On the other hand, this very security may become a disadvantage. Security is apt to breed indolence. Many a good man has degenerated into a mere job holder in public service, who, if he had had the spur of necessity to urge him on, would have been more successful.¹

There are other advantages to be considered. The lower grades of chemical work are better paid in government service than in private practice. Furthermore, compensation conditions are improving. A comparison of the rates of pay to-day with those which existed 10 years ago² will make this apparent. If it is true that the salaries in government service are rather better, on the average, in the beginning, it is equally true, on the other hand, that they are poorer later on. The numbers of high-paying positions in government service are few. As has been stated above, only 10.8 per cent of the chemical positions in the service of the Federal Government, New York State and New York City pay \$3000 or over per annum.

From the standpoint of the value of the experience to be gained by the chemist in public service, it is quite natural to find a condition prevails which is precisely analogous to that of compensation. The experience of the young chemist in his first years of governmental service is most valuable. But, as the years go on, along with a static salary, we find a routine character of work which frequently kills off any initial creative ability of the employee.

Of this state of things, there is but one interpretation possible. Taking it all in all, *public service in chemistry is a good stepping stone but a poor career*. We believe that most chemists are agreed on this point.

May I be permitted one final word of a somewhat more general nature?

The Council of the American Chemical Society, at its meeting of September 27, 1916, unanimously passed the following resolution:

"Resolved, That the Council of the American Chemical Society declares itself to be in favor of an adequate system of national defense. Such a system involving our Army, Navy, coast defenses, natural resources and industrial development, should be so designed as to maintain our liberty and preserve our peaceful pursuit of happiness. The system should also be designed with such reserve power as to maintain our honor and integrity, should the same be menaced by foes within or without. To that end we hold ourselves in readiness to serve our Country in any capacity, but especially in such ways as our abilities best qualify us."

American chemists can devote themselves to no nobler purpose than to the carrying out of the splendid spirit of this resolution. But such devoted action will not achieve its full function, unless we add to the elements of preparedness enumerated in the resolution, another of at least equal importance—*civil preparedness*. No amount of military, naval and industrial preparedness can be effectual unless we have backing it up an army of civil servants disciplined to carry out the administrative needs of the government. If our democracy is to survive, we must discard the haphazard, trust-to-luck methods of the past.

Whatever one's sympathies in the present European conflict may be, one thing is certain—*Germany has been efficient*. And this efficiency has expressed itself as greatly in its civil administration as on the field of battle. Let me quote a passage from

¹ "Public Service Opportunity and Preparedness," *Journal of the Western Society of Engineers*, No. 6, June, 1916.

² This whole question of "success" ought to be gone into more thoroughly than the limits of this paper will permit. What is a "success?"

³ See Bull. 94, Bureau of the Census, p. 125.

a paper by the speaker who immediately preceded me. He says:¹

"On reviewing the remarkable achievements of Germany in the land campaigns, even the most grudging cannot withhold their admiration for the effectiveness and scientific precision with which her gigantic military enterprises are carried out. There is no doubt that the wonderful showing made by that country has been due to something more than the valor and skill of the soldiers on the battlefield. The military authorities would have been impotent if it had not been for the masterful way in which the civil administration of the country has been conducted. If Germany had back of the firing line the kind of civil government which the United States had during the Spanish war—with its scandals of "embalmed" beef and inadequate supplies—administrative imbecility would have wrought more terrible havoc among her own men than all the high-power explosives which the Allies have mustered."

To any one who has given the least thought to this subject, several things are clearly apparent. In the first place, the United States can no longer afford to ignore the lessons to be learned from the experience of other nations. We cannot sit idly by, like immature children, smugly satisfied that democracy and inefficiency are inseparable.

This country is about to go through a second period of reconstruction. Though we have not thus far been in arms in the present world war, our economic interests have been so directly involved, that complete readjustment will be needed at its close. The new conditions which will prevail in Europe will also add to our difficulties. In adapting ourselves to this reconstruction period, our whole scheme of civil service procedure has to be radically revised. To date, we have looked upon our civil service problems in too negative a way. The old slogan "Keep the rascals out of office" will have to be modified to read "Get the best men into office and having got them there, keep them there." The old-fashioned politician—one of the worst of our enemies from within—has to be relegated to the realm of the past along with the ichthyosaurus and the dodo. The new-fashioned office-holder must be of good natural ability, trained for his work and efficient in its performance. He must be assured of a square deal. Nothing is more deadening to an earnest worker than a system which places political subservency above proved devotion and efficiency. Public service must be made a life-career of dignity with recognition of merit as its impelling force and adequate financial return as its tangible reward.

The fear has been expressed that in this manner a "privileged class" will be built up. It is significant that those who are loudest in their protestations in this regard are the very politicians who in themselves constitute a bureaucracy of the most pernicious sort—a bureaucracy of the unscrupulous, the untrained and the unfit. The one thing in the United States which stands forth as the highest expression of a true and thorough going democracy is our system of free education extending from the kindergarten through the college and, in some instances, through the university. If our free democratic system of education is to reap its fullest harvest, surely the graduates of a free public school, a free high school and a free college or university who have received specific training in the work they are to perform, are to be regarded as ideal material for building up a democratic administration which will dispel this favorite bugaboo—this "privileged class"—of the cheap politician.

But before we can attain these highly desirable ends, it is essential, as a preliminary step, to make a complete survey of the entire field of public service as it exists at present. Education and profession must be studied in turn and its relationship to the whole established. The task is a big one. It

involves painstaking application and a reverence for fact to the exclusion of fancy.

Having, in this manner, determined the needs of our public service, our colleges, universities, and technical schools must be called upon—*must* is the word I want to use—to train men for our civil service just as West Point and Annapolis train them for our military and naval services.

Of these larger aspects of the questions involved, this paper cannot treat. It does attempt, however, to present a survey of a very small corner of a very large field.

THE COLLEGE OF THE CITY OF NEW YORK

THE CHEMIST IN THE SERVICE OF THE CITY OF NEW YORK

By OTTO H. KILLEN

The city of New York is well on its way towards becoming the greatest and wealthiest city in the world. In and about it are a score of prominent colleges and universities, in each of which thorough courses in chemistry are well attended, resulting in the graduation each year of an ample supply of well equipped chemists. Additionally, a large number of chemists can at all times be found, from every part of the United States, who are not only willing and anxious to secure employment in New York City, but who are also willing to make a considerable sacrifice in salary for the object of coming to New York. It is evident therefore that no scarcity of chemists, and it may be added very good chemists, exists in this city, and that the city should have a waiting list of very desirable eligibles, from which to recruit its chemical staff.

Withal, up to the present, the competition for employment in the city's laboratories has been characterized by apathy rather than keenness, and while in spite of this fact the personnel of the city's roll of chemists has been maintained at a fairly high standard, this condition has been practically fortuitous rather than the necessary result of deliberate plan.

Recognizing this fact, and with the purpose of stimulating competition among chemists for employment by the city, the Bureau of Standards has formulated a system of specifications which, if finally adopted, should have the effect of attracting the ablest chemists available to the ranks of the city's workers, which is as it should be, the best being none too good for the great work that the city is carrying on. Details of the salary grades have been presented in other publications, and have been referred to by Professor Breithut in his able exposition; *en passant* it is a matter of duty to call attention to the untiring effort of this gentleman in connection with the betterment of the chemist's compensation and to the belief that the municipal chemist owes him thanks. The Bureau of Standards specifications in effect call for separate entrance salaries in the various grades, and a well defined and adequate system of increases for meritorious service. Such features, difficult to bring into immediate body volume and practice, and having therefore contributed to rendering municipal employment unattractive among chemists.

WORK OF CITY LABORATORIES

The work of the various laboratories maintained by the city may be roughly divided into two categories. That of sustaining the city's purse, and that of promoting the city's health. The second and last item of the one is the source of problems rendering the first efforts of the municipal chemist more or less hazy, and the maintenance of the knowledge of different types of materials produced by the city is carrying on its various scientific great employment to determine what are suitable in kind, of doing the best sort of work that is chemically possible.

¹ Charles A. Beard, *Uncle Sam's Government*, *American Historical and Social Science*, Vol. LXIV, March, 1916.

² For a survey of the municipal civil service of New York, see *Municipal Research* No. 208.

³ See *Chemical Engineering*, in the November issue of *Analyst*.

ical work performed in enforcing the specification requirements of the city; suffice it to say that the net result of these labors is a demonstrable saving of money, in sum far exceeding the total cost of the work done.

Needless to say, the variety of chemical work entailed necessitates a definite amount of specialization among the chemists employed, and therefore the assignment of one type of work, or at most, several closely related types of work, to the same chemist, with the desirable permission of a free choice on the part of the chemist where possible. This of course is an ideal condition; in practice a difficulty is encountered when running short-handed, it being then impossible to permit the individual to confine himself to his chosen specialty, or its allied types of work. Under these conditions it is sometimes necessary to thrust widely diverse and unrelated problems upon chemists capable of standing the strain, which, when working at high pressure, is far from being a negligible factor.

A large amount of research work is constantly arising, the prosecution of which makes for the city's best interests, and which should be given the undivided time and attention of those engaged in it. Under ideal conditions this should involve the assignment of a chemist solely to one of these problems, which require original thinking, much searching of the literature, and the highest degree of technical skill for correct solution; usually these problems have to be relegated to spare time, which is a very rare commodity, and even then the frequent calls of routine work break in upon the continuity of application necessary. The completion of one of these tasks has sometimes to be postponed for an unreasonable length of time.

THE CITY CHEMIST

It is apparent from the foregoing that the type of chemist which best fills the city's needs is an unusual one. The training of the city chemist should be of course of the highest degree of completeness as regards analytical work, as the concerns furnishing material to the city almost invariably question the city's analysis in the case of a rejection, and the city's analysis, although nearly always made at top speed and in the press of routine work must be capable of standing the severest scrutiny and in many cases forms the basis of the city's contentions in a court proceeding.

The city chemist should have a thorough working knowledge of industrial processes and plant procedure, in order quickly and accurately to diagnose the shortcomings of a finished product which does not meet the city's requirements. A suggestion of this kind thrown out in a report often saves much time and dispute and is invariably accepted in the proper spirit by the conscientious manufacturer.

Inasmuch as chemical examinations alone are rarely the criterion by which material is accepted by the city, all sorts of specialized physical tests being of daily occurrence, the chemist should be perfectly at home in this field, both as to technique and interpretation.

Expertness with the microscope is a *sine qua non*, the detection of adulterations being in a great majority of cases quickly and accurately verified thereby, and possession of bacteriological technique is of frequent necessity.

A certain amount of engineering training is also necessary, as a great deal of the work presupposes familiarity with the proper use of the materials of construction. The multifarious problems of the various specialized fields such as steel and concrete, eventually play an important part in the work of the city chemist.

Aside from these and a host of related branches such as mineralogy, petrography, electricity and photography, a good grounding in which is really indispensable, it is presupposed that the purely chemical training of the city chemist is thorough and systematic, and that no element of weakness exists in his grasp of inorganic, organic and physical chemistry.

All of this then constitutes his major equipment, his general knowledge of the subject; his prime usefulness to the city, how-

ever, lies in his specialty, be it asphalt, paints, oils, alloys, or whatever branch he may be assigned to. This specialty he must cultivate from every angle; ideally he should be a recognized authority thereon, at least locally, and to the credit of the city's chemists, be it said that these conditions are practically fulfilled in a great many cases.

As the city's competitive examinations are with few restrictions open to all American chemists, who care to qualify, and as actual working experience is a difficult thing to gauge by written examination, it follows that a great many eligibles for the position of municipal chemist do not come seasoned by years of actual professional work. As a consequence, maturity is acquired in the service of the city and as a rule the seasoning process proceeds quickly in consequence of the responsibility thrust upon the incumbent. Needless to say the time required for the acquisition of working methods, of familiarity with systems and of general rapidity and despatch is a gratuitous investment by the city under the competitive system of appointment, but this need not be considered a drawback, as the peculiarities of city service require a preliminary period of education which a veteran chemist of much outside experience would perhaps find irritating and foreign to his preconceived notions. Executive ability, translated into its simplest terms, that of simply being able to get along with men, to command their respect and appreciation, is peculiarly in demand, especially in view of the fact that the commanding officer in the civil service is the general public of the city of New York. Tact and judgment are nowhere more necessary, both in respect to working in unison with one's fellow employees, and in dealing with the sensibilities of purveyors of the city's supplies.

Finally, the keynote of the character of the desirable incumbent may be summed up in the single word—versatility. It is doubtful whether in any post where a chemist's services are required there is as great a need of breadth of information, of ability to undertake various unrelated types of work, to render quick and accurate decision upon the merits of a series of widely differing materials, in short, of every characteristic of the all-round man as there is in the position of the municipal chemist.

That such a type of individual can be found and when found can be held in the city's service, in spite of unattractive compensation and uncertain advancement, is the remarkable factor in the situation. The main influences in retaining these invaluable men have been their devotion to the interesting nature of the work, and their hope that at some no very distant date a widespread realization of the conditions would react towards their betterment. This hope bids fair to be realized, in the schedules worked out by the Bureau of Standards.

The chemists who have remained in the employ of the city in spite of hitherto disheartening conditions have been men of the idealistic type, therefore, who have been able to solace themselves with the slender consolation that this hope offered. This has been the city's unconscious gain. The dawn of equitable conditions is, let us hope, at hand.

Unless a readjustment of affairs is shortly arrived at, it is inevitable, in fact it has begun to come to pass, that a city position be regarded as a mere stop-gap, a temporary occupation rather than a definite career. Already a considerable number of city chemists, some of fairly long standing, have resigned to accept better paying private positions, within the last eighteen months, and replacing these by men of considerably less experience disarranges, temporarily at least, the smooth and efficient working of the civic laboratory system. Undoubtedly, these men were of higher value to the city than they would be to private employers, in whose laboratories even the best of them would be practically of no more value at first than mere beginners, owing to unfamiliarity with private systems. This state of affairs spells an actual monetary loss to the city, for the vacant municipal positions are usually filled at the same salary, and usually by men of less experience. It is the actual reverse of the

ideal condition, which should be that the city by virtue of the higher salaries offered and interesting nature of the work should be able to attract the best available chemical talent wherever employed, rather than to act as a training school for the benefit of other employers.

A few words as to the personnel of the Central Testing Laboratory, the laboratory which is now the city's largest, owing to the consolidation of several formerly important city laboratories. Its chemists are recruited from graduates of Columbia, Cornell, Colgate, Fordham and New York Universities, the College of the City of New York, Rensselaer and Massachusetts Institutes of Technology, and the Philadelphia College of Pharmacy. The bachelor's degree or its fully satisfactory equivalent is possessed by each of the sixteen chemists employed and several have in addition been awarded other degrees. The average age is thirty, average length of time employed in chemical work nine years, average length of time employed by the city as chemist five years.

The enthusiasm retained by the staff is evidenced by the fact that nearly all are active members of some scientific society, a considerable number have published one or more original scientific papers, and in response to a recent questionnaire concerning desirable research work, no less than twenty-seven different lines of investigation were suggested by members of the staff, each problem requiring a great deal of difficult and tedious experimentation and involving the sacrifice of much of the investigators' private time, with no hope of monetary remuneration.

Each chemist, on the average, has been employed in three unrelated divisions of the laboratory's work, voluntarily and with no cases of unfitness manifesting themselves. However, every opportunity is offered to facilitate and further specialization. Frequent conferences have been held, and occasional lectures are invited from outside experts, besides which the members of the staff are encouraged to present their chosen subject to outside audiences, as well as at periodical staff conferences. An excellent working library is at the command of the chemists, liberally supplied with technical periodicals, and thereby saving time required to search literature. Nearly every chemist in the laboratory has repeatedly appeared in court in connection with the city's business, and has, therefore, obtained an excellent grounding in the task of presenting scientific evidence in a manner conformant with legal procedure, requiring absolute confidence in one's technical findings as well as the facility of rapid and clear thinking.

SALARIES

The average entrance salary paid to these men on appointment to the grade of chemist was \$1,530 per annum. This was after an apprenticeship in chemical work served in the city service or outside, but generally outside, averaging four years after graduation from college. The average length of service as chemist has been five years, and the average present salary is \$1,685 per annum; therefore, the average annual increase of salary has been, to the present time, \$111.

In connection with these figures, it may be said that the salaries paid the chemists in this laboratory average higher than the salaries paid throughout the city service, executives excepted, the head of a division in the Central Testing Laboratory receiving much less compensation than the heads of isolated special laboratories in other city departments.

Under the circumstances outlined above, it is evident that the enactment of suitable salary specifications for the chemist in the city service is a real and urgent need both for the city's benefit and for the relief of very uncomfortable financial situations among the chemists.

THE CHEMIST IN THE PUBLIC SERVICE

By H. W. WILEY

The entry of the chemist into the public service is scarcely sixty years of age. In fact, sixty years ago the chemist as a dynamic force was well represented by $x + y = 0$.

The first record I can find of a chemist in the public service is in the Department of Agriculture in 1862. It would be interesting to trace in detail historical data relating to the entry of the chemist into the other departments of the Government. That task I shall have to leave for the historian with more leisure than falls to my lot.

GOVERNMENT CHEMICAL SERVICE

By classification, the chemical service of the United States Government and of the State and Municipal governments may be broadly placed under three heads: *First*, chemists charged with the duties of control; *second*, chemists charged with research; and *third*, chemists charged partly at least with executive duties. The latter classification is a matter of some doubt as my own experience, as well as that of others, has shown that when a chemist begins executive duties they are like the camel's nose in the tent. Much time does not lapse until his duties are wholly executive, but even then he may well retain his classification, as they are executive duties connected with and based upon chemical work.

CONTROL WORK

The nature of the duties of the first class of chemists is well understood. Perhaps, I may best illustrate it by laws relating to fertilizers in the various states. The purpose of these laws was not to give chemists jobs but to protect the farmers against fraud. Practically every state in the union where commercial fertilizers are used in large quantities has chemists controlling the character of the product offered to the farmer. Not infrequently, the chemist who has control of the analysis also has more or less to do with the application of the law, but this is not necessarily nor usually the case. In respect of fertilizer control, not only is the total amount of plant food represented by fertilizer of great importance, but also, even of greater importance, the percentage thereof immediately available. Farmers are not very prone in this country to farm for the future. It is difficult to convince them that if they apply an untreated, fine ground mineral phosphate to their soils, sooner or later it will all be available for crops. They are looking largely to the next crop. Lawes and Gilbert in England were the first to recognize the fact that ordinary phosphates used in homes and mineral phosphates is not readily available. To them we owe the process of treating the phosphates acid by treating the bones and mineral phosphates with sulfuric acid. On this discovery the great acid phosphate industry of the world have been founded. The control chemist determines, therefore, the quantity of phosphoric acid present which may be required or immediately available, that is, within the year. Some residues, of course, are obtained since that those are not lost and return value to the farmer in subsequent crops.

Of similar character also is the work of the chemist in the movement, state and functional relationships in the creation of foods and drugs. The character of this work is also strictly scientific, and it must not be forgotten that the purpose of this function is the same as that controlling the chemistry of muscular processes, namely, the protection of the public against fraud. The responsibility of the chemist, however, is the creation of greater trust in the food consumed. Not only is there a permanent constant trend toward more food for each person, but a higher degree of economy is now demanded primarily the protection of health and the preservation of the national economy as well as the fact, however, that the chemist is not the only one who can protect the public against fraud. In the history of the chemist controlling the

character of foods and drugs is of a higher importance, not from a scientific, but from a humanitarian point of view. With those engaged in the supervision of fertilizers, I may class the chemists connected with insecticide control. With those engaged in food and drug supervision, I class those employed in the water service.

The utility of inspection work such as I have outlined above is patent to every observer. It would be a long step backwards if work of this kind done by the various official organizations of the country, national, state and municipal, should come to an end or if the condition of affairs pertaining to this work were those of 50 or 60 years ago. As long as the farmer used only the manure which he made on his farm and the lime and ashes which he burned on his place, he was in no danger of being defrauded by the fertilizer trade. The very moment, however, commercial fertilizers came into vogue he was helpless before the wiles of the adulterator. It is true he could trade with reputable firms if he were in a position to know the character of the firms with which he traded, but this was not always possible. Presumably, from the very beginning, those firms engaged in the manufacture of fertilizers, employed chemists. They, therefore, fully understood the nature of the products which they offered. They were under no obligation, however, to disclose their formulas to the purchaser. As a matter of fact, they did not do so until the state laws came into vogue. It is rather strange that in so far as fertilizer control is concerned, the National Congress has taken no action looking to the control of the fertilizer trade in interstate commerce. It seems that a law of this kind would be of great value in various states in helping them to secure a more rigid enforcement of the state laws.

EXECUTIVE WORK

I come now to the discussion of the third classification of chemists, namely, those charged with the administration of the laws in which chemical analysis and investigation lay the foundation for the law's enforcement. The head chemists who are employed in the various national, state and municipal laboratories having control of products entering into interstate and intrastate trade are all in the third class of my subject. The amount of time which they give to the executive work of their departments varies. Some of them have important duties in the laboratory, others only supervisory duties, but in all cases they remain in close touch with the work going on in their laboratories and the progress which is made in chemical science. The character of the work of this class of chemists, of course, brings additional responsibilities. The question naturally arises, "What rule of conduct should the executive chemist adopt for his guidance?" The platform on which he stands determines very definitely the character of the work which he does. First of all, it is the duty of every executive chemist under any national, state or municipal law fully to comprehend the purpose of the law under which he is working and the terms in which its provisions are expressed. In this work he should be guided by the universal principle of the courts in interpreting an act intended for some public benefit, and practically all acts are so intended. The principle of construction adopted by the courts is extremely simple, namely, if the law be capable of more than one interpretation that one should be adopted which more nearly carries out the provisions and purposes of the act. If, for instance, the law requires that the steel which is used for the manufacture of ordnance should be of a certain fine quality and that the impurities in the steel which tend to impair its quality should be as nearly as possible eliminated, the chemist has a fairly good working hypothesis. He will ascertain just what composition of the steel is best suited for the purpose, especially its tensile strength, endurance and tenacity. If he finds these conditions are based upon a certain minimum or maximum, as the case may be, of carbon, manganese, etc., he will require that the manufacturer of the steel prepare it according to these ideas.

If the standard which he sets is reasonable, it, of course, is one which can be maintained. Whether or not it is reasonable depends upon the terms of the law and the conditions surrounding the production of the best material. The law may be specific, in which case the executive chemist has no responsibility. But if the law is general as to the quality then the responsibility of getting the best quality rests upon him. The materials which are employed in the manufacture of standards, for instance, are required to be of such a character as to be the least variable under the conditions in which standards are utilized. The degree of expansion by heat, or contraction by cold, resistance to oxidation and all other properties which go to make an excellent standard are to be carefully studied and only those materials accepted which confirm to the required chemical and physical tests. Another illustration which is very patent is in the supervision of therapeutic reagents by the public health bureaus of the Treasury Department. The various sera, vaccines, etc., which pass from state to state are subject to inspection and approval by this Bureau. The tests which are made are chemical, physical and pharmacological, and the chemist bears with the physicist and pharmacologist his share of the responsibility of securing a serum or vaccine of maximum vitality and of minimum threatening content. Much of the objection which has been made to serum therapy and vaccine prophylaxis has been due to carelessness in the manufacture of these bodies. Occasionally a product is made which is infected with streptococcus, and staphylococcus and tetanus bacillus or some other dangerous infection and the result is always disastrous and will result very greatly in the production of opposition to these procedures. While it is true that the chemist exercises only a minor part of this control, it is at least an important part.

The chemists in the Bureau of Mines shoulder a very heavy responsibility. Accidents in mines are usually of a chemical character. They are produced very generally by the explosion of combustible gases. The origin of these gases, their control and the precautions which are necessary to minimize the danger are almost purely chemical problems. The head chemist of the Bureau of Mines is, therefore, called upon to discharge not only chemical duties of the highest character but also executive duties in the proper interpretation of his efforts for the greater safety of life.

In the Geological Survey the chemist has a very great responsibility as an executive head in addition to his skill as an analyst and a student of chemical theories and problems. The development of the industries of the country depends largely on a proper census of natural and national wealth, and the best means, as far as chemistry is concerned, of utilizing this natural wealth in a manner best suited to the interests of the public at large. The executive chemist, therefore, has this duty always in mind, that in the exercise of his functions in the interpretation and application of data he should always keep in mind the cardinal principle of public benefit.

There is perhaps no field in which the executive chemist is called upon to exercise a greater responsibility, in the nation, states and municipalities, than in the duties which fall upon him in connection with the food and drug laws. Here we have a wide field of activity which I can speak of with some degree of authority because of my long service in an executive capacity in connection with work of this kind. The food and drug laws of the state and also of the different states which are modeled largely on the federal law, leave a large discretion to the executive officer in charge of the laboratories. This officer is charged by law with ascertaining whether or not a given sample is adulterated or misbranded. First of all before he reaches any conclusion in this matter the nature of the substance must be known; a rigid chemical and physical examination of the sample is therefore precedent to any executive action or to any interpretation of data. It is the duty of the executive chemist to pro-

vide the proper supervision over the work of his assistants, and to know by personal inspection and test that this work is accurate and thorough. Slipshod methods of analysis will easily grow up in a laboratory if the executive head thereof does not take an active part in the supervision of the work. It is his duty also to direct the research chemists in that line of investigation which to his mind seems most fruitful of good and if he be trained in research work to aid and support the research work of this kind. Most of all, however, his responsibility is greatest when he is called upon to come to the final decision as to whether or not the given sample is in harmony with the general principles of the law under which he is working. In the national and municipal laboratories chemists are required to take an oath faithfully to support the constitution of the United States or state and to discharge the duties of his office in harmony with the requirements of the law. He, therefore, cannot evade his duty. He must perform it. The principle which guides his work is practically the same as that which has already been enunciated. He must use his judgment in such a way, when there is conflicting evidence, as to carry out best the purpose of the act. The executive chemist in this case is not the judge or jury; his action is to determine whether or not a court should pass upon and review his decision. If he comes to the decision that the given article is not adulterated or misbranded, whether it be a drug or food, that settles the question, in so far as further proceedings are concerned. There is no one who can review his work. If, therefore, he makes a mistake and decides in the wrong way, he incurs a very heavy responsibility or rather he fails to discharge a duty. As far as I am personally concerned, I always had one invariable rule in all cases of this kind; namely, if there were conflicting evidence to give the benefit of the doubt to the public. This rule I also applied in all synthetic foods to which materials had been added other than nature had provided. Unless it was evident beyond question that the addition of extraneous materials had for its purpose a better product for the public, their presence was always considered as a suspicious circumstance worthy of further review before the courts. If for instance the manufacturer of butter used a moderate amount of salt to meet the general requirements in this country of a salted butter, such an addition would not be considered a violation of law. If, on the other hand, he added a preservative agent with no organoleptic property, such as borax, this would be regarded as an adulteration under the law and warrant the executive chemist in citing the offending parties to the proper officials to defend their action in court. We all know as a matter of history what a tremendous pressure has been brought to bear upon executive chemists in control of foods and drugs to influence their decision favorably to the trade rather than to the public. I do not, however, intend here to go further into this important principle as, if I should, it would be writing a history rather than a paper. I will only add, however, that all efforts made by executive officers to minimize the possible danger of addition of substances to foods and to condone or favor such activities have been, in my opinion, wholly illegal, contrary to the public welfare, and violative of the fundamental principle of the law.

RESEARCH WORK

In the Advisory Board, appointed to aid the Secretary of the Navy in the proper discharge of his duties and for other purposes in connection with the welfare of the people of the country, our society is represented. Importance of research along the line of economical and industrial development cannot be overrated. Of still greater importance, however, is the necessity of a rigid investigation of the causes which are preventing the physical efficiency of our nation. When we realize that more than 60 per cent of the young men who offer their services to the Army and Navy are rejected for physical reasons, the low condition of physical efficiency in our country is made apparent. To my mind, the principal cause of this physical inefficiency

is due to improper nutrition. Important subsidiary causes are the use of alcohol, tobacco, habit-forming drugs and other bodies that have specific effects upon the nerves. The chemist of necessity must take the leading part in the researches which shall lead to a better physique and freedom from moral and intellectual deficiency. The supreme importance of a better physical manhood and womanhood, which would bring a better mental and moral efficiency of the people is slowly becoming recognized. The work of the research chemist in public life is too often curtailed by supervisory and executive duties. An increasing field for the exercise of research activities will undoubtedly be open in official service.

It would be of interest to have a census of the number of chemists found in official service.¹ I hope that some statisticians will take up this subject especially for the archives of the Society. The Chemical Society of Washington has made a beginning of this work and in their list of members printed in November, 1915, they have given the number employed in the various departments of the Federal Government, the Army and Navy, and in schools and institutions. I do not mention this at all with a view of indicating that all chemists in the public service are members of our Society, but this list does give the number in each department that are members. For instance, in the Department of Agriculture, the number of chemists in the Bureau of Chemistry is 93; in the Bureau of Soils, 25; in the Bureau of Plant Industry, 13; in the Bureau of Animal Industry, 13; miscellaneous, 3; total, 147. The number of chemists in the Geological Survey, Department of Interior, is 9; Patent Office, 11; Bureau of Mines, 2; National Museum, 1; total, 23 in the Department. There are 38 chemists in the Department of Commerce, 15 in the Treasury Department, 4 in the Army and Navy, 28 in schools and institutions, and 43 in the miscellaneous and unclassified service. There are 14 members of the Society employed in Maryland. This makes a total of the members of the Chemical Society, employed in the Government Laboratories at Washington and near-by, 315. In addition to these members also, it is not to be forgotten that the Department of Agriculture and the Treasury maintain a number of laboratories in different parts of the country and the chemists in those laboratories are not included in the membership of the Washington branch, but will be found in the local branches where they are situated, such as New York City, Philadelphia, etc. The total number in these laboratories is probably as large, if not larger, than those in the Bureau of Chemistry. The total number of chemists employed by the United States is probably about 1000.

In addition to these official chemists, we should not forget that almost every state has a chemical service consisting of from five to fifteen or twenty persons, which multiplied by the total number of states will give an approximate idea of the total number of chemists thus employed. The municipal chemists are perhaps more numerous, even than the state chemists, although I have not endeavored to make a serious count, but assuming they are of the same number, then we have approximately, a membership of the Chemical Society (unclassified chemists who are considered in official work of some kind or another). This is indeed a formidable number and does not by any means include all the chemical service which is given by chemists employed in the United States. These latter service chemists, that of course, chemists are employed in public work in the country.

I cannot close this paper without referring to one special cause which the organization of the American chemists has had upon the official members. I am here, I am sure, with the entire industry, when I tell you that the American Chemical Society has given little or no attention. I have often suggested that I had not been one of the chemists to pursue to the grave the cause of the chemist in public service. I have often suggested that I had not been one of the chemists to pursue to the grave the cause of the chemist in public service. I have often suggested that I had not been one of the chemists to pursue to the grave the cause of the chemist in public service.

of Priestley in 1874 and take part in the original membership of our organization. This, however, was the first year of my chemical activity and I either had no notice of this meeting or failed to take advantage of it. At that time, although connected with the agricultural education in Indiana, I had no official control of any product. It was not until several years later that Indiana established the office of State Chemist and placed me at its head, by designating as that official the Professor of Chemistry at Purdue University. Since that day, continuously, until my separation from the public service, in March, 1912,

I held official positions in which as an executive officer I felt the obligations of trying to serve as well as possible the people of the United States. It was, therefore, with pleasure that I accepted an invitation to give a short paper on this subject because I feel that through our organization a higher spirit of service has been imparted to our membership and a deeper sense of the obligations under which we rest to do well and faithfully the things confided to our care.

WOODWARD BUILDING,
WASHINGTON, D. C.

DEDICATION OF THE NEW CERAMIC ENGINEERING BUILDING UNIVERSITY OF ILLINOIS

On December 6th and 7th, the University of Illinois dedicated its new Ceramic Engineering Building. The dedication exercises were opened at 1.30 P.M. on Wednesday, December 6th, by a meeting of the Advisory Board of the Department followed by a reception in the building, at which all of the laboratories were thrown open to the visiting guests and the University public.

On the evening of Wednesday an introductory session was held in the University Auditorium, presided over by Dr. Edmund J. James, President of the University. At this session, Dr. S. W. Stratton, Director of the National Bureau of Standards, gave an address of "The Ceramic Resources of America." This was followed by an address on "Science as an Agency in the Development of the Portland Cement Industries," by Mr. J. P. Beck, General Manager of the Portland Cement Association of Chicago. Dr. Stratton discussed the organization and formation of the different types of clay deposits together with their most prominent geological and geographical positions in the United States. This was followed by a discussion of the reactions occurring during the burning of clay products. A detailed classification of the various clay products fashioned from ceramic materials was also presented. The whole address gave a very clear idea of the great variety and extent of the clay resources of the nation and the multifold products which are manufactured from them.

The second dedicatory session was of a technical nature and assembled on Thursday morning in the University Auditorium. It was opened with an address on "The Manufacturer's Dependence upon Ceramic Research," by Mr. W. D. Gates, president of the American Terra Cotta and Ceramic Company, of Chicago. This was followed by further discussions by Mr. Ross C. Purdy, Research Engineer of the Norton Company, and by Mr. L. E. Barringer, Engineer of Insulations for the General Electric Company. Mr. C. H. Kerr, who was to discuss the same topic from the standpoint of the problems of the clay industries, was unable to be present, but sent his discussion for presentation.

The second address of this session was given by Mr. W. W. Marr, Chief State Highway Engineer of Illinois, upon the topic "The Use of Ceramic Materials in Highway Construction." This paper was discussed in a very interesting manner by Mr. Plair, Secretary of the National Paving Brick Manufacturers' Association, of Cleveland, Ohio, and by Mr. G. G. Wooley, Engineer for the Road Bureau of the Portland Cement Association, Chicago.

A paper on the topic "Ceramic Products as Structural Materials" was presented by Mr. H. J. Burt, Structural Engineer, of Chicago, and discussed by Mr. A. V. Bleining, Ceramic Chemist and Head of the Clay Products Laboratory of the United States Bureau of Standards.

The last topic for discussion at this session was "The Use of Ceramic Products in the Artistic Embellishment of Buildings." The discussion was opened with a paper by Mr. Claude Bragdon, author and architect, of Rochester, New York, which was dis-

cussed by Mr. G. C. Mars of St. Louis. Mr. F. Wm. Walker, who was to have discussed the same topic, was unable to be present.

At the close of the forenoon session, the speakers and guests of the University were entertained at luncheon at the University Club by the dean and heads of departments of the College of Engineering. The formal session of dedication convened at the University Auditorium in the afternoon. It was presided over by Dean W. F. M. Goss of the College of Engineering. Introductory addresses were made by the Honorable Edward F. Dunne, Governor of the State of Illinois, and by Honorable W. L. Abbott, President of the Board of Trustees of the University of Illinois. The principal address of this session was then given by Professor Charles F. Binns, Director of the New York State School of Clayworking and Ceramics, upon the topic "The History of the Ceramic Arts." The exercises were closed with an address by the President of the University, describing the history of the growth of the Department of Ceramic Engineering. After singing "America," the audience marched to the new building where the prayer of dedication was delivered by the Rev. John Mitchell Page.

On the evening of the 7th, an Illinois student branch of the American Ceramic Society was formally installed by Mr. L. E. Barringer, President of the Society.

The addresses by Mr. Beck, Mr. Gates, Mr. Barringer and Mr. Kerr appear in full below.

DESCRIPTION OF THE CERAMIC ENGINEERING BUILDING

The Ceramic Engineering Building, exclusive of the kiln laboratory to which it is connected by means of a corridor, covers a ground area of 67×189 feet, with a basement under all. It is a three-story building and is constructed of materials which are representative of the ceramic arts, high-grade brick, tile, terra cotta, cement and gypsum products being used throughout.

The entire basement is given over to the fan system and storage rooms. The first floor contains the ceramic materials laboratories and an office and private laboratory. On the second floor will be found the offices of the department, offices and private laboratories for two professors, the library, lecture, class and drafting rooms, and several laboratories devoted to chemical and physical work and to high temperature investigations. For the present, the offices and laboratories of the Geological Survey occupy the third story of the building, and a portion of the first floor is also given over to the concrete testing laboratory. Space is provided on a fourth floor for the distilling apparatus which furnishes a supply of pure distilled water for the building.

The walls of the main corridor on the first floor have been decorated with display panels showing different styles of face brick. These panels were donated and erected by the following firms:

Western Brick Company, Danville, Illinois.

Sheldon Brick Company, Urbana, Illinois.

Hydraulic-Press Brick Company, St. Louis, Missouri; Indianapolis, Indiana; Aledo, Illinois.

West Salem Hollow Brick and Tile Company, West Salem, Illinois.

Streator Brick Company, Streator, Illinois.

Decatur Brick Company, Decatur, Illinois.

Acme Brick Company, Cayuga, Indiana.

Brazil Clay Company, Brazil, Indiana.

La Salle Pressed Brick Company, La Salle, Illinois.

C. E. Poston, Attica, Indiana.

THE LABORATORIES AND THEIR EQUIPMENT

The laboratories of the building are provided with outlets for water, gas, compressed air, vacuum, distilled water, and alternating and direct current.

The laboratories on the first floor are arranged for the preparation and handling of ceramic materials. In the store-room, the supplies of ceramic materials are stored in large bins ranging in capacity from 2 tons to 100 pounds. The ceramic materials laboratory is equipped with laboratory tables and lockers to meet the needs of 40 students. Adjoining it is the glaze laboratory with tables and lockers for 24 students. The glaze prepara-

press. A large drying closet and a damp closet are also included in the equipment for the work in pottery.

The plaster shop is intended for the preparation of models and molds for pottery and other clay wares. It is equipped with a bench whirler, two potter's wheels and a potter's lathe. Concrete-topped tables for modeling terra cotta forms and casting molds, together with shelving for the storage of models and molds, complete the equipment of this room.

The kiln laboratory, which is in a separate structure connected with the main building by a corridor, is equipped with two open fire downdraft test kilns with chambers of one cubic yard capacity and one muffle kiln with two-thirds of a cubic yard capacity. These kilns are fired with coal or coke. A round downdraft kiln with a 2-foot chamber, a load-test kiln for testing refractories under load at high temperatures, and a muffle furnace for enameling and decorating work are arranged for oil firing. A battery of 4 gas-fired frit furnaces, a small gas-fired test kiln with a pre-heating arrangement for the gas and air, a Monarch tilting furnace for the fusion of glass batches, and several small pot



THE NEW CERAMIC ENGINEERING BUILDING, UNIVERSITY OF ILLINOIS

tion laboratory is provided with machinery for grinding and mixing slips and glazes. This equipment consists of ball mill racks for the accommodation of twenty 1-gallon jars; two double racks for 5-gallon jars, three 12 inch Buhrstone mills, 3 power mortar mills and 8 slip blungers; and a large porcelain lined ball mill; all driven from a line shaft.

The pottery laboratory is provided with the necessary equipment for the manufacture of tile and of tableware. It includes a mixing unit consisting of a blunger and agitator, a levener, and a filter press with a capacity of 30 to 40 pounds of clay per charge. A pulldown and jigger with heads and rings suitable for the making of large pieces of hollow ware, and two friction jolleys with heads and rings for the manufacture of medium and small sizes of flat and hollow ware are also provided. One of these is arranged for use as a thrower's wheel. The other apparatus in this laboratory includes a tile press with die for the preparation of ware by the dust process, a potter's lathe of the most modern type, bench whirler, and a decorator's printing

furnace for firing work are also provided. The various kilns and furnaces are connected by underground flues to a dust test stack. A small room adjoining the kiln laboratory is equipped with indicating and recording instruments which are connected to thermocouples in the kilns. A continuous Madsen carbon dioxide recorder is connected with the three gas fired kilns for the study of atmospheric conditions in the firing. A steam-heated closet is provided for the drying of ware and test pieces.

The machinery equipment of the kiln laboratory consists of a 4-ft. dry pan elevator and a Jeffrey shaking screen; a 4-compartment steel box for storing ground clay above the 8-ft. double shaft pug mill; a 4-ft. wet pug and mixer truck machine with a capacity of 600 lbs. per day with a take-off belt and a hand power side delivery cutting table; a measuring meter brick machine, a hand power regenerator, and a hand power dry press for full-sized brick as well as a measuring dry press for inspection; two hand power blunger machines for limpet molding; a sugar press; a tile press; a 14 x 28 in. iron ball mill,

a set of laboratory rolls and a small jaw crusher. An air compressor is provided for special needs and a rotary blower and oil pump supply the oil burners. The kiln building also provides bins for the storage of fuel, clays and refractories; and a small classroom and a laboratory equipped with tables for the testing of clays and specimens burned in the kilns.

The department library is provided with a well selected set of books dealing with ceramics and its allied sciences, as well as complete sets of the ceramic journals.

The museum has a small but growing collection of ceramic wares and samples of raw materials.

The lecture room has seating capacity for 90 students, and is equipped with the necessary lecture table and lantern facilities. Wall cases for the storage of mineral and clay samples and specimens required for class demonstration, will be provided in this room.

The drafting room provides space for the accommodation of 16 students, as well as filing cases for the storage of plans and blueprints of the various types of industrial plants.

The chemical, physical and research laboratories on the second floor are equipped with the usual laboratory desks and other equipment necessary in such laboratories. The high temperature laboratory is intended for research work with electric furnaces. A 5-kilowatt motor generator set and a 10-kilowatt transformer are provided in this room.

The department also possesses a variety of measuring instruments, such as indicating and recording pyrometers and optical pyrometers for the measurement of high temperatures, ammeters, voltmeters, various types of electric furnaces and petrographic microscopes for general research work.

The buildings and equipment of the Ceramic Engineering Department represent an investment of about \$200,000.

An illustrated booklet describing the Department of Ceramic Engineering, its organization, purposes, and equipment was published by the University for distribution at the dedication exercises.

SCIENCE AS AN AGENCY IN THE DEVELOPMENT OF THE PORTLAND CEMENT INDUSTRIES

By J. P. Beck

General Manager Portland Cement Association

Probably few laymen are aware of the debt which modern industries owe to scientific research. To Dr. Stratton, fellow alumnus of this University, the Portland cement industry, as one example, is indebted to a remarkable degree. Under his able guidance, the United States Bureau of Standards, of which he is the distinguished head, has been of incalculable benefit not only to the Portland cement industry itself but to the many industries which have sprung from it as parent. Leaders of industry recognize that in the face of present-day conditions, correct standards of measurement, quality or performance call for continuous scientific, technical research of the highest order. To this end the Bureau of Standards has contributed far more liberally in many industries than is generally known.

The topic which has been assigned to me might lead you to think that I am a scientist. Let me disabuse your minds of that thought. When I received Dr. Goss' invitation to address you at my alma mater on this occasion, I could look at it only in the light of a command. I feel that he might have chosen more wisely, because although my varied connections with the cement industry have afforded me some opportunities to learn what an agency science has been in developing the Portland cement industries, these connections have not qualified me to discuss this development from the scientist's aspect. I shall, therefore, disclaim originality for the thoughts which I shall endeavor to present to you, because they have been gleaned largely from the writings of those really responsible for placing the Portland cement industry and the industries dependent upon it, in the position which they occupy to-day.

For a number of years, all manufacturing industries have recognized the importance of conducting scientific research and applying the disclosures which such research has made. Science has improved processes and has disclosed a better knowledge of the properties of materials upon which the useful qualities of those materials depend. Science helps modern industry to meet competition, to raise standards of product, to decrease cost of production, to raise standards of living. Science has been at the base of all these ends at least to a contributory extent in practically every industry of any magnitude. For years it has been the underlying policy of all great industrial leaders to surround themselves with and make partners of competent experts, the best scientific equipment and that keen intuition supplemented by long experience such as the laboratory expert, for instance, possesses.

The manufacture of Portland cement combines the mechanical and chemical—processes largely suggested by the mechanical engineer and the chemist.

As time is measured, Portland cement is still something of a youngster. It may be said to have had its origin in 1756 from researches made by John Smeaton, an English engineer. Smeaton was employed by the English Government to build a lighthouse upon a group of partly exposed rocks in the English Channel. His work demanded a cementing material that would set under water as well as in air, and in searching around for such a material he discovered that an impure or clayey limestone, when burned and slaked, would meet requirements better than anything so far known. The clayey limestone which he used was found in Cornwall. From it he made a hydraulic lime which, when mixed with puzzolana, a pumice-like material of volcanic origin, produced a satisfactory mortar which he used when building the Eddystone Lighthouse.

But although Smeaton's cement was undoubtedly an excellent structural material, it was never widely used because puzzolana is found only in a few volcanic regions, notably Italy, where from almost time immemorial it has been used in the making of the so-called Roman cements.

Smeaton's discovery, however, paved the way for that improvement and development in the lime and cement industries which ultimately led up to the original Portland cement, made and patented by Joseph Aspdin, in England in 1824. The fact that Aspdin's product resembled in color, after hardening, the famous old English Portland stone, is responsible for the name Portland cement. Aspdin's patent involved calcining a mixture of limestone and clay, these materials being raised to a temperature sufficient to result in a clinker. Scientific knowledge was scant during the early stages of the development of the Portland cement industry in England, so proper proportions of limestone and clay to be used were discovered by burning experimental mixtures and testing the physical properties of the resulting product.

THE CHEMISTRY OF CEMENTS

The first knowledge of the chemistry of cements probably came from various investigations carried on in France. Of these early researches the ones that have no doubt done most to establish studies which followed, were those of M. Vicat. Vicat made an attempt to determine the relation between the quality of hydraulic lime, cement and the chemical composition of the stone from which they are derived; likewise the nature of the chemical compounds formed during burning and the changes which took place when the cement was mixed with water and hardened. Although Vicat did not attain the ends which he sought, his studies resulted in some interesting theories that have done much to guide scientific research since his time.

When the manufacture of Portland cement was first undertaken in the United States, the natural tendency was to follow closely the practice prevailing in Europe, both as to raw materials and processes. Then nearly all of the European plants used

soft natural raw materials which were mixed and ground in a wet condition and burned in stationary vertical kilns, the resulting clinker being then ground in a manner similar to the grinding of wheat into flour by the old familiar millstones. But this process was not best adapted in all instances to the great bulk of raw cement materials in the United States. It involved reducing them to powder or to a wet paste or "slurry," or forming the materials into bricks or balls and feeding them by hand in these forms into a vertical kiln in which they were burned. The kilns also had to be unloaded by hand and the clinker finally ground in a way that to-day would be regarded as particularly ineffective and inexpensive. When both of the raw materials were naturally wet and naturally soft, as when marl and clay were used, the earlier stages of the wet process were, of course, considerably simplified and relatively inexpensive.

But with the hard dry raw materials, such as those so abundant in the Lehigh district, for instance, the wet process was not only expensive but absurd. It was soon recognized by those who had commenced experimentally the manufacture of Portland

greater attention because of its important effects on the cement industry.

THE ROTARY KILN

It will be sufficient to describe briefly the rotary kiln as a steel cylinder lined with fire brick and set at a slight inclination to the horizontal. The raw mixture is conveyed in at the upper end and travels slowly by gravity as the kiln is revolved. The fuel is blown in at the lower end where the burned clinker also falls out. When the rotary kiln was first planned for use in this country it was expected that producer gas would be the fuel, but as a matter of fact petroleum was used and for some years this continued to be current American practice. The rotary kiln was first used successfully in this country at South Rondout, N. Y., in 1899. At the South Rondout plant it was found possible to charge the mixed and ground raw materials direct to the kiln without wetting. This marked another step in the progress of science in the Portland cement industry. In 1891, at Montezuma, N. Y., naturally wet raw materials (marl and clay) were charged into the kiln without preliminary drying.



EAST END OF KIEN LABORATORY SHOWING BRICK AND MARL MACHINERY.

cement in the United States, that the relatively higher priced labor and cheap fuel of America as contrasted with the cheap labor and expensive fuel of Europe, would call for great changes in the technology of the industry if it were ever to be established on a firm commercial basis.

The most interesting features of the days that marked the early development of the cement industry in this country were a realization of these conditions and the careful search for alternative methods. In the general effort to cut down the excessive labor cost of the product, two distinct, though closely allied points of attack, were obvious. Both the burning and the grinding processes would have to be cheapened by mechanical improvements. These received prompt consideration and careful study. Advancement became a reality when the old stationary kilns and millstones were displaced respectively by the rotary kiln and by modern grinding machinery. On the first change, substitution of the rotary for the stationary kiln demanded the

The two main types of present American practice in Portland cement manufacture were then possible: one continuous, the dry process, mixed with limestone or cement rock, and the wet process, mixed with marl. On the basis the dry process has become the most thoroughly tested.

The first step in the development of American cement manufacturing methods began about 1850, when powdered coal, first used as fuel, petroleum oil, and then kerosene, replaced wood throughout the United States and in a short time New England alone produced or consumed ten thousand tons.

The most timely development in the rotary kiln was the continuous method of burning. By 1890 these kilns had become practically standardized in size and capacity. Almost every kiln in the country used wet raw materials, most being long, 100 to 150 ft. and a total capacity of 100,000 to 200,000 cu. ft. The process, with the removal of marl, kiln and fuel, had nearly reached its present stage. When was built about 1900, most when

nothing like fixed standards in length have prevailed. Kilns now installed range from 100 to 150 feet in length and have an output of from 400 to 800 barrels a day. A few kilns 250 feet in length are in operation.

In line with changes in type and capacity of kilns, it is natural that there should be changes in crushing and grinding machinery which have also contributed to the enormous tonnages of raw and finished material. The cracker crushers and millstones of the early days of the cement industry have been replaced by larger and more efficient reducers. At present the gyratory crusher is almost exclusively used for the first stage of reduction.

In 1905 the United States Geological Survey published as its Bulletin 243, a report of the cement materials and industry of the United States, prepared by Edwin C. Eckel. The introduction to this bulletin was written in 1904 and called attention to the marvelous growth of the Portland cement industry during the ten years preceding. Mr. Eckel then said:

"In its importance to our present-day civilization, cement is surpassed among mineral products only by iron, coal and oil. In rate of increase in annual production during the last decade, even these three products cannot be compared with cement. In 1890 the total production of Portland cement in the United States was 335,000 barrels, valued at \$439,050. In 1903, it exceeded 22,000,000 barrels, while the value was over \$27,000,000.

"During the 16 years which witnessed the development of the American Portland cement industry, two of the greatest gold discoveries in the world's history were made in Colorado and Alaska. The annual gold production of Alaska and of the Cripple Creek District in Colorado have impressed themselves on every citizen of the United States, while the Portland cement industry has attained its growth in comparative obscurity. Yet on comparison it will be seen that the gold production of Cripple Creek is only slightly greater than the output of Portland cement, while the production of Alaska sinks into comparative insignificance. Moreover, the greater part of this increase has been within the last decade. The production of Portland cement has risen from a little less than \$2,500,000 in 1896 to over \$27,000,000 in 1903."

These figures now have only a historical interest. But they are interesting because of the growth which the Portland cement industry has undergone since they were published. In 1915 the total production of Portland cement in the United States was 85,914,907 barrels valued at \$73,886,820. The recent growth of the American Portland cement industry has been so rapid that its present relative standing among our great industries is realized by few, sometimes not even by those most directly interested.

Nature has provided an abundance of calcareous and argillaceous materials suitable for the manufacture of Portland cement and its manufacture does not involve a secret process. Portland cement is but one of a dozen chemical compounds which harden or set when mixed with water. It has attained its great importance because of the ease and relative cheapness with which it can be manufactured and not because of any peculiar properties not possessed by certain other compounds. But simple mechanical mixing of silica, alumina and lime in the proportions usually found in standard Portland cements will not yield a compound possessing the required properties. It is essential that the ingredients be properly combined, not exactly as a true chemical compound but rather as a physical chemical solution of one or more chemical compounds in each other. The best, and practically the only way, in which such a union can be attained is by a complete or partial fusing of the silica, alumina and lime, in other words, reducing this mixture to a clinker, then grinding it to a fine powder.

Knowing the chemical ingredients of Portland cement and the steps necessary to combine these materials properly, it is evident

that plants of the industry should be widely distributed. A mixture of clay and limestone can be so prepared artificially that when the combined water in the clay and the carbonic acid of the limestone are driven off by heat, the residue will form clinker of the desired composition. Assisted by the mechanical equipment devised and perfected by the mechanical engineer, the chemist then controls the process of cement manufacture.

The Portland cement industry is a chemical industry in that Portland cement is the result of reactions going on at high temperatures between the silica, alumina and lime in predetermined proportions. For this reason it is necessary that the scientific side of the industry be given proper recognition and research work be highly developed and persistently maintained. Chemical research may be and has been directed in various directions in industries which involve chemical principles. Take, for example, the manufacture of dyes, in which chemistry, by the manipulation of coal tar, has evolved practically every conceivable color. Chemical research may also be directed toward the development of new processes or the modification of old methods, and toward a proper interpretation of the reactions to which the formation of different products are due, in order that the conditions under which they originate may be made the most favorable for producing the highest grade of material at the lowest cost.

The Portland cement industry, like many other industries, has benefited because of persistent research and study along the last two lines. In the early days of its development, manufacturing processes were carried on largely by rule of thumb methods, and the preëminence of Portland cement has been made possible solely because of the control which the chemist can exercise over the finished product before and during its manufacture.

THE AMERICAN CEMENT INDUSTRY

John W. Eckert has been called the father of cement chemists in this country. While working as an assistant at Lehigh University, South Bethlehem, Pa., he was asked to make analyses of rocks from the different beds in the quarries of the Coplay Cement Works, of which D. O. Saylor was then President. Mr. Eckert was finally engaged by the Coplay Cement Works to devote his entire time and knowledge to the process of manufacture and in this way became the first cement chemist in the United States. His efforts resulted in more certainty and less chance in the preparation of proper mixtures. A more nearly uniform product naturally resulted. This was in the latter seventies. Somewhat later, Robert W. Lesley, one of the pioneer manufacturers of the country, in cooperation with George W. de Smedt, then a Government chemist, worked at various problems that had been puzzling cement manufacturers; among these was a search for something to retard the setting time. Chance brought to light the fact that gypsum added in certain quantities accomplished the desired end.

But although chemistry has had a great deal to do with progress made in the manufacture of Portland cement, the work of the chemist has been most effective in perfecting technical processes. Only within the past year has it seemed likely that the chemical structure of the material will soon be disclosed. Studies now in process at the Geophysical Laboratory, Carnegie Institution, Washington, appear to point to this conclusion.

The chemist has shown that a true Portland cement can be made from blast-furnace slag, once a waste product, and has thus been responsible for a great industry producing considerably over 10 per cent of the total Portland cement manufactured in the country. He has proved that the cement rocks, as found, for instance, in the so-called Lehigh district, need not be depended upon as a source of high-grade product. He has found that almost every state in the Union contains materials which, when properly combined, will produce Portland cement of high quality. He is able to control even variations in composition of raw materials and as the requirements of engineering speci-

fictions have called for a material of better quality, the demands have been met.

The first semblance in this country to anything like standard specifications for Portland cement was a report of a committee of the American Society of Civil Engineers, January 7, 1885, which served for a few years; but it soon proved too indefinite for the growing needs of engineering as applied to concrete. In 1896, at the suggestion of Mr. Richard L. Humphrey, a series of editorials appeared in the *Engineering Record* calling attention to the inadequacy of the 1885 report of the committee mentioned, and urging the appointment of a new committee to revise and amend the first committee's work. Following this, a resolution was presented at a meeting of the American Society of Civil Engineers held November 4, 1896, requesting the Board of Direction to report on the advisability of appointing a committee to report on the proper manipulation of the tests of cement. The Board reported at the annual meeting of the Society, January 20, 1897, and after a vote by letter ballot, appointed in July of the same year a committee which may be considered as the first definite organization delegated to prepare comprehensive cement specifications.

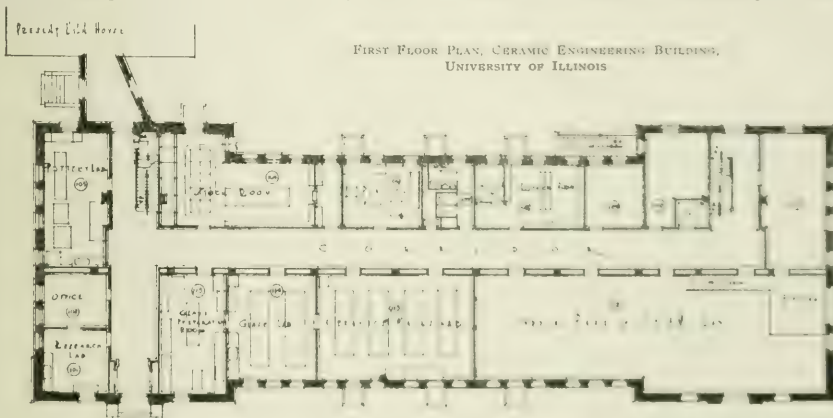
With the rapid development of concrete engineering, further changes in standard specifications have been necessary. Various

materials; but as the science of concrete design developed, rapid recognition was given to concrete as a distinctive building material. It has many desirable qualities peculiarly its own. Probably none is greater than its resistance to fire, when properly manufactured and used.

It differs from all other structural materials in that it is not a finished product until some weeks after fabricated. Other building materials are either provided by nature ready for use or are made and finished in a plant in which rigid inspection of all processes is possible.

The fact that concrete is composed largely of inert materials called aggregates, which are bound together by Portland cement, has led many to believe that as a building material the quality of concrete depends largely upon the Portland cement used in its manufacture.

In order that the engineer may be able to make a proper selection of materials, to proportion them properly, and to mix and place the concrete, it is necessary that the influence of each ingredient entering into it be fully understood. No other material used in building construction depends so much for its value upon the widest possible knowledge obtainable as to the influence of each step in the process of manufacture. So science has extended its researches in determining the value of concrete



committees of different societies have worked both independently and jointly in perfecting cement specifications. But so many societies or different bodies brought forth cement specifications that little short of chaos has existed until within the past year, when various societies and interests united in efforts to evolve one specification that would serve all interests best. These are the specifications of the American Society for Testing Materials which will become effective on the 1st of January, 1917. It is an end to be desired—one that has long been sought not only by cement manufacturers but by many recognized leaders in engineering lines.

CONCRETE

The industries dependent on Portland cement to-day are numerous. As a binder for the finished product known as concrete, Portland cement has no equal. The uses for concrete are many. It is employed in the construction of road, street, alleys, sidewalks, houses, dams, bridges, tunnels, office and factory buildings, farm structures, ornamental products, building units such as block and brick, sewers, both monolithic and pipe, for pipe and tile used in drainage, and for many scores of other uses, practically all that have heretofore been satisfied by the older building materials and many that have not.

When concrete first won popularity, it was often almost exclusively looked upon as a substitute for some of the older structural

aggregates. The studies which have been made along these lines would form many printed volumes. Only within comparatively recent times has it been proved that the aggregates determine in a far greater degree than most people know, what qualities the resulting concrete will possess.

In making aggregate determinations, many laboratories, individuals and scientific bodies have been leaders. Probably it would be impossible to refer to any one of these without seeming to slight the others. Yet at the present time the Structural Materials Research Laboratory, located at Lewis Institute, Chicago, perhaps stands foremost, at least in the diversity of its research. The studies on concrete, for instance, which have been made during the past year or more in this laboratory mentioned, have been remarkable for their range and important implications in the structural applications of the Portland cement. The aggregate determinations that have been made and are now being made in this laboratory will, it is judged, eventually disclose how little in relative mass has been known in the past, both of cement and concrete.

One of the earliest studies of the properties of concrete was carried out by G. A. Gifford, of the United States Army, who was invited to deliver a paper on concrete at New York during the World Fair (1901). A more extensive study, entitled "Concrete Treatment in Acid, Hydrated Cement and Mortar," was the result

of these studies. A second volume was published in 1871 which gave the results of other studies. Paul Alexandre and R. Feret, French scientists, made important contributions to our knowledge of the strength and other properties of hydraulic mortars and concrete during the years 1888-1892.

The first uses of concrete considered taking advantage only of its compressive strength, that is, its ability to bear loads placed directly upon it. But like building stones, for instance, concrete is strong in compression but weak in tension and little progress was made in developing the possibilities of concrete as a structural material until it was combined with metal, such as iron or steel rods or other fabricated reinforcement, to compensate for its deficiency in tension. To-day the value of concrete as a structural material is due largely to the development of reinforced construction. Such concrete has been referred to in various ways, the terms "ferro concrete" or "armored concrete" were once general and even to-day are in popular use abroad. The combination of steel and concrete has resulted in a building material different in properties from any other and for which the usual formulas of design, such as those involving stress distribution, do not apply. Therefore, it has been necessary for a time to assist in developing the men of science who have aided in solving the problems that were and are still sometimes encountered in making the best use of this most modern building material.

REINFORCED CONCRETE

The early history of reinforced concrete is most interesting. It appears that the first use made of metal reinforcing in combination with concrete was by certain French artisans about 1855 to 1865, in making small boats and flower pots. These men conceived the plan of strengthening their concrete products by embedding iron wires in the fresh concrete. Little did they dream at this period of the importance this principle would have.

The first instance of any importance in which the principles of reinforced concrete construction were applied was in a dwelling at Port Chester, N. Y., built in 1875 by W. E. Ward. This was the first example of reinforced concrete construction which in any way approached our present conceptions of this material. The further development of reinforced concrete construction was extremely slow, as fifteen years elapsed before we find another example of its use in any important structure in the United States. It is probable that reinforced concrete would still be one of the curiosities of building construction were it not for the fact that men of science have searched for and discovered the principles underlying the action of this material, and have shown how structures of reinforced concrete may be designed in a rational way.

The first scientific study of a combination of concrete and iron in the form of reinforced concrete was carried out about 1875 by the laboratory of David Kirkaldy, of London, at the request of Thaddeus Hyatt. Hyatt was a citizen of the United States at that time residing in London. In 1877 a book was published by Hyatt giving the results of these investigations. Although this book was printed for private circulation and has long been out of print, it has attained rank as a classic in the literature of reinforced concrete. Hyatt was probably the first to recognize the fundamental principle of reinforced concrete which involves the use of reinforcement to take the tensile stresses which would otherwise be thrown upon the concrete. At the same time he recognized the necessity of a permanent bond between the concrete and the reinforcing metal, and the importance of similar action of the two materials when subjected to changes in temperature. The tests described by Hyatt were carried out for the purpose of securing information on these subjects.

The use of concrete as a structural material has given rise to many problems which have commanded the attention of scientists. The combination of two materials of entirely different

characteristics into a single structural unit has made it essential that new principles be developed which could be applied to the analysis of members of this character. For the first time we are able to construct buildings in such a way that they are of monolithic nature. This has made it essential that methods of analysis be developed which would apply to continuous beams and slabs, and combinations of beams, columns, walls, etc., in a manner that has not been necessary with other materials.

The experiments carried out by Hyatt attracted considerable attention and showed the true principles of the action of reinforced concrete beams under load. However, developments in the uses of reinforced concrete were limited until about the beginning of the present century. Prior to this time a few isolated experiments had been conducted in Germany, Switzerland and France in promoting the use of certain so-called "systems" of reinforced concrete construction. These consisted of patented arrangements of reinforcing steel, many of which were of poor design and wasteful of materials. Practically no research work was done in the United States on the subject of reinforced concrete prior to the year 1900. Since that date the combined efforts of many investigators in the United States, Germany and France have furnished us with a large stock of information concerning the action of reinforced concrete.

The year 1903 saw the inauguration of several independent researches in the United States on the properties of reinforced concrete beams. Professor A. N. Talbot, of the University of Illinois, made his first experiments on reinforced concrete beams during this year. Experiments along similar lines were carried out during the same year by Professor W. K. Hatt, of Purdue University, Professor Edgar Marburg, of the University of Pennsylvania, and by Professor M. A. Howe, of the Rose Polytechnic Institute. Since 1903 numerous other experiments have been carried out by the above-mentioned institutions and by the University of Wisconsin, the United States Geological Survey, The United States Bureau of Standards and others. Prior to these extensive experimental studies, reinforced concrete was designed by purely empirical methods. It was impossible for reinforced concrete to reach its proper development until such experimental studies as those mentioned above had shown that:

- (1) There is a definite and positive adhesion or bond developed between concrete and steel which can be depended upon to transmit the stresses from one material to the other.
- (2) Iron or steel embedded in well-made concrete is perfectly protected against corrosion and deterioration of all kinds.
- (3) The coefficients of linear expansion of concrete and steel due to changes in temperature are practically the same.
- (4) Rational analyses may be applied in determining the stresses developed in reinforced concrete members due to applied loads.

It seems probable that no one institution has contributed more to the literature of this subject than the Engineering Experiment Station of the University of Illinois. This experimental work was begun by Professor A. N. Talbot in the year 1903, and has been continued up to the present time. Large numbers of tests have been carried out each year on reinforced concrete beams, columns, slabs, bridge girders, culvert pipes, footings, rigid frames, and on completed structures. A great deal of the development of reinforced concrete construction has come about as a direct result of the scientific studies of this subject which have been carried out by Professor Talbot and his assistants. The importance of Professor Talbot's contributions to this subject may be seen from the fact that the nomenclature used by him in some of the earliest publications of the Illinois Engineering Experiment Station has become the universal language in the literature of reinforced concrete.

To the Engineering Experiment Station of the University of Illinois the world is also indebted for the comprehensive tests tabulated in Bulletin 71 of the Engineering Experiment

Station entitled "Tests of Bond between Concrete and Steel." These tests, which were made by Professor D. A. Abrams, then Associate in Theoretical and Applied Mechanics at this University, and now Professor in Charge of the Structural Materials Research Laboratory, Lewis Institute, Chicago, have been a valuable contribution of science in furthering a number of the industries dependent upon Portland cement.

In a class by themselves stand the group of bulletins, monographs or whatever you choose to call them, that has been issued by the Bureau of Standards in its series of Technologic Papers. These constitute a contribution of inestimable value to those studies which have made many of the Portland cement industries realities, or have advanced them to a higher plane of efficiency than would have otherwise been possible. Among the Technologic Papers of the Bureau of Standards are these reporting:

Results of Tests on the Strength of Reinforced Concrete Beams.

Tests of Absorptive and Permeable Properties of Portland Cement Mortars and Concretes, together with Tests of Damp-proofing and Waterproofing Compounds and Materials.

The Effect of High-Pressure Steam on the Crushing Strength of Portland Cement Mortar and Concrete.

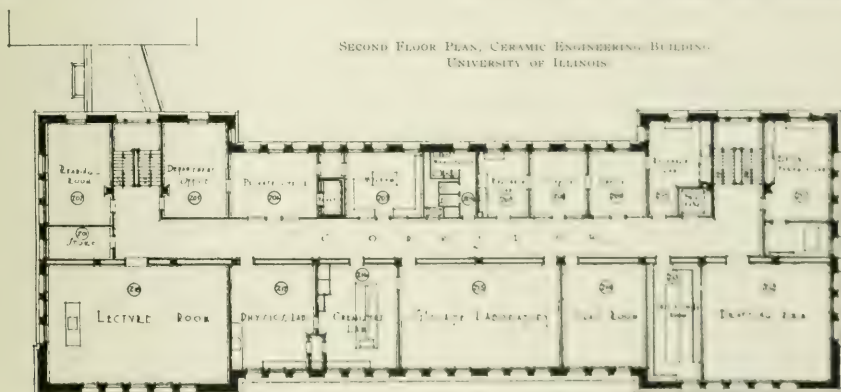
Action of the Salts in Alkali Water and Sea Water on Concrete.

Special Studies with a View to Preventing the Action of Electrolysis.

the European war, recovery of potash is likely to be a profitable side issue of cement manufacture.

The pioneer experiments of this kind were made by the Riverside Portland Cement Company in its plant at Riverside, Cal. Experiments have been carried on also by the Security Cement & Lime Company, near Hagerstown, Md., and were made the subject of a quite comprehensive article in the *Manufacturers' Record* of May 11th, this year. While the recovery of potash from cement manufacture is in itself so new a development that its possible significance is not yet generally appreciated, it has, however, gone far enough to arouse many cement manufacturers to its possible importance. I refer to it only for the purpose of citing one more instance to prove that unthought-of possibilities in industry lie dormant awaiting the magic touch of the scientist.

To-day we find that concrete has attained a point where its application is almost universal in the construction field because of its practically unlimited usefulness. Yet those who are familiar with the cement industries realize that there is still need for the scientist to advance further our knowledge of the properties and uses of this material. I believe that to-day we stand only on the threshold of concrete's possibilities. I have no doubt that those who are most active in the cement and allied industries to-day will, ten or fifteen years from now, look back



SECOND FLOOR PLAN, CERAMIC ENGINEERING BUILDING,
UNIVERSITY OF ILLINOIS

Variations and Results of Sieving with Standard Cement Sieves.

The Standardization of Cement Sieves.

Studies on the Hydration of Portland Cement

Investigation of the Durability of Cement Drain Tile in Alkali Soils.

Strength and Other Properties of Concrete as Affected by Materials and Methods of Preparation, etc.

Some of these studies are being extended at the present time with a view to reaching more nearly definite or final conclusions.

Without the studies and tests that have been made of concrete and reinforced concrete with a view to determine the resistance of this material to fire and other destructive agencies, there would be no reinforced concrete buildings, no concrete roads, streets nor alleys, no concrete sewers, no cement drain tile—none of the many other structures and products of concrete which science has made possible.

Among the latest achievements of science in the Portland cement industry itself are experiments tending toward conservation of resources, in the possible recovery of potash, a by-product of Portland cement manufacture. Experiments which have been made within the past year or two indicate that our supply of potash from Germany has been cut off because of

our present practices with cement and concrete with pity for the little we really know of their wonderful possibilities.

CHICAGO, ILLINOIS.

THE MANUFACTURERS' DEPENDENCE ON CERAMIC RESEARCH

By W. D. LEITCH

President American Terra Cotta and Ceramic Companies, and President American Ceramic Society

All things in all times, change. It is the law, the established order of things. Progress—speeding on, faster and more constant, better wares and better service are strictly and rapidly demanded in each and every line of work. The wheel does not halt, who holds that what was good enough for his father is good enough for him, will be discarded, cast away, and left rotting in the lumber yard of the business life of to-morrow. It is absolutely the survival of the fittest.

From the days of the Great Mays, in the matter of manufacturing personal fidgets, the days are long away to the way early, that to the first strike to the last product to the finish of the line. The machine goes, and the man must follow. Many great things have been done in the world, and many more are being done by improved tools, and by the use of the machine, and by the use of the

not see and that could not see him. He condensed mighty gases into compact form that he might suddenly loosen them with all their terrific power for his use, to do his bidding, to work his vengeance. He learned to govern them absolutely, to bind more power into a smaller package. When their smoke bothered him he stopped their smoking and made smokeless powder, so that the men he fought could not locate his hidden retreat. Man is like all animals in that he fights but unlike any animal in that he laughs, and this trait of his leads him to other things than war and slaughter.

Thank God not all his conquests are by war. There are other ways than by blood, others than by physical force. Chemistry can work out other things than high explosives, things useful and beneficent rather than destructive and abhorrent. Mechanical and Chemical Arts have been advanced far beyond the fondest dreams of our fathers. Man talks across the ocean, travels under its surface, flies in the air; from using the lightning as a plaything he makes it his servant and commands its mighty power, binding and harnessing it to do his bidding, even before he really knows just what it is. He hunts out its laws and, knowing them, compels it to do his will. Utilizing the force of gravity in our lakes and rivers, he has harnessed that power, and, compelling it to make lightning, has lit up his cities with it and turned night to day with water. What would your grandfather have thought of the statement that the waters of Lake Michigan would eventually light the city of Chicago? Jules Verne's dream is no longer a dream and ships go under the water. Darius Green and his flying machine are no longer a joke, for man flies at an hundred miles an hour, outstripping the birds, and not that only but he fights other men there. From the big things to the little, the invisible, man has made a new eye and sought out the little, invisible, teeming microscopic life; has hunted disease germs and, having found them, has fought them and conquered. Life has thus been prolonged and saved. The great doctrine of prevention has been established without which such great achievements as the Panama Canal could not have been accomplished.

Manufacture has always been dependent on research, from the time of the first manufacturer, and ceramic research is one of the oldest of all such lines employed. It was not a lack of research but of quality and extent and the effort and energy employed. Ceramists have always been enthusiasts, optimists in the extreme, dreamers. The very first experimenter when he, or more probably she, found she could shape a cup in a plastic mass of clay, hesitated not at all but proceeded at once in the attempt to make a better one, in the which, every ceramist since has followed her example. Nothing was so good that a better was not sought. Perfection was always sought but never acknowledged as achieved. Always a better body, better glass, better shape and greater beauty were sought. Utility and beauty were the objects ever pursued. To make the best possible has been the effort and to this end all the workers have wrought tirelessly, enthusiastically and intelligently to the very best that was in them. Their effort was right but they had small opportunity. It was individual and not collective effort and the problems were too much for an individual; team work was required. At first there was no fund of research accumulated and it had to be hunted out, built up and made available. This necessity being apparent, this first discoverer of the fact that clay was plastic, could be fashioned, made into a cup that would hold water, did not stop. It was a memorable discovery but not final. The discoverer, having the true spirit of the potter, kept at it and made the further discovery that it would dry and harden. Undoubtedly, the very next discovery was the disconcerting one that it would wet up and dissolve when wet again. Long research must have been exercised here to correct this which, however, resulted finally in utilizing the great mystery of fire to fix it lastingly. This changed its whole

nature and made it indeed a new material, useful, beautiful and lasting. From the first experimenter on, through countless ages, beauty of form has been the objective. Utility was a pressing requisite but effort to make it beautiful was always shown, and protected and preserved the article when made, causing it to be treasured and cared for. I have no doubt but that the first discoverer, in fashioning her cup, shaped its form to lines of beauty, possibly crude but seeking beauty none the less. Ceramic research had thus progressed to the forming of a cup, doubtless crude, probably porous, but a great achievement and prophetic of the future. Later on research brought out the quality of vitrification—nonabsorbent and waterproof—and, later on, wedded the cup to glass and glazed it. This one thing of the glaze bound the art irrevocably to close ceramic research and committed every succeeding potter to cast aside all else in the fervent, tireless effort to surpass, to make a better body and a better glaze than any one before him had made, and, in his fervent, tireless effort to surpass, and in his enthusiasm to this end, make any sacrifice, endure any privation, surmount any obstacle and never give up hope. Pallis was not the only potter who burned furniture. All potters have done so: burned furniture, bridges, luxuries, clothes, necessities even, and to-day, all over the world, they are feeding their kilns with clothes and automobiles and sacrificing their luxuries and comfort, they are eating dry crusts instead of cake, that they may feed their kilns, try their experiments and make something better and more beautiful than has yet been wrought. All this has brought clay wares into a very extended use. You drink your morning coffee from a cup of clay, more than a thousand times a year you eat your food from a plate of clay, you wash your face in a clay bowl and you take your bath in a clay tub. All the modern use of electricity would fail were it not for clay insulators. The paper you write on and the paper on your walls are largely composed of it and even the sugar you put in your tea is more than likely to have made its acquaintance but in the latter case not through ceramic research.

While the ceramic art is perhaps the most ancient of all the arts of to-day it has been probably, through the past ages, the most secretive. Progress in it has been, of necessity, by means of a multitude of experiments, mostly of necessity failures, being wrought so crudely and blindly. Occasionally one proves good and capable of reproduction. Many were freaks and depended on chance conditions which were not present on the next attempt and were, therefore, discontinued and lost. Sometimes, however, these were traced out and led to new processes, thus utilizing these very accidents. When these processes stood the tests and produced a new effect, the process was surrounded by every possible safeguard to hold it secret; often so closely guarded that it was lost on the death of the discoverer. Often, too, it was handed down, from father to son, as a family heirloom, thus remaining in use for generations. Imitation, however, prevailed more than invention. Men feigned idiocy to get into factories, living on crusts and being kicked and buffeted about, that they might finally worm out the secret and then go and imitate. Even where invention was used it was employed in a blind fashion, feeling the way with this and that material, and with very little real knowledge as to real possibilities. So earnest was the work, however, and so extensive the experimentation, that much of good was accomplished, and these experimenters are entitled to very great credit for having, under such conditions, wrought out methods many of which are used to this day.

But even the excessive secretiveness of the potter has had to yield to the modern spirit. Men have become broad-minded enough to subserve their personal interests to the good of their Art: to add their contribution to that of the one who had gone before them, and not only that, but to hand over their contribution to the fellow coming after them, and thus get the whole,

cumulative effect. They have learned to glory in the upbuilding of their art as an Art indeed.

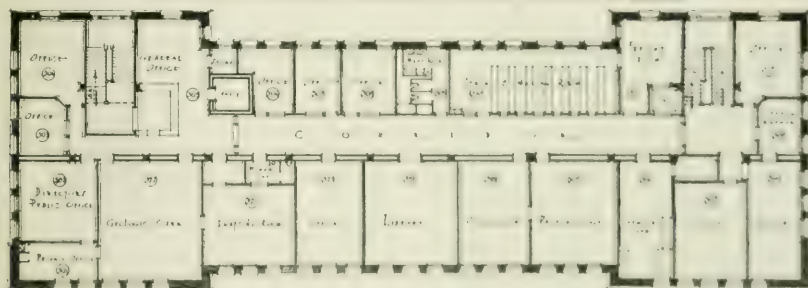
The Almighty has prepared the material in abundance. In the great laboratory of Nature, He ground it with mighty glaciers, chemicalized it through countless ages, washed it, spread it out, compressed it under millions of tons pressure and covered it over deeply for man's use when required. Men have constantly labored and schemed with this crude material. They have dug deep but, as yet, have only scratched the surface. They have mixed one clay with another clay and have thus improved their wares by the mixing process. They have earnestly and faithfully sought to find out and follow Nature's Laws and have broadened from ancient usage radically in publishing their findings for the good of the Art and for the benefit of those coming after. The active work of the American Ceramic Society and the work done in the Ceramic Departments of our State Universities have done much and will yet accomplish wonders in the clay art in the future history of our country. The names of Orton and Bleining will be spoken in reverence by the workers in clay in generations yet to come. The taking of a crude, waste material and making it into a thing of utility and beauty is indeed something of which to be proud. The digger of the clay, working with the pugger, the presser, the chemist, the modeller and the burner, all working earnestly and honestly, each giving the very best there is in him, will produce useful and beautiful wares, as yet undreamed of, out of this hidden, unused

extend over quite a period of time. The experiment started to-day may require a week or a month or more. The intimate chemical changes that occur when the material is molten are very perplexing and intricate. To all the complexity of mixtures of flint and spar, of flux and frit, there is added that of color, for the production of which the ceramist's palette is extremely limited. Only a few metallic oxides will withstand the heat and even these are of a most erratic nature, as for instance copper which is capable of making black, blue, green or red according to the atmosphere in which it is produced.

But ceramic research is not confined to chemistry. Engineering and general management enter largely into the field of this research. Large quantities of crude material must be handled, must be plentifully and economically provided and, to this end, there must be the most intelligent treatment. Machinery must be largely used and great intelligence exercised in its construction and employment. Men must be selected for the various places and as nothing varies more than men, very great intelligence must be exercised in their selection and placing. The right man in the wrong place or the wrong man in the right place is as disastrous with men as with machines, so a properly balanced working plant for manufacture is really a complicated mechanism, and like any other complex piece of machinery, a bad cog in the wheel will throw the whole out of gear and stop all perfect working of the machine.

Beyond these generally recognized essentials of ceramic re-

THIRD FLOOR PLAN, CERAMIC ENGINEERING BUILDING, UNIVERSITY OF ILLINOIS



material that has so long been waiting under the prairies of Illinois. Lying crude and hidden, the material does no one any good. He who fashioned it, who so patiently prepared it and laid it away, left it lacking in admixture with one thing in particular—brains. Unless mixed with these it will never come into its own. The clays must be good and the brains must be good, and the mixture must be right. Both may be good but lack the mixture. In Italy, to-day, there is crude clay, still in the bank, from beside which other clay was dug five hundred years ago. That other clay, under the touch of Della Robbia, grew into a beauty that has placed it, worth its weight in gold, yes priceless, treasured in the choicest museums of the world, while this mud-g clay, untouched by a skilled hand, unmixed with brain, remains inert, despised, unused, awaiting the touch of another hand to bring it into the life, the individuality, that shall make of it a thing of beauty, shall fix into it the vigor and enthusiasm of him who fashions it into lasting beauty. So there lies all under this State of Illinois a wealth of this crude material waiting the touch that shall give it life and beauty. I believe that the men who will do this are those that shall go out from this school with brain skilled and trained for that work, working, not blindly as of old, but with trained intelligence.

Ceramic research has largely to do with chemistry. The various admixtures are formed when the materials are cold but the chemical changes occur when heated to a high degree of heat and are hence shut out of sight. They also, necessarily,

search there is another, often missed in the general summing up, but of the utmost importance, that of Art. Unless it have artistic beauty, no matter how skillfully composed, the product will be a failure. The primitive Indian woman, fashioning the first clay pot, forming it for ordinary domestic use, recognized this requirement, shaping it to pleasant form, of beauty. Having so formed the first, she went on to add something, of ornament for her children, an ornament desired in that universal, never ceasing effort to add beauty to utility. This effort of the first worker has never stopped, but has acquired momentum in the years since. Beauty has found a position as well. Many of the vessels that tell of the mud and burned part are very fragile and the big heavy vessels that shatter breakable but beautiful things, whose beauty appeared in all and for which they were prized and protected. I look forward confidently to the time when this will be better recognized and when this University will have a distinct department, housed in the beautiful clay building, in the clay state, in which trained, enthusiastic artists will lead and touch more deeply in molding clay into lasting beauty. I believe that I can not, undervaluing Della Robbia in glory and his only real encouragement and inspiration, to bring them out. If we can not do this work ourselves, if we have not the hand trained to the single touch, if we have not the eye to see the highest beauty in that crude material, if we cannot materialize the hidden beauty ourselves, if we have not the brain nor the training required to bring out of beauty

and fix it lastingly, for the good of mankind, we can still so arrange things that the tools are here for the good of others, so the way shall be open, all the material provided, building and instructors ready, the opportunity shall be afforded those coming after us to use facilities we did not have and, lacking these, we came to know their value.

There is a wide field of experimentation that really cannot be done elsewhere than in a school such as this. Individuals have not the time to devote to it. It is broadly in the line of the advancement of the science, requires much time and careful attention, and would never be worked out except in such a school and by students who were building themselves up in the working out of just such problems. Instance of this is the formula for crystalline glaze given the American Ceramic Society and the eighteen hundred experiments made in this school with it in which very much of interest was added that never would have been worked out except under these conditions.

The manufacturers of Germany demonstrated their belief as to the value of such research and, utilizing it in every available form, they went conquering the world. They were indeed far on their way in such conquest up to the time that the war lords fell out and so stopped their work and dragged them back to the old, old aboriginal manifestation of brute force and the lust for blood. Had they but kept to their work, utilizing scientific research in their manufacture as they had been doing, their conquest of the world would seem to have been assured, but the war lords decided otherwise and chose the way of blood.

This gathering here to-day is not just an accident, not something that happened without cause or reason. This gathering itself is a complete demonstration of the pressing importance and insistence of the subject of which I am speaking. You are gathered here to-day because of the persistent demand of the manufacturers for more ceramic research. They have not only clamored for it, they have worked for it, earnestly and self-denyingly. They have labored personally and collectively. This department of ceramic engineering came into being because of their demands and their effort. They labored with the University authorities; they worked with every succeeding Legislative Assembly; they begged appropriations, and then, rallying the clay workers throughout the State, demanded appropriations, and they got appropriations. All this labor and effort has crystallized and materialized in tangible form in this building we here dedicate to-day to the furtherance of our Art, for the good of those who are to come after us and who will, we know, surpass us. We dedicate that they may not lack the facilities that we lacked, that they may grow to do the things that we could not do. We dedicate in reverence and hope as our best contribution to the progress and good of the work we love.

I have treated my subject in a wandering fashion, possibly in a wandering fashion, for the reason that the need of the manufacturers for ceramic research is, and always has been, so great, so well known, so constant and insistent as to be self-evident and needing no demonstration. This dependence has existed from the earliest times, the want has always been felt. What was needed was a proper opportunity for research. A place was needed and tools and then education in using the tools. Men must be educated to becoming skilled in knowing how to use material and tool. Must be so trained that when reactions occur they must know why they occur and work intelligently to the desired end, and not blindly, as in the past. The quest has been much of the time blindly, gropingly, in the dark, but now is coming to be openly, understandingly, and in broad daylight. State universities like this, and buildings and appliances like these, are the tools which shall furnish the opportunities and appliances, for the training of the brains to mix with the clays that will then place our Art where it belongs, and our pioneer work shall not have been in vain.

I may only add that the men on this board who have really

done the most in the pioneer labor to bring this work to fruition are so modest and diffident and fearful of receiving the praise they so well merit for their efforts that they are sitting very tight, keeping very quiet and, following usage from time immemorial, are now putting forward that member of the board who probably did the very least in the real past work to now do the talking.

CHICAGO, ILLINOIS

DISCUSSION

By L. E. BARRINGER

President American Ceramic Society
Engineer of Insulations, General Electric Company

I prefer not to launch into the troubles of the electrical engineer, as I am afraid that would take a great deal of time because it is true that a large part of the electrical engineer's troubles to-day may be attributed to insulation and frequently to ceramic insulation. There are many forms of electrical insulation but true ceramic insulation forms a large part of the material used. I should like to tell you something about these electrical insulation problems but would prefer at this time to discuss the general aspects of ceramic research work as covered by the paper which has just been read.

In the first place, there is one point in Mr. Gates' paper to which I wish to take exception, and that is his last statement that the man who had done the least had now been put forward to do the talking. Mr. Purdy and I did not know whether he referred to us or to himself, but assuming that Mr. Gates referred to himself, in his modest way, I want to say that eighteen years ago, in his factory at Terra Cotta, Illinois, I was given the privilege of going into that factory and working during my summer vacation. I was then in the first engineering class in ceramics in Ohio State University and was given the opportunity of working in that factory, from the plaster shop to the decorating room, and of learning all that I could pick up in this way. While there I found that Mr. Gates had employed one of the first short-course students from Ohio State University and that he had set this young man experimenting upon all sorts of problems in colors and shapes of pottery, new kinds, unknown kinds, trying to develop something new and more beautiful, so I wish to say that in my opinion Mr. W. D. Gates is one of the pioneers in present day ceramic research. He had one of the very first laboratories, if I am not mistaken, and while Mr. Gates' motives may have been partly philanthropic (as he was always ready to encourage ceramic education and ceramic research), I suspect he had placed some dependence upon ceramic research for something that he really desired to obtain and that, therefore, he is a good example to put before you of the manufacturer's dependence upon ceramic research. Mr. Gates wanted something and he tried to get it by putting a technically trained man at work upon the necessary research.

Ceramic research is not different, or at least fundamentally different, from any other research. There is nothing to differentiate it in a general way. It requires the same sort of preparation and endeavor and the same attitude of mind but it is different in this respect—that it has taken longer to assume its proper place in the world's work. Personally, I think that this is largely because we have been handicapped by tradition. Ceramic industry is as old as the hills and from the ages past, we have record of the Chinese and Japanese potters producing most beautiful ceramic objects that are very rarely equalled, or excelled, to-day. We know that these old Chinese and Japanese potters worked by passing the secrets along from father to son. It was their greatest pride to discover something new and beautiful and then to have that live in the family as an heirloom, to be passed down to coming generations. That was the standard practice in China and Japan. Unfortunately the Germans, when they learned the secret of making pottery, particularly

porcelain, in imitation of the wares from the Orient, followed the same course and produced the wares in secret, nay, even with royal approval and protection in maintaining such secrecy.

I think that ceramic research has been largely handicapped by this tradition, a tradition which is now fast being broken down and dispersed. Other industries have, I might say, been born in a new era, as the electrical industry, and have not been subject to this old traditional habit of passing these discoveries on from father to son.

I was looking around the other day for a definition of research and I ran across this statement in the Encyclopedia Britannica: "Without research no authoritative works have been written, no scientific discoveries made, no theory of any value propounded." That is a very broad statement, but I think, after due consideration, it will be admitted that it is generally correct. When I read that, I tried to think of discoveries which might be termed "accidental." We hear of "accidental discoveries" but in nearly every case I could think of I knew that the discovery had been made simply as a side issue or as a by-product of research in some other line, but that it was almost invariably the result of something some man had found or observed in the course of research work started for some particular purpose. As a matter of fact, the most skilled research men closely watch every development, not only to attain what they seek as the ultimate result, but to avoid missing anything by the way, something perhaps that may be useful, or new or valuable.

In this connection I recall Mr. E. G. Acheson having told me of his discovery of carborundum. While he was experimenting in electric furnace work in the Edison laboratories he observed in his arc furnace a few tiny iridescent crystals, crystals so small and so few in number that I dare say they would undoubtedly have escaped the attention of most investigators. He immediately focused his attention upon this tiny crystal and separated it from the other material, and in his interest tested the hardness by scratching a diamond in his ring and thus the discovery of carborundum, a hard abrasive of which he realized the value immediately. That might be termed accidental "discovery," but yet it was made by a research man endeavoring to find something, but with his eyes wide open so as to make sure of missing nothing while trying to find something, and to my mind such discoveries are legitimately the product of research.

The country was never in greater need of research than at the present time, and particularly "organized research" where groups of investigators are working shoulder to shoulder to advance some particular field of knowledge. The great industries have recognized the value of research and particularly the value of organized research, as is evidenced by the research activities of the General Electric Company, the Westinghouse Company, the National Carbon Company, the Pittsburgh Plate Glass Company, the Norton Company and others I might mention. Then there are the groups in the colleges and the United States Government service. As an example of organized research I would say that I represent a company that employs over a hundred men engaged in research work, a company which has invested heavily and has invested because it pays, and not only pays, but the progress of the electrical industry is absolutely dependent upon systematic research and effort to advance. One of the best examples is electric lighting which has progressed from a humble in the last ten years. The old carbon filament was quite common, used ten years ago. Since then it has rapidly gone through the stages of metallized filaments, pressed tungsten filaments, drawn tungsten filaments, and gas-filled lamps (nitrogen, etc.) all this has resulted from the determined effort of the General Electric Co. and its research men to advance that particular field, which they have accomplished in a tremendously systematic way. We have lighting today at a cost of one-third of what

as a few years ago, giving three times as much light at the same cost as in those days.

I do not believe, then, that there need be any very strenuous argument as to the value of research to the manufacturer.

As another example I would say that Mr. M. T. Herrick, in addressing the American Ceramic Society at its annual meeting last February, spoke of early research work by the National Carbon Co., with which he is closely identified, and stated that when that company was first formed it had great difficulty in producing electrode brushes and other forms of molded carbon to compete in quality and in price with the European articles. There was no high protective tariff available and it became necessary that his company either compete successfully or go to the wall. Representatives were sent to Europe to study methods. They traveled from factory to factory but very rarely were given the real secrets of the success of these European factories, and the representatives of the National Carbon Company came back empty-handed with this exception—that they had observed that there was one thing that every European factory had in common and that was a laboratory. Quite blindly, Mr. Herrick stated, the National Carbon Company put up a laboratory. Then they hired a man from the Massachusetts Institute of Technology and within a year he had introduced two or three valuable features. This is another example of the absolute dependence of the manufacturer upon research, and not only in this country but the world over. The Germans have been pioneers in the line of industrial research.

A few years ago we were called upon to develop porcelain bushings for high-voltage transformers. As you all know, very much greater voltages are being transmitted to-day over high-tension lines than a few years ago. Transformers had to be built for these higher voltage and where five or six years ago a transformer of 60,000 volts was considered large, the development rapidly made necessary transformers to be tested at 300,000 volts or more, and insulation had to be devised accordingly. We had been building comparatively small porcelain bushings to stand 50,000 to 70,000 volts and when it became necessary to go 300,000 we naturally thought the porcelain ought to be larger and thicker, so that we were soon making porcelain bushings five or six feet high. These large pieces proved very difficult to manufacture successfully and even when constructed did not entirely give the desired results. The interested electrical engineers studied the problem and after several months investigation found that the trouble was not in the porcelain but in the distribution of potential over the bushings and so it was the potential had piled up at certain points to such a degree as to be able to break the surface of the porcelain of almost any size or thickness. By devising the proper design and proper voltage distribution appliances the voltage was so distributed that instead of making bushings five or six feet high and consequently thick, we were actually able to reduce the size very considerably.

Now in this same development our next problem was to develop the leading insulator quickly. I want to say in connection with this problem that it is always that research is not sufficient by the company engaged in it, but it must be the company engaged in it. I think at the end that it had been to do with some of the most important and with some of the most important, and I think that the research men, with their knowledge and their experience, had seen the problem and had seen the solution and had seen the solution and that problem was solved. After the research men had provided the proper method of solution. That was the research men's problem, but the company had to say that it was solved, it was solved, it was solved.

I have stated that this is a company in which the research men are the research men, and the research men are the research men.

upon the other side of the balance he is entitled to a just return for his investment and to insure that just return the research engineer or the research chemist must be broad enough and big enough to recognize all phases of the subject and to carry along his work accordingly.

I think one of our commonest perils in research work is to get too close to the problem. It is a good thing, I think, to get away from one's work occasionally, to back off from the picture as the artist does, in order to acquire a perspective, to see it differently and then return better equipped and with a better understanding of the work as a whole.

It is this kind of research that the manufacturer expects. I hope then that the research work which this new Ceramic department undertakes will be of such a character as will have a vision of the whole field, and that in teaching ceramics to the undergraduates the point will be emphasized as to the value of organized research, group research, and of the great value of cooperative effort and of always maintaining proper vision and perspective. When it is shown that the manufacturer is dependent upon research, this places a responsibility upon the research engineers which they must prepare to meet successfully.

SCHENECTADY, NEW YORK

DISCUSSION

By C. H. KERR

Director Research Laboratory, Pittsburgh Plate Glass Company

That the practical status of any industry cannot proceed in development without the growth of the fundamental scientific facts upon which that industry is based must be evident to any well-informed man, be he scientist or layman. Or as Dr. Clarke, of the United States Geological Survey, has aptly stated it, "There can be no applied science until there is a science to apply."

To the glass and enamel divisions of the ceramic industry this thought is especially applicable—in fact, it should be written in italics and kept constantly before the minds of those men who in their respective positions are instrumental in regulating the course of new developments in the industry.

An extended discussion of the problem of surface tension as it relates to glasses took place in one of our courts not long ago and the nature of that discussion illustrates as well as anything could illustrate it, the great lack of scientific knowledge and to an even greater extent the real need of such knowledge in the industry.

Let us acknowledge at once that in the field of glasses, enamels and other similar fused silicates the present state of development of chemical and physical science does not permit us to presuppose an ability to arrive at a completely satisfactory scientific solution of most of our problems. The extent of our knowledge concerning the laws governing systems with as many components as usually are present in the silicates with which we are concerned, is decidedly limited and developing but slowly. But, let us at the same time emphasize very strongly these two things: (1) that there are many incidental problems in connection with each branch of the industry that are capable of easy and complete solution and these problems can be taken care of while the main work is in progress and in all cases it is safe to assume that the solution of these problems alone will more than repay the employer for all laboratory expenditures; (2) that in studying the main problems of reactions in the silicate melts of many components it will always be found to be true that while answers which are complete from a scientific point of view are rarely possible, still as the study progresses there are constantly occurring ideas based on reasoning along lines of analogy which are susceptible of adaptation to practice. In the actual operation of the laboratory it will always be found that where

a worker would (or certainly should!) hesitate to offer a complete solution to any certain problem he will have ideas based on essentially sound data that extend beyond the range of present-day experimentation possibilities, but which nevertheless offer the best and safest foundations upon which to proceed with practical development work.

To name some of the unsolved problems in the glass industry is to show in the most conclusive possible manner the necessity of much greater development in the fund of scientific data and the manufacturers' dependence upon research. To name approximately all of the problems which present themselves to-day in an important bearing would exhaust the time of this meeting to the exclusion of everything else, but to name a few such problems will illustrate the present state of comparative ignorance in which the industry is struggling. Much work has been done within the past decade but it represents a mere beginning which is not more than an introduction to the real work which must inevitably follow.

What is seed or bubble in glass? This defect in glass is one that is common to all kinds of ware and one that causes enormous losses either directly in the manufacturing losses, or indirectly in the loss of business because of superior quality met with in competition. The defect is known under a variety of names, seed, blister, boil, bubble, etc., but practically nothing is known about it except its existence. Many assumptions as to the nature of this defect have been made, most of them based upon reasoning that proceeds from a highly questionable chemical reaction which looks well when written on paper, but nothing is known about the origin of the bubble, the nature of the material, if any, filling the void in the glass, or the conditions necessary to prevent its formation or accelerate its liberation.

Concerning the color of glass (meaning the great mass of commercial glasses which are supposed to be substantially colorless) there has been considerable investigation but the subject is still in a very unsatisfactory state. *What is the real nature of the coloring effect or iron impurities and how can it be controlled? When once standardized in control how can variations in purity of the raw materials be properly provided for? If neutralizing or decolorizing agents are required what is the best theory of overcoming the residual color effect of the original glass and how can this be applied?*

One great source of industrial loss is breakage traceable directly or indirectly to the annealing process. *What are the relations existing between the composition of the glass and its required annealing treatment? And the converse of the problem may be equally important—what is the correct annealing treatment as applied to the particular glass composition concerned?* Another question along the same line is of perhaps greater immediate importance—*what are the relations between certain common impurities in the glass and the necessary corresponding changes in annealing treatment?*

Another very large problem or field of problems lies in the relation existing between the glass and the containing pot or tank. *What defects are introduced from this source and how may the composition of the glass or of the containing vessel be altered to produce beneficial effects, or how may the process of manufacture be changed to avoid the resulting troubles?*

This list of problems might be added to indefinitely but it must be evident from even this small list that the fundamental problems of the glass and allied industries are far from a basis of satisfactory solution. Mechanically the glass industry has developed wonderfully, even magically, within the past quarter century and especially within the past decade. Chemically, the glass industry has stood still. There must be an awakening and a real development and the dedication of this building to-day is a very significant fact in this awakening. An industrial awakening is always of necessity a slow and tortuous process,

but when the awakening once starts, its progress while often erratic must be in the right direction. The whole field of development in glass technology is before us and the future will undoubtedly bring forth progress resulting from scientific application that will certainly be more startling than the wonderful progress we have already seen as a result of mechanical developments.

Even this brief review of the status of the technology of the industry and the manufacturers' dependence upon ceramic research would be incomplete without reference to the pioneer

work of the famous German glass firm at Jena. If any manufacturer doubts the dependence of developments in glassmaking upon scientific data, let him refer to the growth of the firm of Carl Zeiss in Jena where the development of manufacturing has gone hand-in-hand with the development of the scientific facts upon which the manufacturing is based. There is no more complete answer now available than this marvellous development. It is but typical of what the future must bring forth.

PITTSBURGH, PENNSYLVANIA

CURRENT INDUSTRIAL NEWS

FRENCH DYESTUFFS SYNDICATE

The Paris correspondent of the *Morning Post*, London, states that some interest is being taken in financial circles in the announcement that a French national dyestuffs syndicate is to be formed with a capital of \$8,000,000 to act in conjunction with the British Dyes, Ltd. The shares will probably be issued at the end of November and the Banque de Paris et des Pays Bas will be at the head of the issue. An agreement, it is understood, is also about to be reached—if it has not already been reached—by leading producers of aluminum in France and a strong organization is to be formed for the development and control of aluminum there.—A. McMILLAN.

SOUTH AFRICAN MINERAL PRODUCTION

The total value of the mineral output of the Union of South Africa for 1915 was \$216,948,843, as compared with \$217,757,875 in 1914. The production of the various minerals was as follows:

	Tons		Value	
	1914	1915	1914	1915
Copper.....	29,326	28,970	\$3,283,304	\$5,003,107
Tin.....	3,429	3,441	1,494,676	1,190,816
Asbestos.....	1,191	2,138	96,417	172,275
Graphite.....	34	41	4,616	6,579
Magnesite.....	572	627	6,964	7,526
Lead.....	136	180	6,700	8,812
Zinc.....		352		10,627
Salts (including by-products)	40,290	45,104	324,710	394,037
Lime.....	66,095	68,989	523,396	530,688

No new discoveries of new minerals of any importance were made in South Africa in 1915. Small quantities of nickel, mica, iron pyrites, kaolin and talc were produced during the year.—M.

NICKEL PRODUCTION IN CANADA

The total production of matte in 1915 was 67,703 tons, containing 39,216,165 lbs. copper and 68,077,823 lbs. nickel valued by the producers at \$10,352,344. The tonnage of ore smelted (part being previously roasted) was 1,272,283. The production in 1914 was 46,396 tons of matte containing 28,895,824 lbs. copper and 45,517,937 lbs. nickel, valued at \$7,189,031. The reported recovery of nickel from the ores of the cobalt district was 55,324 lbs. of the metal and 200,032 lbs. of nickel oxide. The recovery in 1914 was 392,512 lbs. of nickel oxide. The exports of nickel are reported by the customs department as 66,410,400 lbs., valued at \$7,394,446.—M.

SMOKELESS COMBUSTION AND BY-PRODUCT RECOVERY

According to the *Iron and Coal Trade Review*, Mr. C. Wilkinson, Harrogate, England, has designed and patented a new type of boiler with the object of eliminating the smoke nuisance and furnishing by-products that, otherwise, would be discarded. It is claimed to have the following characteristics: (1) The coal is distilled, tar and ammonia liquor being extracted as by-products; (2) the coke obtained from the coal, while in incandescent gravitates into the furnace and is there consumed without

smoke; (3) the gas after being denuded of by-products is also passed into the furnace under considerable pressure with the necessary air and burns with a smokeless flame until it enters the retort flue, where it is transformed into radiant heat. This radiant heat is absorbed partly by the retort and partly by the water in the boiler. Thus, very active steaming surfaces are produced, not only in the furnace, but upon the whole flue-surface. On an average the inventor expects to get from 20 to 25 lbs. evaporation per sq. ft. of heating surface. The boiler is automatically fed with the coal which passes automatically through the various stages of distillation and combustion.—M.

DEHYDRATION OF TAR

The distillation of tar being now organized in France in accordance with an order prescribing its delivery to the distillers with not more than 4 per cent water, M. Mallet has published some recommendations to gas makers. These were drawn up at the suggestion of the Société Technique and appear in the *Journal des Usines à Gas* (October 20). He remarks that, some 14 yrs. ago, at Marseilles, tar was dehydrated in a Hignette centrifugal plant by which water was reduced to 1 per cent with a production of 6 1/4 tons per day. This is the most perfect process but is not within the power of every works—decantation methods depending on difference of density being, in many instances, alone possible. In adopting this method, it is pointed out that hot tar containing free carbon, if cooled in the presence of water, absorbs a considerable quantity of the latter in the form of an emulsion and causes difficulties in the subsequent separation. Thus, as far as possible, supernatant liquid should be separated at the outlet of the hydraulic main and run off by a separate system of pipes from that along which the tar passes and thereby cools. Tar pumped from tanks may be conveyed into a raised receptacle of capacity considerably higher than the railway tank and provided with a steam coil in its base by which tar is heated to 100 or 120° F. In this case, as the heating will produce a satisfactory result at required dehydration. In filling the railway tank from the intermediate receptacle, at least a 3 ft. depth of tar should remain in the latter after discharging. The pipe delivering the tar should lead down to the floor of the receptacle in order to avoid the emulsification of the tar in its passage with supernatant water, which latter should be returned to the main tanks by an overflow.—M.

FIRE PROTECTION ON SHIPS

In July 1905 a report, L22 (1905), on the British Fire Prevention Committee named Red Book No. 101, dealing with the essential question of fire protection for passenger ships. Having special regard to the fact that much shipbuilding work is under consideration with a view to packing up the wreckage of the war, the committee has now issued Red Book No. 102, implementing the earlier one and dealing with "constructed fire ships and passenger ships." The new publication may be said to deal with the construction of passenger ships from the fire point of view, with the specific intention of advising

subdivision of passenger ships and use of fire-resisting material, so that a fire at any given point may be more readily limited to a small area, much as water-tight compartments exist for limiting the area of submersion. The new book comprises a chapter on fire compartments and one on fire-resisting materials and also some useful appendices, one of which deals with certain features of the Board of Trade report on bulkheads, and another on charcoal as an insulating material on board ship. Both books taken together may be said to cover the whole field of fire protection for passenger ships both from the shipbuilding and equipment aspects, and the question of administration.—M.

SYNTHETIC RUBBER

The *Pall Mall Gazette*, London (October 9), learns from a well-informed source that the most recent synthetic rubber is of little or no practical value. A prominent Swiss chemist who has been in Germany recently states that authorities there attach no importance whatever to the production which is still in the experimental stage and extremely expensive. The relative durability of the latest synthetic rubber still remains to be proved and it is generally conceded that, after the war, the natural product will hold its own with ease.—M.

MACHINE TOOLS IN JAPAN

It is only within the last 10 yrs., says the *Times Engineering Supplement*, quoting from a contemporary, that Japan has taken up the manufacture of machine tools seriously, and little progress was made until about 4 yrs. ago, when the government decided that it was time to encourage domestic manufactures with the object of checking the flow of specie abroad and of rendering the markets less dependent on foreign supplies. Large works containing, roughly, 1,000 engine lathes, 300 capstan lathes and 150 drilling machines were recently completed within 3 mos. of the first orders being given out, over 90 per cent of the machines being made in Japan. In regard to methods of manufacture, jigs and fixtures are not used to any great extent and as most of the works will accept any order that comes their way within their capacity, there is little opportunity for specialization.—M.

POSITION OF TIN

According to an article in the *Cornish Post*, quoted in *Mining World*, 90 (1916), 468, the position of tin is somewhat interesting at present: 50 per cent of the world's production of tin (say 60,000 out of a total of 120,000 tons) is consumed by the United States. The Welsh tin plate industry is said to be 50 per cent smaller, owing to the war. France and England are restricted in their use of tin for commercial purposes and America makes more than 60 per cent of the world's tin plates. It is evident that, whereas there may be a slump in the price of mining commodities after the war, a declaration of peace would be followed by a substantial rise in the price of tin. Even during the interim there may be an advance in price of \$50 to \$100 per ton, or there may be a similar falling back owing to market operations. At present prices, it seems that the world can get all the tin it needs. The general position seems to be fairly cheerful for Cornish mines if properties like Dolcoath, Crofty, East Pool, Grenville, Tincroft and others can return good quantities of tin at not too exorbitant a price, owing to scarcity of labor, cost of coal, explosives and other materials.—M.

NATURAL DYE FROM PORTO RICO

The British Vice-Consul at Mayaguez, says *Chemical Trade Journal*, 59 (1916), 420, has forwarded to London a sample of a native root known as "sweet ginger (*gengibrillo*)," from which seemingly a dye can be extracted. "*Gengibrillo*" is the root of a plant which grows wild in the mountainous parts of Porto

Rico, especially in damp places and along the banks of small rivers and streams. No accurate data seems to be given as to the quantity in which the root is obtainable but the British Consul thinks that a fair estimate of the production of the Mayaguez district would be 50 tons per yr. The price at which the product is being bought at Mayaguez from the farmer is \$1 per 100 lbs. in the raw state. The root, which contains 75 per cent moisture, is prepared for shipment by slicing into very fine pieces and then exposing to the sun for drying, during which operation it shrinks considerably.—M.

SIBERIAN METALLURGY

According to a report in *Engineering*, 102 (1916), 436, new iron and steel plants seem to be in contemplation in Siberia. A meeting was recently held between representatives of the Russian government and the Russian iron trade and it was decided to raise a capital of \$10,300,000, the interest to be guaranteed. The government is to lease for a term of 40 yrs. the district of Kusnezsk where the proposed works are to be situated and the company is to supply a fixed tonnage of rails and other railway material annually. The district has coal and iron deposits estimated at a total of over 26,000,000 tons and the ore yields from 58 to 65 per cent iron.—M.

CEMENT INDUSTRY IN JAPAN

The cement industry in Japan which seems to have been at a low ebb for a long time after 1911, owing to the reduced demand and increased output, experienced a marked improvement last year, which has developed during 1916. According to a London contemporary, the present price is about double that ruling at the beginning of the year, as a result of the great activity of the export market and the increased domestic demand. Exports have gone up steadily from 67,651 bbls., worth \$163,500 in 1911 to 668,613 bbls. worth \$1,229,000 last year. It is expected that the current year's exports will be about 1,000,000 bbls. Stocks of European cement in oriental markets have been exhausted. There are 16 cement companies in Japan and 20 factories.—M.

MINERALS IN PANAMA

There is evidence, says *Mining World*, 91 (1916), 492, of the existence of coal, copper, gold, iron, petroleum and salt in Panama, but, beyond gold, none of these minerals are at present worked. Coal mines and petroleum wells exist in the districts of Macaracas and Tonosi in the Province of Los Santos. Practically all the gold exported comes from the Darien gold mines which are in the Province of Panama. Nearly all the streams of the country bear evidence of gold but the difficulties in the way of practical working seem to be insurmountable; 6,807 oz. fine gold valued at about \$144,475 and 118,435 oz. silver valued at \$74,745 were produced in the course of a single year.—M.

EFFECT OF ACID ON ALUMINUM

At the opening meeting of the Chemical Society, London, a series of strips of an aluminum alloy were exhibited, demonstrating the effect of traces of water in inhibiting the action of organic acids in particular upon the metal. It was shown that, whereas 99.9 per cent acetic acid had a solution rate of 4 mg., the removal of the last traces of water to form the anhydrous acid raises the solution rate to over 200 mg. Other strips of similar alloys illustrated the local action of acids under certain conditions of temperature and concentration, the factors determining whether pitting takes place or not. This exhibit forms part of an extensive research on the subject being carried out by Messrs. Seligman and Williams.—M.

SCIENTIFIC SOCIETIES

COAL ANALYSIS

FINAL REPORT OF THE JOINT COMMITTEE OF THE AMERICAN SOCIETY FOR TESTING MATERIALS AND THE AMERICAN CHEMICAL SOCIETY

The *Joint Committee on Coal Analysis*, which has been at work on the subject since the fall of 1911, consists of the following members: W. A. Noyes, *Chairman*; Perry Barker, H. C. Dickinson, A. C. Fieldner, Frank Haas, W. F. Hillebrand, S. W. Parr, S. S. Voorhees, A. H. White.

The work of the joint committee has been carried on chiefly through the agency of the following sub-committees:

I—Preparation of Laboratory samples including loss of moisture in sampling: Fieldner, *Chairman*; Haas, Hillebrand, Voorhees, Parr and Barker.

II—Moisture: Hillebrand, *Chairman*; Fieldner, Parr.

III—Deterioration: Parr, *Chairman*; Fieldner, Haas, Dickinson.

IV—Volatile Matter: Parr, *Chairman*; Fieldner, Haas, Dickinson.

V—Fixed Carbon and Ash: Parr, *Chairman*; Fieldner, Hillebrand.

VI—Sulfur: Barker, *Chairman*; Voorhees, Dickinson.

VII—Phosphorus: Hillebrand.

VIII—Ultimate Analysis: Fieldner, *Chairman*; Parr, White.

IX—Calorimetric Determination: Dickinson, *Chairman*; Haas, Barker.

Three preliminary reports have been published, one in *THIS JOURNAL*, 5 (1913), 517; a second as the Report for 1914 of Committee E-4 in Vol. XIV of the Proceedings of the American Society for Testing Materials; the third as the tentative final report in 1915. The present report is the same as the report submitted in 1915 with the exception of a few verbal changes. The report has been accepted by letter ballot as the official, final report of the American Society for Testing Materials and is recommended for the use of chemists and as a basis for specifications to be used in the purchase of the coal. (Many details given in the preliminary reports are not repeated here.)

The report has been unanimously approved by the members of the committee and has been approved by the Supervisory Committee on Standard Methods of Analysis of the American Chemical Society.

Respectfully submitted on behalf of the joint committee,

W. A. NOYES, *Chairman*

PREPARATION OF LABORATORY SAMPLES

APPARATUS

Air-Drying Oven—The oven is to be used for air-drying wet samples and may be of the form shown in Fig. I. This is not absolutely necessary but is economical where many wet samples are received.¹

Galvanized-Iron Pans 18 by 18 by 1½ in. Deep for air-drying wet samples.

Balance or Solution Scale for weighing the galvanized-iron pans with samples. It should have a capacity of 5 kg. and be sensitive to 0.5 g.

Jaw Crusher for crushing coarse samples to pass a 4-mesh sieve.

Roll Crusher or Coffee-Mill Type of Grinder for reducing the 4-mesh product to 20-mesh. The coffee-mill type of grinder should be entirely enclosed and have an enclosed hopper and a

receptacle capable of holding 10 lbs. of coal. This is to reduce the moisture losses while crushing.

Abbé Ball Mill, Planetary Disk Crusher, Chrome-Steel Bucking Board, or any Satisfactory Form of Pulverizer for reducing the

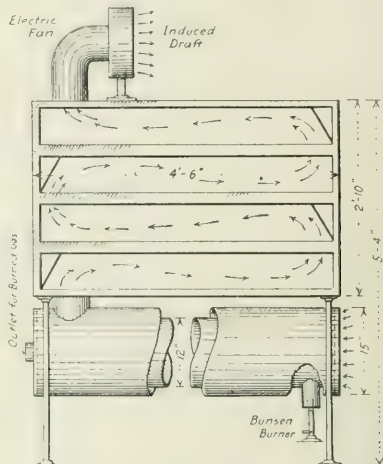


FIG. I—DRIER FOR COARSE SAMPLES

The outlet for air at the top may be connected with a chimney or any other device which will furnish a suitable draft. (*Bulletin No. 9, Geological Survey of Ohio, p. 312*)

20-mesh product to 60-mesh. The porcelain jars for the ball mill should be approximately 9 in. in diameter and 10 in. high. The flint pebbles should be smooth, hard and well rounded.

A Large Riffle Sampler, with 1½- or 5/8- in. Divisions for reducing the 4-mesh sample to 10 lbs. (Fig. II).¹

A Small Riffle Sampler, with 1/4 or 3/8 in. Divisions for dividing down the 20- and 60-mesh material to a laboratory sample (Fig. II).

An 8-in. 60-mesh Sieve with Cover and Receiver.

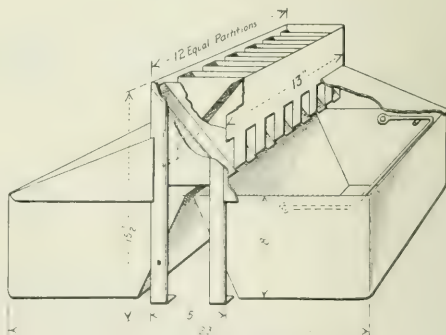


FIG. II—RIFLE SAMPLER

(*Bulletin No. 9, Geological Survey of Ohio, p. 313*)

Containers for Shipment to Laboratory—Samples in which the moisture content is important should always be shipped in moisture-tight containers. A galvanized-iron or tin can with a

¹ E. E. Somermeier, "Coal, Its Composition, Etc.," McGraw-Hill Book Co. (1912).

¹ For details of air-drying oven see Bownocker, Lord and Somermeier, "Coal," *Bull.* 9, 4th Series, Ohio Geological Survey, p. 312 (1908); or F. M. Stanton and A. C. Fieldner, "Methods of Analyzing Coal and Coke," *Technical Paper No. 8*, Bureau of Mines, p. 4 (1912); or E. E. Somermeier, "Coal, Its Composition, Analysis, Utilization and Valuation," p. 71, McGraw-Hill Book Co. (1912).

screw top which is sealed with a rubber gasket and adhesive tape is best adapted to this purpose. Glass fruit jars sealed with rubber gaskets may be used, but require very careful packing to avoid breakage in transit. Samples in which the moisture content is of no importance need no special protection from loss of moisture.

METHOD OF SAMPLING

(A) *When Coal Appears Dry*—If the sample is coarser than 4-mesh (0.20 in.) and larger in amount than 10 lbs., quickly crush it with the jaw crusher to pass a 4-mesh sieve and reduce it on the larger riffle sampler to 10 lbs.;¹ then crush at once to 20-mesh by passing through rolls or an enclosed grinder, and take, without sieving, a 60-g. total moisture sample, immediately after the material has passed through the crushing apparatus. This sample should be taken with a spoon from various parts of the 20-mesh product, and should be placed directly in a rubber-stoppered bottle.

Thoroughly mix the main portion of the sample, reduce on the small riffle sampler to about 120 g., and pulverize to 60-mesh by any suitable apparatus without regard to loss of moisture. After all the material has been passed through the 60-mesh sieve, mix and divide it on the small riffle sampler to 60 g. Transfer the final sample to a 4-oz. rubber-stoppered

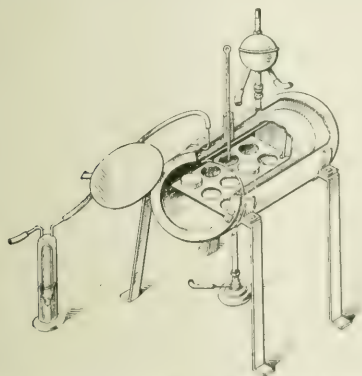


FIG. III.—TOLUENE OR GLYCERIN AND WATER OVEN FOR DETERMINING MOISTURE

(Technical Paper No. 76, Bureau of Mines, p. 16)

bottle. Determine moisture in both the 60- and the 20-mesh samples by the method given under moisture.

Computation—Compute the analysis of the 60-mesh coal, which has become partly air-dried during sampling, to the dry-coal basis, by dividing each result by 1 minus its content of moisture. Compute the analysis of the coal "as received" from the dry-coal analysis by multiplying by 1 minus the total moisture found in the 20-mesh sample.

(B) *When Coal Appears Wet*—Spread the sample on tared pans, weigh, and air-dry at room temperature, or in the special drying oven, shown in Fig. I, at 10 to 15° C. above room temperature, and weigh again. The drying should be continued until the loss in weight is not more than 0.1 per cent per hour. Complete the sampling as under dry coal.

Computation—Correct the moisture found in the 20-mesh, air-dried sample to total moisture "as received," as follows:

$$\frac{(100 - \% \text{ Air-drying Loss}) \times \% \text{ Moisture in 20-mesh Coal}}{100} = \% \text{ Air-drying Loss} \times \text{Total Moisture "as received"}$$

Compute the analysis to "dry-coal" and "as-received" bases as under dry coal, using for the "as-received" computation the

¹ If the sample is crushed to pass a 6-mesh screen it may be reduced to 5 lbs.

total moisture as found by the formula in place of the moisture found in the 20-mesh coal.

NOTES—Freshly mined or wet coal loses moisture rapidly on exposure to the air of the laboratory, hence the sampling operations between opening the container and taking the 20-mesh total-moisture sample must be conducted with the utmost dispatch and with minimum exposure to air.

The accuracy of the method of preparing laboratory samples should be checked frequently by resampling the rejected portions and preparing a duplicate sample. The ash in the two samples should not differ more than the following percentages.

	Per cent
No carbonates present.....	0.4
Considerable carbonate and pyrite present.....	0.7
Coals with more than 12 per cent ash, containing considerable carbonate and pyrite.....	1.0

DETERMINATION OF MOISTURE

APPARATUS

Moisture Oven—This must be so constructed as to have a uniform temperature in all parts and a minimum of air space. It may be of the form shown in Fig. III. Provision must be made for renewing the air in the oven at the rate of two to four times a minute, with the air dried by passing it through concentrated sulfuric acid.

Capsules with Covers—A convenient form, which allows the ash determination to be made on the same sample, is the Royal Meissen porcelain capsule No. 2, $\frac{7}{8}$ in. deep and $\frac{1}{2}$ in. diameter; or a fused silica capsule of similar shape. This is to be used with a well-fitting flat aluminum cover, illustrated in Fig. IV.

Glass capsules with ground-glass caps may also be used. They should be as shallow as possible, consistent with convenient handling.

METHOD

1.1 Sixty-Mesh Sample—Heat the empty capsules under the conditions at which the coal is to be dried, stopper or cover, cool over concentrated sulfuric acid (sp. gr. 1.84) for 30 minutes, and weigh. Dip out with a spoon or spatula from the sample bottle approximately 1 g. of coal; put this quickly into the capsule, close, and weigh at once.

An alternative procedure (more open to error), after transferring an amount slightly in excess of 1 g., is to bring to exactly 1 g. in weight (± 0.5 mg.) by quickly removing the excess weight of coal with a spatula. The utmost dispatch must be used in order to minimize the exposure of the coal until the weight is found.

After removing the covers, quickly place the capsules in a preheated oven at 100 to 110° C. through which passes a current of air dried by concentrated sulfuric acid. Close the oven at once and heat for 1 hour. Then open the oven, cover the capsules quickly and place them in a desiccator over concentrated sulfuric acid. When cool, weigh.

(B) *Twenty-Mesh Sample*—Weigh a 60-g. sample weighed with an accuracy of 2 mg. and heat for $1\frac{1}{2}$ hours. The procedure is otherwise the same as with the 60-mesh sample. Methods of greater accuracy for the determination of moisture are given in the preliminary report.

The precision attainable in ash analysis is summarized as follows:

	Same Analyst	Different Analysts
Moisture under 1 per cent.....	± 0.01 per cent	± 0.02 per cent
Moisture over 1 per cent.....	± 0.02 per cent	± 0.03 per cent

DETERMINATION OF ASH

APPARATUS

Crucible—Platinum. **Moisture Furnace**—This must be a good one, and should be used for the purpose of drying the temperature. Temperature should be 100 to 110° C.

Porcelain Capsules—Royal Meissen porcelain capsules No. 2 $\frac{7}{8}$ in. deep and $1\frac{1}{4}$ in. in diameter or similar shallow dishes.

METHOD

Place the porcelain capsules containing the dried coal from the moisture determination in a cold muffle furnace or on the hearth at a low temperature and gradually heat to redness at such a rate as to avoid mechanical loss from too rapid expulsion of volatile matter. Finish the ignition to constant weight (± 0.001 g.) at a temperature between 700 and 750° C. Cool in a desiccator and weigh as soon as cold.

The permissible differences in duplicate determinations are as follows:

	SAME ANALYST	DIFFERENT ANALYSTS
No carbonates present	0.2 per cent	0.3 per cent
Carbonates present	0.3 per cent	0.5 per cent
Coal with more than 12 per cent of ash, containing carbonates and pyrite	0.5 per cent	1.0 per cent

NOTES—Before replacing the capsules in the muffle for ignition to constant weight, the ash should be stirred with a platinum or nichrome wire. Stirring once or twice before the first weighing hastens complete ignition.

The result obtained by this method is "uncorrected" ash. For "corrected" ash see the preliminary report. The actual mineral matters in the original coal are usually very different in weight and composition from the weight of the "uncorrected" ash.

DETERMINATION OF VOLATILE MATTER

APPARATUS

Platinum Crucible with Tightly Fitting Cover—The crucible should be of not less than 10 nor more than 20 cc. capacity; of

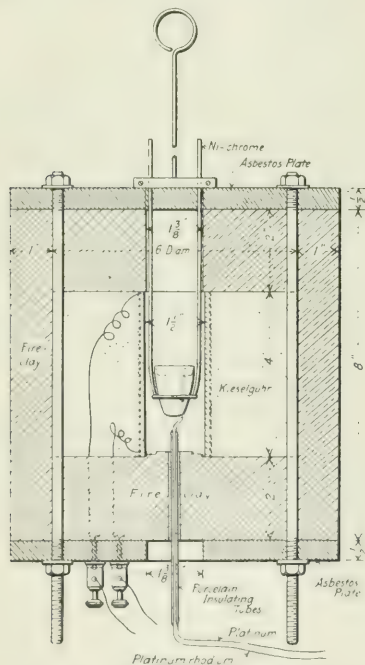


FIG. V.—ELECTRIC TUBE FURNACE FOR DETERMINING VOLATILE MATTER
For 110-volt alternating current, 60 ft. of nichrome wire, No. 17 B. & S. gauge, will give the required temperature. The temperature must be controlled by an external resistance.

(Technical Paper No. 76, Bureau of Mines, p. 21)

not less than 25 nor more than 35 mm. diameter; of not less than 30 nor more than 35 mm. height.

Vertical Electric Tube Furnace; or a Gas or Electrically Heated

Muffle Furnace—The furnace may be of the form shown in Fig. V. It is to be regulated to maintain a temperature of 950° C. ($\pm 20^\circ$ C.) in the crucible as shown by a thermocouple kept in the furnace. If the determination of volatile matter is not an essential feature of the specifications under which the coal is bought a Méker burner may be used.

METHOD

Weigh 1 g. of the coal in a weighed 10 to 20 cc. platinum crucible, close with a capsule cover and place on platinum or nichrome-wire supports in the furnace chamber, which must be kept at a temperature of 950° C. ($\pm 20^\circ$ C.). After the more rapid discharge of volatile matter has subsided, as shown by the disappearance of the luminous flame, tap the cover lightly to seal the crucible more perfectly and thus guard against the admission of air. After heating exactly 7 minutes remove the crucible from the furnace and without disturbing the cover allow it to cool. Weigh as soon as cold. The loss of weight minus moisture equals the volatile matter.

Modification for Sub-Bituminous Coal, Lignite and Peat—Mechanical losses are incurred on suddenly heating peat, sub-bituminous coal, and lignite; therefore they must be subjected to a preliminary gradual heating for 5 minutes; this is best done by playing the flame of a burner upon the bottom of the crucible, in such manner as to bring about the discharge of volatile matter, at a rate not sufficient to cause sparking. After the preliminary heating, transfer the crucible to the volatile-matter furnace and heat for 6 minutes at 950° C. as in the regular method.

The permissible differences in duplicate determinations are as follows:

	SAME ANALYST	DIFFERENT ANALYSTS
Bituminous coals	0.5 per cent	1.0 per cent
Lignites	1.0 per cent	2.0 per cent

NOTES—The cover should fit closely enough so that the carbon deposit from bituminous and lignite coals does not burn away from the under side. Regulation of temperature to within the prescribed limits is important.

DETERMINATION OF FIXED CARBON

Compute fixed carbon as follows:

$$100 - (\% \text{ Moisture} + \% \text{ Ash} + \% \text{ Volatile Matter}) = \text{Fixed Carbon}$$

DETERMINATION OF SULFUR BY THE ESCHKA METHOD

APPARATUS

Gas or Electric Muffle Furnace, or Burners for igniting coal with the Eschka mixture and for igniting the barium sulfate.

Porcelain, Silica, or Platinum Crucibles or Capsules for igniting coal with the Eschka mixture.

No. 1 Royal Meissen porcelain capsule, 1 in. deep and 2 in. in diameter. This capsule, because of its shallow form, presents more surface for oxidation and is more convenient to handle than the ordinary form of crucible.

No. 1 Royal Berlin porcelain crucibles, shallow form, and platinum crucible of similar size may be used. Somewhat more time is required to burn out the coal, owing to the deeper form, than with the shallow capsules described above.

No. 0 or 00 porcelain crucibles, or platinum, alundum or silica crucibles of similar size are to be used for igniting the barium sulfate.

SOLUTIONS AND REAGENTS

Barium Chloride—Dissolve 100 g. of barium chloride in 1000 cc. of distilled water.

Saturated Bromine Water—Add an excess of bromine to 1000 cc. of distilled water.

Eschka Mixture—Thoroughly mix 2 parts (by weight) of light calcined magnesium oxide and 1 part of anhydrous sodium carbonate. Both materials should be as free as possible from sulfur.

Methyl Orange—Dissolve 0.02 g. in 100 cc. of hot distilled water and filter.

Hydrochloric Acid—Mix 500 cc. of hydrochloric acid (sp. gr. 1.20) and 500 cc. of distilled water.

Normal Hydrochloric Acid—Dilute 80 cc. of hydrochloric acid (sp. gr. 1.20) to 1 liter with distilled water.

Sodium Carbonate—A saturated solution: approximately 60 g. of crystallized or 22 g. of anhydrous sodium carbonate in 100 cc. of distilled water.

Sodium-Hydroxide Solution—Dissolve 100 g. of sodium hydroxide in 1 liter of distilled water. This solution may be used in place of the sodium-carbonate solution.

METHOD

Preparation of Sample and Mixture—Thoroughly mix on glazed paper 1 g. of coal and 3 g. of Eschka mixture. Transfer to a No. 1 Royal Meissen porcelain capsule, 1 in. deep and 2 in. in diameter, or a No. 1 Royal Berlin crucible or a platinum crucible of similar size, and cover with about 1 g. of Eschka mixture.

Ignition—On account of the amount of sulfur contained in artificial gas, the crucible shall be heated over an alcohol, gasoline or natural gas flame as in procedure (a) below or in a gas or electrically heated muffle as in procedure (b) below. The use of artificial gas for heating the coal and Eschka mixture is permissible only when the crucible are heated in a muffle.

(a) Heat the crucible placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter, which tends to prevent complete absorption of the products of combustion of the sulfur. Heat the crucible slowly for 30 minutes, gradually increasing the temperature and stirring after all black particles have disappeared, which is an indication of the completeness of the procedure.

(b) Place the crucible in a cold muffle and gradually raise the temperature to 870–925° C. (cherry-red heat) in about 1 hour. Maintain the maximum temperature for about 1½ hours and then allow the crucible to cool in the muffle.

Subsequent Treatment—Remove and empty the contents into a 200 cc. beaker and digest with 100 cc. of hot water for ½ to ¾ hour, with occasional stirring. Filter and wash the insoluble matter by decantation. After several washings in this manner, transfer the insoluble matter to the filter and wash 5 times, keeping the mixture well agitated. Treat the filtrate, amounting to about 250 cc., with 10 to 20 cc. of saturated bromine water, make slightly acid with hydrochloric acid and boil to expel the liberated bromine. Make just neutral to methyl orange with sodium hydroxide or sodium carbonate solution, then add 1 cc. of normal HCl. Boil again and add slowly from a pipette, with constant stirring, 10 cc. of a 10 per cent solution of barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$). Continue boiling for 15 minutes and allow to stand for at least 2 hours, or preferably over night, at a temperature just below boiling. Filter through an ashless filter paper and wash with hot distilled water until a silver nitrate solution shows no precipitate with a drop of the filtrate. Place the wet filter containing the precipitate of barium sulfate in a weighed platinum, porcelain, silica or aluminum crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. Smoke the paper off gradually and at no time allow it to burn with flame. After the paper is practically consumed, raise the temperature to approximately 925° C. and heat to constant weight.

The residue of magnesia, etc. after leaching, should be dissolved in hydrochloric acid and tested with great care for sulfur. When an appreciable amount is found the residue should be determined quantitatively. The amount of sulfur retained is by assumption a negligible quantity.

Blanks and Correction—In all cases a correction must be applied either by running a blank exactly as described, placing the same amount of all reagents that were employed in the regular determination or more surely, as by determining a

known amount of sulfate added to a solution of the reagents after these have been put through the prescribed series of operations. If this latter procedure is adopted and carried out, say, once a week or whenever a new supply of a reagent must be used, and for a series of solutions covering the range of sulfur content likely to be met with in coals, it is only necessary to add to or subtract from the weight of barium sulfate obtained from a coal, whatever deficiency or excess may have been found in the appropriate "check" in order to obtain a result that is more certain to be correct than if a "blank" correction as determined by the former procedure is applied. This is due to the fact that the solubility error for barium sulfate, for the amounts of sulfur in question and the conditions of precipitation prescribed, is probably the largest one to be considered. Barium sulfate is soluble¹ in acids and even in pure water, and the solubility limit is reached almost immediately on contact with the solvent. Hence, in the event of using reagents of very superior quality or of exercising more than ordinary precautions, there may be no apparent "blank," because the solubility limit of the solution for barium sulfate has not been reached or at any rate not exceeded.

As shown in the preliminary report,² the Atkinson and sodium peroxide methods give results in close agreement with the Eschka method. Regester³ has shown that if 5 per cent of nitrogen is present in the gases contained in the bomb calorimeter the sulfur of a coal is almost completely oxidized to sulfuric acid and the washings of the calorimeter may be used for the determination of sulfur.

The permissible differences in duplicate determinations are as follows:

	NAME ANALYST	DIFFERENCE ANALYSES
Sulfur under 1 per cent	0.05 per cent	0.10 per cent
Sulfur over 1 per cent	0.10 per cent	0.20 per cent

DETERMINATION OF PHOSPHORUS IN ASH

METHOD 1 TO COVER ALL CASES

To the ash from 5 g. of coal in a platinum capsule are added 10 cc. of nitric acid and 3 to 5 cc. of hydrofluoric acid. The liquid is evaporated and the residue fused with 3 g. of sodium carbonate. If unburned carbon is present to a $\frac{1}{2}$ g. of sodium nitrate is mixed with the carbonate. The melt is leached with water and the solution filtered. The residue is ignited, fused with sodium carbonate alone, the melt leached and the solution filtered. The combined filtrates, held in a flask, are just acidified with nitric acid and concentrated to a volume of 100 cc. To the solution brought to a temperature of 85° C. is added 50 cc. of molybdate solution and the flask shaken for 15 minutes. If the precipitate does not form promptly and copiously, add enough ammonium nitrate to cause it to do so. The precipitate is washed six times, or until free from acid, with a 1 per cent solution of potassium nitrate, then returned to the flask and treated with saturated sodium hydroxide solution. The clear solution may well be made equal to a weight of 100 g. phosphorus, i.e., 100 g. per cent for a 1 g. sample of coal and 10 to 100 cc. of one with molybdate, by the phosphorus in the precipitate is determined by the color and titration of the molybdenum with potassium permanganate.

NOTE. The amount of 10 per cent potassium permanganate solution added to the molybdate solution must be such as to cause a slight excess of potassium permanganate to be present in the solution after the molybdate has been added. The amount of 10 per cent potassium permanganate solution added to the molybdate solution must be such as to cause a slight excess of potassium permanganate to be present in the solution after the molybdate has been added.

METHOD 2

(This method is not to be used in cases where the ash is determined by Method 1, but examination is started only in a case of about 1 g. of coal. The solution is started with water.)

1. The sample is 1 g. of coal, the ash is 1 g. of coal.

2. The sample is 1 g. of coal, the ash is 1 g. of coal.

3. The sample is 1 g. of coal, the ash is 1 g. of coal.

4. The sample is 1 g. of coal, the ash is 1 g. of coal.

¹ J. Am. Chem. Soc., 21, 1899, 1435.

to 30 cc., boiled and filtered. If the washings are turbid they are passed again through the filter. The residue is ignited in a platinum crucible, fused with a little sodium carbonate, the melt dissolved in nitric acid and its solution, if clear, added to the main one. If not clear it is filtered. The subsequent procedure is as under Method I. The fusion of the residue may be dispensed with in routine work on a given coal if it is certain that it is free from phosphorus.

ULTIMATE ANALYSIS

CARBON AND HYDROGEN

The determination of carbon and of hydrogen is made with a weighed quantity of sample in a 25-burner combustion furnace of the Glaser type. The products of combustion are thoroughly oxidized by being passed over red-hot copper oxide and lead chromate, and are fixed by absorbing the water in a weighed Marchand tube filled with granular calcium chloride (CaCl_2) and by absorbing the carbon dioxide in a Liebig bulb containing a 30 per cent solution of potassium hydroxide (KOH).

The apparatus used consists of a purifying train, in duplicate, a combustion tube in the furnace, and an absorption train. The purifying train consists of the following purifying reagents arranged in order of passage of air and oxygen through them: sulfuric acid, potassium hydroxide solution, soda lime, and granular calcium chloride. One of the trains is for air and one for oxygen. In the sulfuric acid and potassium hydroxide scrubbing bottles the air and the oxygen are made to bubble through about 5 mm. of the purifying reagent. Both purifying trains are connected to the combustion tube by a Y-tube, the joint being made tight by a rubber stopper.

The combustion tube is made of hard Jena glass. Its external diameter is about 21 mm., and its total length is 1 meter. The first 30 cm. of the tube are empty; following this empty space is an asbestos plug (acid-washed and ignited) or in its place a roll of oxidized copper gauze may be used; the next 40 cm. are filled with "wire" copper oxide; a second asbestos plug separates the copper oxide from 10 cm. of fused lead chromate, which is held in place by another asbestos plug 20 cm. from the end of the tube. The end of the tube is drawn out for rubber tubing connection with the absorption train.

The absorption train consists, first, of a Marchand tube filled with granular calcium chloride (CaCl_2) to absorb moisture. The CaCl_2 should be saturated with CO_2 before using. The Marchand tube is followed by a Liebig bulb containing a 30 per cent potassium hydroxide (KOH) solution, in which any possible impurities, as ferrous iron or nitrites, have been oxidized by a little potassium permanganate (KMnO_4). A guard tube, containing granular calcium chloride and soda lime, is attached to the Liebig bulb to absorb any carbon dioxide escaping the potassium hydroxide solution and any water evaporating from that solution.

The train is connected to an aspirator which draws the products of combustion through the entire train. A guard tube of calcium chloride prevents moisture from running back into the absorption train. The suction is maintained constant by a Mariotte flask. The advantage of aspirating the gases through the train rather than forcing them through by pressure is that the pressure on the rubber connections is from the outside, so that gas-tight connections are more easily maintained than if the pressure is on the inside of the tube. The connections are made as tight as possible. The usual test for tightness is to start aspiration at the rate of about three bubbles of air per second through the potash bulb, and then to close the inlet for air and oxygen at the opposite end of the train; if there is no more than one bubble per minute in the potash bulb, the apparatus is considered tight.

Before starting a determination when the train has been idle some hours, or after any changes in chemicals or connections, a blank is run by aspirating about 1 liter of air through the train,

which is heated in the same manner as if a determination on coal were being made. If the Liebig bulb and the tube containing calcium chloride show a change in weight of less than 0.5 mg. each, the apparatus is in proper condition for use.

A porcelain or platinum boat is provided with a glass weighing tube of suitable size, which is fitted with an accurately ground glass stopper. The tube and empty boat are weighed. Approximately 0.2 g. of the air-dry coal (60-mesh and finer, or better, 100-mesh if much free impurity is present) are quickly placed in the boat. The boat is at once placed in the weighing tube, which is quickly stoppered to prevent moisture change in the coal while weighing, and transferring to the furnace. The absorption tubes are connected and the boat and sample are transferred from the weighing tube to the combustion tube, which should be cool for the first 30 cm. The copper oxide should be red hot and the lead chromate at a dull-red heat. The transfer of the boat from weighing tube to combustion tube should be made as rapidly as possible. As soon as the boat is in place near the asbestos plug, at the beginning of the copper oxide, the stopper connecting with the purifying train is inserted and the aspiration started with pure oxygen gas at the rate of three bubbles per second. One burner is turned on about 10 cm. back from the boat, and the aspiration is continued carefully until practically all the moisture is expelled from the sample. The heat is then increased very gradually until all the volatile matter has been driven off. In driving off the volatile matter the heat must be applied gradually in order to prevent a too rapid evolution of gas and tar, which may either escape complete combustion or may be driven back into the purifying train. The heat should be slowly increased by turning on more burners under the open part of the tube until the sample is ignited; then the temperature can be increased rapidly, but care should be taken not to melt the combustion tube. Any moisture collecting in the end of the combustion tube, or in the rubber connection joining it to the calcium chloride tube is driven over into the calcium chloride tube by carefully warming with a piece of hot tile. The aspiration with oxygen is continued for 2 minutes after the sample ceases to glow, the heat is then turned off and about 1200 cc. of air are aspirated. The absorption bulbs are then disconnected, wiped with a clean cloth, and allowed to cool to the balance-room temperature before weighing.

$$\text{Per cent Hydrogen} = \frac{11.19 \times \text{Increase in Weight of } \text{CaCl}_2 \text{ Tube}}{\text{Weight of Sample}}$$

$$\text{Per cent Carbon} = \frac{27.27 \times \text{Increase in Weight of } \text{KOH Bulb}}{\text{Weight of Sample}}$$

The ash in the boat is weighed and carefully inspected for any unburned carbon, the presence of which would destroy the value of the determination.

Method with Electrically Heated Combustion Furnace—An electrically heated combustion furnace of the Heraeus type is used by the Bureau of Mines.¹

It consists of three independent heaters, two of which are provided with sheave wheels, and are mounted on a track so that they are movable along the tube; the third heater which surrounds the lead chromate is stationary.

The furnace as provided by the manufacturer does not include the small stationary heater. This can be made in the laboratory by winding an alundum tube 12 cm. in length with No. 20 nichrome II wire and enclosing it in a cylinder packed with magnesia-asbestos. The movable heaters have very thin platinum foil, weighing about 9 g. in all, wound on a porcelain tube of 30 mm. internal diameter. The larger one, which heats the copper oxide, is 350 mm. in length, and the smaller one, which heats the sample in the boat, is 200 mm. in length. The Jena glass or fused silica combustion tube, of about 21 mm. external diameter and 900 mm. in length, is supported by an asbestos-lined nickel trough. The current through each heater

¹ Technical Paper No. 8, Bureau of Mines, revised edition 1913, p. 22.

is regulated independently by separate rheostats, mounted on the frame of the furnace. The two platinum-wound heaters require an average current of about 4.5 amperes at a pressure of 220 volts, although for heating rapidly a larger amperage is necessary.

The oxygen or air entering the combustion tube is purified by passing through a Tauber's drying apparatus, which contains the following reagents arranged in order of the passage of air or oxygen through them: sulfuric acid, for removing possible traces of ammonia, 30 per cent potassium hydroxide (KOH) solution, granular soda lime, and granular calcium chloride. One side of the train is connected directly to a Linde oxygen tank, which is provided with a reducing valve for regulating the oxygen pressure; the other side of the train is used for purifying the air supply.

The absorption train consists of a 5-in. U-tube, filled with granular calcium chloride (CaCl_2) to absorb moisture. Before using, the calcium chloride should be saturated with carbon dioxide to avoid possible absorption of carbon dioxide during a determination by any traces of calcium oxide that may be present. This saturating is done most conveniently by placing a quantity of calcium chloride in a large drying jar, and filling the jar with carbon dioxide. After standing over night, dry air is drawn through the jar to remove the carbon dioxide. The treated calcium chloride is kept in well-stoppered bottles.

The calcium chloride tube is connected to a Vanier potash bulb containing a 30 per cent potassium hydroxide solution and granular calcium chloride. Six to eight determinations can be made without recharging this bulb. The potash bulb is connected to an aspirator through a guard tube containing granular calcium chloride and soda lime, and a Mariotte flask. The Mariotte flask keeps the pressure constant.

In general, the method of determination is the same as the one used with the gas furnace. By removing the heaters toward the end of the tube where the gases enter, and cutting in the electric current, the air can be warmed enough to dry the tube and its contents thoroughly. The current is then cut off from the small heater, and the large heater is moved over the copper oxide; about 250 mm. of that part of the combustion tube between the two heaters where the boat containing the sample is to be placed is kept exposed. The full current is then turned on the large heater to bring the copper oxide to a red heat. When this temperature is reached it is necessary to reduce the current with the rheostat to avoid melting the tube. In the meantime the absorption train is weighed and connected, and the boat containing the sample is placed in the exposed and cooler part of the tube between the two heaters.

The current is then passed through the shorter heater. By manipulating the rheostat and by gradually pushing this heater toward the boat, the rate of evaporation of moisture and evolution of volatile matter can be readily controlled.

After combustion is complete, the electric current is turned off the smaller heater and this heater moved back to allow the tube to cool for the next determination. The final aspiration of air and the weighing of the absorption train is conducted as described under the gas furnace method.

NOTES.—In place of granulated coal, concentrated sulfuric acid may be used for collecting the water formed by combustion. In such cases the air and oxygen entering the combustion tube and the gas leaving the potash bulb must also be dried by sulfuric acid.

Other suitable forms of absorption vessels than those indicated in the above procedure may be used.

NITROGEN

The Kjeldahl-Gunning method is recommended for the determination of nitrogen. This method has the advantages over either the simple Kjeldahl or the Gunning method in requiring less time for the complete oxidation of the organic matter, and in giving the most uniform results.

The Kjeldahl-Gunning Method.—One gram of the coal sample

is boiled with 30 cc. of concentrated sulfuric acid (H_2SO_4), 7 to 10 g. of potassium sulfate (K_2SO_4), and 0.6 to 0.8 g. of metallic mercury in a 500 cc. Kjeldahl flask until all particles of coal are oxidized and the solution is nearly colorless. The boiling should be continued at least 2 hours after the solution has reached the straw-colored stage. The total time of digestion will be from 3 to 4 hours. The addition of a few crystals of potassium permanganate (KMnO_4), after the solution has cooled enough to avoid violent reaction, tends to insure complete oxidation.

After cooling, the solution is diluted to about 200 cc. with cold water. If the dilution with water has warmed the solution, it should be again cooled and the following reagents added: 25 cc. potassium sulfide (K_2S) solution (40 g. K_2S per liter) to precipitate the mercury; 1 to 2 g. of granular zinc to prevent bumping; and finally enough strong sodium hydroxide (NaOH) solution (usually 80 to 100 cc.) to make the solution distinctly alkaline. The danger of loss of ammonia may be minimized by holding the flask in an inclined position while the sodium hydroxide solution is being added. The alkaline solution runs down the side of the flask and forms a layer below the lighter acid solution. After adding the alkaline solution, the flask is at once connected to the condensing apparatus and the solution mixed by gently shaking the flask.

The ammonia (NH_3) is distilled over into a measured amount (10 cc.) of standard sulfuric acid solution, to which has been added sufficient cochineal indicator for titration. Care should be taken that the glass connecting tube on the end of the condenser dips under the surface of the standard acid. The solution is slowly distilled until 150 to 200 cc. of distillate have passed over. To avoid mechanically entrained alkali passing over into the condenser, the rate of distillation should not exceed 100 cc. per hour. The distillate is titrated with standard ammonia solution (20 cc. NH_4OH solution = 10 cc. H_2SO_4 solution = 0.05 g. nitrogen). Standard NaOH or KOH solution with methyl orange or methyl red as indicator may be used instead of ammonia and cochineal.

A blank determination should be made in exactly the same manner as described above, except that 1 g. of pure sucrose (cane sugar) is substituted in place of the coal sample. The nitrogen found in this blank determination is deducted from the result obtained with the coal sample.

The potassium sulfide and sodium hydroxide may be dissolved in a single stock solution. Sufficient potassium sulfide is dissolved in the water before adding the sodium hydroxide, to make a solution in which the quantity necessary for a nitrogen determination. So to 100 cc. contains 1 g. of potassium sulfide. Twelve grams of potassium sulfide and 500 g. of sodium hydroxide in one liter of water are required for the above proportions.

Coal and anthracite coal should be ground to an impalpable powder, as they are very difficult to oxidize. Even if this is done the digestion may require 10 to 16 hours.

OXIGEN

There being no satisfactory direct method of determining oxygen, it is computed by subtracting the sum of the percentages of hydrogen, carbon, nitrogen, sodium, water, and ash from 100. The results obtained are affected by all the errors incurred by the other determinations, and especially by the change in weight of the ash-forming constituents on oxidation from pyrite, lignin to ferric oxide, increasing the ash and causing a heavier loss in the oxygen equivalent of the volatile in the pyrite solution. On the other hand, there is also a loss in weight of water of composition from the strong and stable constituents common double bond carbonates, etc., which tends to counteract the assumption of oxygen.

General Method.—Weigh 3 more or more grams of coal as desired. It may be determined by making the combustion indicated by the following formula:

Corrected oxygen

$$= 100 \rightarrow [(C - C') + (H - H') + N + H_2O] + S' + \text{Corrected Ash}]$$

in which

C = Total Carbon

C' = Carbon of Carbonates

H = Total Hydrogen — Hydrogen of Water

H' = Hydrogen from Water of Composition in Clay, Shale, Etc.

N = Nitrogen

H_2O = Moisture as found at 105° C.

S' = Sulfur not present as pyrite or sulfate (This is usually small and in many types of coal it may be disregarded.)

Corrected Ash = Mineral Constituents originally present in the coal. (For most purposes this can be determined with sufficient accuracy by adding to the ash, as found, five-eighths of the weight of pyritic sulfur, the CO_2 of carbonates and the water of composition of clay, shale, etc. See also *Ash Determinations*.)

CALORIMETRIC DETERMINATION

APPARATUS

Combustion Bombs—The Atwater, Davis, Emerson, Mahler, Parr, Peters, Williams, or similar bombs may be used. The bomb shall have an inner surface of platinum, gold, porcelain enamel, or other material which is not attacked by nitric and sulfuric acids, or other products of combustion.

Calorimeter Jacket—The calorimeter must be provided with a water-jacket having a cover to protect the calorimeter from air currents. The jacket must be kept filled with water within 2 or 3° C. of the temperature of the room (except in calorimeters which are totally submerged, where the jacket temperature is controlled by a thermostat) and should be stirred continuously by some mechanical stirring device.

Stirring of the Calorimeter Water—The water in the calorimeter must be stirred sufficiently well to give consistent thermometer readings while the temperature is rising rapidly. The speed of stirring should be kept constant. A motor-driven screw or turbine stirrer is recommended and the speed should not be excessive. This may be determined by adjusting the temperature of the calorimeter to equality with that of the jacket and allowing the stirrer to run continuously for ten minutes. If the temperature of the calorimeter rises more than about 0.01° C. in this length of time, the rate of stirring is excessive. Accurate results cannot be obtained when too much energy is supplied by the stirring device or when the rate of stirring is irregular. The portion of the stirring device immersed in the calorimeter should be separated from that outside by nonconducting material, such as hard rubber, to prevent conduction of heat from the motor or outside air.

Thermometers—Thermometers used shall have been certified by a government testing bureau and shall be used with the corrections given on the certificate. This shall also apply to electrical resistance or thermo-electric thermometers. Correction shall also be made for the temperature of the emergent stem of all mercurial thermometers, and for the "setting" of Beckmann thermometers. For accurate work, either Beckmann or special calorimetric thermometers graduated to 0.01 or 0.02° C. are required. Such thermometers should be tapped lightly just before each reading to avoid errors caused by the sticking of the mercury meniscus, particularly when the temperature is falling. A convenient method is to mount a small electric buzzer directly on the top of the thermometer and connect it up with a dry cell and a push button. The button should be pressed for a few seconds immediately before each reading.

Oxygen—The oxygen used for combustions shall be free from combustible material. The bomb when filled should contain at least 5 per cent of nitrogen to insure complete oxidation of the sulfur.¹ The total amount of oxygen contained in the bomb for a combustion shall not be less than 5 g. per gram of coal. But the combustion must be complete, as shown by

the absence of any sooty deposit on opening the bomb after firing.

Firing Wire—The coal in the bomb may be ignited by means of either iron or platinum wire. If iron wire is used, it should be of about No. 34 B. & S. gauge and not more than 10 cm. (preferably 5 cm.) should be used at a time. A correction of 1600 calories per gram weight of iron wire burned is to be subtracted from the observed number of calories.

Standardization—The water equivalent of a calorimeter can best be determined by the use of the standard combustion samples supplied by the Bureau of Standards. The required water equivalent is equal to the weight of the sample multiplied by its heat of combustion per gram and divided by the corrected rise in temperature.

The calorimeter shall be standardized by the combustion of standard samples supplied by the Bureau of Standards and used according to the directions given in the certificates which accompany them. A standardization shall consist of a series of not less than five combustions of either the same or different standard materials. The conditions as to the amount of water, oxygen, firing wire, method of correcting for radiation, etc., under which these combustions are made shall be the same as for coal combustions. In the case of any disagreement between contracting parties a check standardization may consist of two or more combustions of standardizing samples.

MANIPULATION

(1) **Preparation of Sample**—The ground sample is to be thoroughly mixed in the bottle and an amount, approximately 1 g., is to be taken out and weighed in the crucible in which it is to be burned. Coals which are likely to be blown out of the crucible should be briquetted. After weighing, the sample should preferably be immediately placed in the bomb and this closed. This procedure is necessary to avoid sublimation in the use of naphthalene for standardization.

(2) **Preparation of the Bomb**—The firing wire, if iron, should be measured and coiled in a small spiral and connected between the platinum terminals, using, if necessary, a piece of platinum wire somewhat heavier than the iron wire, to make the connection. The platinum and the iron must both be clean. About 0.5 cc. of water should be placed in the bottom of the bomb to saturate with moisture the oxygen used for combustion. When the crucible is put in place in the bomb, the firing wire should touch the coal or briquette of standard material. For the combustion of standardizing samples iron wire is preferable to platinum.

(3) **Filling the Bomb with Oxygen**—Oxygen from the supply tank is to be admitted slowly to avoid blowing the coal from the crucible, and the pressure allowed to reach 20 atmospheres for the larger bombs or about 30 atmospheres for the smaller bombs, so that the bomb shall contain an amount of oxygen sufficient for complete combustion, namely, at least 5 g. per gram of coal, or other combustible. This method of filling will insure 4 per cent of nitrogen in the larger bombs, irrespective of the nitrogen contained in the oxygen.

(4) **Calorimeter Water**—The calorimeter is to be filled with the required amount of distilled water, depending upon the type of calorimeter. The amount may be determined either by measurement in a standardized flask or by weighing. The amount must be kept the same as that used in standardization of the apparatus.

(5) **Temperature Adjustments**—The initial temperature in the calorimeter should be so adjusted that the final temperature, after the combustion, will not be more than 1° C., preferably about 0.5° C., above that of the jacket, under which conditions the total correction for heat gained from or lost to the surroundings will be small when the rise of temperature is 2 or 3° C. and the effect of evaporation will also be small.

(6) **Firing Current**—The electric current used for firing the

¹ Regerster, THIS JOURNAL, 6 (1914), 812.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS NINTH ANNUAL MEETING

The Ninth Annual Meeting of the American Institute of Chemical Engineers will be held in New York City, January 10 to 13, 1917, with headquarters at the Chemists' Club. A Smoker and the Subscription Dinner will be held at the Chemists' Club on Wednesday and Thursday evenings.

PROGRAM OF PAPERS

- Unpreparedness. *President, GEO. D. ROBINSON*.
Recent Developments in Chemical Engineering Equipment. H. D. MILES.
Corrosion of Ingot Iron, Containing Cobalt, Nickel or Copper. H. T. KALMES and K. B. BLAKE.
The Human Side of the Development of Chemical Industries. C. W. THOMPSON.
The Fixation of Nitrogen. J. E. BUCHER.
The Decatur Sewage Disposal Plant of the Electrolytic Sanitation Company. WM. HORSKINS.
The Effect of Centrifugal Force on Colloidal Solutions. E. E. AVRES, JR.
Recent Developments in the Absorption and Distillation of Volatile Liquids. C. L. CAMPBELL.
Chemical Engineering Aspect of Renovating a Sulfide Mill. H. K. MOORE.
Recovery of Benzol from Coke Oven and Illuminating Gas. C. J. RAMSBURG.

EXCURSIONS

David Bournonville Company, Jersey City, N. J.; Pierre Lorillard Tobacco Company; American Smelting & Refining Company, Maurer, N. J.; German-American Stoneware Works, Keasbey, N. J. Additional excursions are being arranged for. Members only will be permitted to attend excursions.

PROGRAM FOR THE LADIES

A special program for the ladies has been arranged which includes: automobile, theatre and musical parties; a tea party at the residence of Dr. and Mrs. Chas. F. Chandler; and the Subscription Dinner on Thursday evening.

ADJOURNED MEETING AMERICAN CHEMICAL SOCIETY WITH THE AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE

A symposium "On the Structure of Matter" was given at a Joint Meeting of the Sections on Physics and on Chemistry of the A. A. S., the American Physical Society and the American Chemical Society, on Wednesday, December 27, 1916. A Joint Meeting of the Chemistry Section of the A. A. S. and the American Chemical Society was held at the College of the City of New York, on Thursday, December 28, 1916.

PROGRAM OF PAPERS

- Radiation and Atomic Structure. Presidential Address of the American Physical Society. ROBERT A. MILLIKAN.
The Atom and Chemical Valence. GILBERT N. LEWIS.
Molecular Resonance and Atomic Structure. ROBERT W. WOOD.
The Evolution of the Elements as Related to the Structure of the Nuclei of Atoms. WM. D. HARKINS.
Discussion. OPENED BY PROF. WM. DUNNELL of HARVARD UNIVERSITY and PROF. JOHN M. NELSON of COLUMBIA UNIVERSITY.
The Relations of Magnetism to the Structure of the Atom. WM. J. HUMPHRIES.
The Relations of Magnetism to Molecular Structure. ALBERT P. WELLS.
The Structure of Solids and Liquids and the Nature of Interatomic Forces. IRVING LANGMUIR.
Electromerism, a Case of Chemical Isomerism Resulting from a Difference in Distribution of Valence Electrons. LAUDER W. JONES.
Discussion. OPENED BY K. G. FALK of the HARTMAN Research Laboratory.
Asymmetric Syntheses and Their Bearing upon the Doctrine of Vitalism. WILLIAM McPHERSON.
The Individuality of Tissue Elements. PHOEBUS A. LEVENE.
The Photo-Chemistry of the Chlorination Processes. HUGH S. TAYLOR.
Preparedness Chemistry Exhibit of the United Chemical Societies at the American Museum of Natural History. GEORGE F. KUNZ.
The Influence of Substitution Groups in Organic Compounds. C. J. DREYER.
The Application of Atomic Theories in Chemistry. S. DUSHMAN.

THE PERKIN MEDAL AWARD

The Perkin Medal for 1917 has been awarded to Dr. Ernst Twitchell, Ph.D., Superintendent of the Emery Candle Company and of the American Oil Treating and Hardening Company, Ivorydale, Ohio. The medal will be presented to Dr. Twitchell at the regular meeting of the New York Section of the Society of Chemical Industry, to be held at the Chemists' Club, January 19, 1917. A full account of the proceedings will be printed in the next issue of THIS JOURNAL.

Dr. Twitchell was born at Cincinnati, Ohio, on February 26, 1863, and received the degree of B.S. in 1886 from the University of Cincinnati. He was given an honorary degree of Ph.D. by the same University this spring.

In 1891 he published his method for the determination of rosin in the fatty acids of soap. The Twitchell method for rosin has to this day been the standard analytical process and is recommended by Lewkowitsch in the last edition of his "Oils, Fats and Waxes" as giving the best results of all methods proposed hitherto.

Dr. Twitchell's work is best known, however, in his invention of a catalytic agent for the saponification of fats. This agent is a sulfo-oleic acid and will split up fats when as little as 0.5 per cent is digested with the melted fat and water. The saponification is practically complete and may be effected in wooden tanks at the temperature of exhaust steam and at atmospheric pressure. The reaction may be carried out on a scale limited only by the size of the tank. The reagent is to a large extent recovered in the fatty acid obtained. Recently an improved form has been brought out as a dry salt which is still more effective. Prior to this discovery free fatty acids could be obtained only by the autoclave process, involving a heavy capital outlay for copper apparatus which could be used only in small units and at a high temperature and pressure, making the operation expensive and somewhat dangerous. The autoclave saponification was used only in the preparation of fatty acids in candle manufacture, as the process was too costly to be used in the production of fatty acids to be used in soap. The Twitchell process has made possible the large scale saponification of fats for the production of crude glycerin free from salt and of fatty acids for direct combination with soda ash to make soap instead of using the more expensive caustic lye on the neutral fat.

Low-grade fats, such as garbage grease, cottonseed oil foots, etc., were formerly with difficulty used in the soap or candle industry. Such materials can now be readily worked up by the Twitchell process, the fatty acids being distilled to remove color before use. This releases a large quantity of the higher grade fats for use as food products.

The bulk of the soap used in Belgium, Holland, Germany and Scandinavia is said to be prepared from fatty acids direct, and 75 per cent of these acids are made by the Twitchell method. Millions of pounds of fat are saponified yearly in the United States by this process, and practically all of the larger soap factories have Twitchell plants.

All of the recent books in German and English on the soap and fat industries discuss the Twitchell process in full.

NICHOLS MEDAL NOT AWARDED THIS YEAR

The Nichols Medal Committee met December 15th, and after a lengthy and careful deliberation and consideration of all papers published in the Journals of the Society during the year, decided that there were none of sufficiently original merit to be awarded the Nichols Medal. They have, therefore, this year passed the award.

NOTES AND CORRESPONDENCE

ON ANALYZED CHEMICALS

To the Council of the American Chemical Society:

We respectfully request that you take some action looking towards the definition of an "Analyzed Chemical."

That the need of such a definition exists is shown, we believe, by the following extracts from some correspondence between one of our members and a manufacturer of "Analyzed Chemicals."

CONSUMER TO MANUFACTURER

"We purchased recently from _____ a 1-lb. bottle of your ZINC METAL C P. POWDER, 30-MESH, your lot _____. The published analysis on this bottle shows it to contain Lead 0.005 per cent. Shortly after using this zinc, we found a discrepancy in our lead work and have made a careful analysis of a portion of the zinc, finding it to contain Lead 0.80 per cent * * * * *"

"We shall be very glad to hear from you in regard to this matter, as the presence of lead in the zinc has caused us considerable trouble * * * * *"

MANUFACTURER TO CONSUMER

"* * * Since writing we have further investigated the matter and it looks now as if there had been some mistake made by an inferior grade being sent out with the wrong label. We are investigating this matter carefully with a view of avoiding further mistakes of this kind, and will be glad to replace the lot of zinc which you purchased, if this will be satisfactory."

CONSUMER TO MANUFACTURER

"* * * Answering your question as to whether it would be satisfactory to have you replace the lot of impure zinc with a pure and equal amount of zinc, I will say emphatically that it would not. As explained in my former letter, we, based upon the advertisements and claims of your Company, purchased a bottle guaranteed to contain not over a stated minimum of lead. We used this in making a series of high-grade analyses. We reported these to our several clients. Our results were questioned, and it was only after making some fifty determinations and eliminating every other possible cause of error that we suspected the zinc used in this work and found by analysis that it was not pure. This has put us in a very unfortunate position with our clients, and we certainly do not propose to adjust the matter by having you substitute one or two bottles of guaranteed product for those in our possession, which are impure * * *"

MANUFACTURER TO CONSUMER

"We have your letter of _____ in reference to zinc and note that you have taken the analysis on the label as a standard for making a series of high-grade lead analyses. While we endeavor to have the analysis correct, at the same time we do not pretend to do work equal to the Bureau of Standards, and we always advise our customers when they intend to use any analyzed chemicals as a standard to first check up the analysis and satisfy themselves that it is correct. In doing our work we depend upon our men who handled these chemicals and put them up, and mistakes will sometimes occur. In this instance we believe a different grade of zinc was put up under the label furnished. We can only offer our apologies and assure you that notwithstanding this unfortunate incident we shall do our best to maintain the reliability of our analyzed chemicals, and trust you will not be discouraged about using them."

The instance here cited is, by no means, an isolated one, and we have been able to obtain from other members of our Section many similar instances where the analysis failed to reveal some impurity which was present in considerable quantity

or where the impurities in the substance far exceeded the printed analysis.

It seems to us of the greatest importance to all chemists that a distinct understanding should be arrived at concerning the accuracy of such an analysis. Many chemists are undoubtedly depending upon the printed label, and from the data in our possession it is quite evident that in many cases these analyses are entirely unreliable.

As the American Chemical Society is the largest association of chemists in the world, it seems to us further advisable that this Society should take up the question of analyzed chemicals with a view to determining, after a free and fair discussion of the matter, exactly what is meant by the term "Analyzed Chemical," and whether the manufacturer should be in any way responsible for the accuracy of an analysis when printed on the label of a container.

Respectfully yours,

CALIFORNIA SECTION AMERICAN CHEMICAL SOCIETY,

BRYANT S. DRAKE,

Secretary

A HIGHLY UNSATURATED HYDROCARBON IN SHARK LIVER OIL—CORRECTION

In the article under above title printed in THIS JOURNAL, 8 (1916), 889, the following corrections should be made:

Page	Column	Line	
891	right	4	"20° C." should read "—20° C."
893	left	22	Omit, "of a colorless liquid."
893	right	9	"292.5" should read "292-5."
893	right	9	"293-303° C." should read "298-303° C."
893	right	29	"368" should read "268."
893	right	31	"0.8546" should read "0.8646."
893	right	32	"1.4968" should read "0.4965."
894	left	9	"C ₂₁ H ₃₈ " should read "C ₂₅ H ₃₈ ."
894	left	40	"100 g." should read "150 g."
895	left	10-11	"C = 20.78 per cent, H = 3.72 per cent. Br = 60.50 per cent should read "C = 26.29 per cent, H = 3.68 per cent. Br = 70.03 per cent"

M. TSIJIMOTO

IMPERIAL INDUSTRIAL LABORATORY

YOKOHAMA-KU, TOKYO, JAPAN

NOVEMBER 21, 1916

NOTE ON THE RECOVERY OF MOLYBDIC ACID¹

By FRED. REINSTEK AND R. D. COOPER

Of the many published methods for the recovery of molybdic acid that described by W. D. Browne² seemed to us to be the most suitable since it obviates the necessity of drying and weighing the recovered molybdic acid. The wet precipitate is at once dissolved and made up into a solution of the required strength.

The essential changes from the method described by Browne are the following:

(1) Molybdic acid is recovered from the filtration liquor as well as from the filtrate containing the excess of ammonium molybdate.

(2) The quantities of materials have been changed so as to produce the solution required by the official method of the A. C. A. C.

The process as method used in this laboratory may be briefly described as follows:

¹ Presented at the Meeting of American Chemical Society, New York City, September 13-16, 1916.

² *Trans. American Chem. Soc.*, 37, 1111 (1915).

The phosphomolybdate solutions after titration are filtered through glass wool to remove paper pulp and combined with the filtrates and washings separated from the yellow precipitates. To this is added an excess of a saturated solution of ammonium phosphate, and after standing at least over night, the supernatant liquid is siphoned off. When a convenient amount of ammonium phosphomolybdate has been collected in this manner, it is washed by decantation with hot water until the washings begin to come through cloudy, requiring about 2 l. of water for each 100 g. of precipitate. After washing, the precipitate is dried on the steam bath and contains approximately 92 per cent of molybdic acid (85 per cent MoO_3).

Five hundred and ten grams of the dry salt are dissolved in ammonium hydroxide made by diluting 620 cc. of ammonia (0.90 sp. gr.) to 1000 cc. To this a solution of 85 g. of magnesium nitrate in 200 cc. of water is added, and after settling for 2 or 3 hrs. the filtrate is tested for phosphorus by adding a

few cc. to double the amount of nitric acid (1 : 2.5). It is important not to add the acid to the ammoniacal filtrate so as to avoid the precipitation of molybdic acid which might be mistaken for phosphomolybdate. If a yellow precipitate is formed, more magnesium nitrate must be added. When precipitation is complete the magnesium ammonium phosphate is filtered off, washed, and the filtrate made up to a volume of 2 l.

Two liters of concentrated nitric acid are diluted to 4668 cc. and both solutions are allowed to cool. The ammonium molybdate solution is now added very slowly to the nitric acid with constant stirring, preferably by means of filtered compressed air, timing the addition so that it will require at least an hour. The solution is allowed to stand over night, or preferably several days, and after filtering 320 cc. of concentrated nitric acid are added. The resulting solution is ready for use.

CHEMICAL LABORATORY, ARMOUR & COMPANY
UNION STOCK YARDS, CHICAGO

PERSONAL NOTES

The Youngstown Chemists' Club, recently organized, held its first regular meeting on December 14, 1916. The officers elected are: *President*, Edwin G. Pierce, consulting chemist; *Secretary*, Carl Weesner, Carnegie Steel Company; *Treasurer*, H. E. Moyer, Brier Hill Steel Company.

Mr. Ellwood Hendrick lectured on "Science in the Humanities," at Columbia University, on December 4, 1916, under the combined auspices of the Gamma Chapter of Phi Lambda Upsilon and the Institute of Arts and Sciences.

The Dyestuffs Census compiled by the Bureau of Foreign and Domestic Commerce is now available in its revised form.

Provost Edgar F. Smith, of the University of Pennsylvania, visited Wittenberg College, Springfield, Ohio, where he was professor of Natural Science in the early eighties, and the Ohio State University, Columbus, Ohio, on November 24, 1916, where he delivered a lecture before the Columbus Section of the American Chemical Society on "Robert Hare, a Pioneer American Chemist."

Dr. O. R. Sweeney, for the past six years instructor in qualitative analysis at the University of Pennsylvania, has been appointed instructor in industrial chemistry at the Ohio State University where he formerly graduated from the chemical engineering course.

Mr. George A. Burrell, consulting chemical engineer and president of the Natural Gas Products Company of Pittsburgh, was in Louisiana last month making tests of natural gas for gasoline content with the view of installing absorption plants. The Natural Gas Products Company uses an absorption process, worked out by Mr. Burrell, that is independent of other processes.

The President and Council of the Royal Society, London, have made the following awards: A "Royal" Medal to Dr. J. S. Haldane for research in chemical physiology; a "Royal" Medal to Mr. H. M. Macdonald for research in mathematical physics; "Copley" Medal to Sir James Dewar for research in physical chemistry; "Rumford" Medal to Prof. W. H. Bragg for research in X-ray radiation; "Davy" Medal to M. Henri Louis Le Chatelier for research in chemistry; "Darwin" Medal to Prof. Yves Delage for research in zoology and botany; "Sylvester" Medal to M. Jean Gaston Darboux for research in mathematical science; "Hughes" Medal to Prof. Elihu Thomson for research in electricity.

Dr. H. E. Armstrong has been elected a manager of the Royal Institution, to succeed the late Prof. Sylvanus P. Thompson.

The Massachusetts Institute of Technology has appointed the following assistants, with the grade of instructors, to the new chemical engineering stations: Bangor, Me., Wilfred A. Wylde; Everett, Mass., William B. Leach, Jr.; Niagara Falls, Winthrop E. Caldwell; Stamford, Conn., Edwin S. Wallace; Allentown, Pa., John S. Little. Azel W. Mack has been appointed research assistant in applied chemistry.

Emeritus Professor John Ferguson, who held the regius chair of chemistry in the University of Glasgow from 1874 to 1915, died November 3, 1916, aged seventy-nine years.

Dr. Rudolph R. Rosenbaum, formerly of the Central Commercial Company, Chicago, has opened the "Western Chemical Laboratories" at 53 West Jackson Boulevard, Chicago.

It is reported that the Swedish Academy of Science has decided not to award this year the Nobel prizes for physics and chemistry.

Mr. Clarence W. Marsh, engineer, announces the establishment of his New York office at 101 Park Ave.

Dr. G. H. A. Clowes, director of the Gratwick Research Laboratory, spoke on "Colloidal Equilibrium" at the December 8th meeting of the Indiana Section of the A. C. S. Dr. Wilder D. Bancroft will address the Indiana Section on March 9, 1917, and Dr. E. V. McCollum on May 11, 1917.

Dr. Severance Burrage, of the Indiana Section, is leaving Eli Lilly & Company, Indianapolis, to take up a new work at the Massachusetts Institute of Technology, Boston. Dr. Burrage has been in Indiana for 21 years as professor of biology at Purdue University and later as director of the biological laboratories of Eli Lilly & Company.

The new address of the General Bakelite Company is 2 Rector Street, New York City.

It is planned to erect a memorial at the University of Vermont to the late Prof. N. S. Merrill, of the department of chemistry. Prof. E. C. Jacobs has been appointed chairman of a committee for this purpose.

The University of Washington campus has been selected as the site of the government mining and metallurgical station for the Pacific Northwest states, to the maintenance of which Congress appropriated \$25,000 a year. Dorsey A. Lyon, formerly professor of mining engineering at the University of Washington, will be in charge of the station.

Dr. V. A. Coulter, Ph.D., has been appointed assistant professor of chemistry in the University of North Carolina.

GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

GEOLOGICAL SURVEY

Artesian Water for Irrigation in Little Bitter-Root Valley, Montana. OSCAR E. MEINZER. Water Supply Paper 400B; from Contributions to the Hydrology of the United States, 1916, pp. 9-37; published November 22nd. This report was prepared in cooperation with the Montana State Department of Public Health and the College of Agriculture and Mechanic Arts. It includes a discussion of the quality of the water and presents a number of analyses of samples.

The Yukon-Koyukuk Region Alaska. HENRY M. EAKIN. Bulletin 631, 80 pp. Paper, 20 cents. "The economic results of the investigation are largely negative, for but few mineral deposits occur in the region. The only mining has consisted in the small-scale placer operations in the Indian River district. On the other hand, certain intrusive granites which are shown to be the mineralizing agents are rather widely distributed and, therefore, the region, in spite of the meager results thus far achieved by the prospectors, should be classed as one in which there is hope of finding auriferous deposits."

Gypsum in the Southern Part of the Bighorn Mountains, Wyoming. CHARLES T. LUFTON AND D. DALE CONBIT. Bulletin 640H; from Contributions to Economic Geology, 1916, Part 1, pp. 139-157; published November 29th.

Geology of the Upper Stillwater Basin, Stillwater and Carbon Counties, Montana, with Special Reference to Coal and Oil. W. R. CALVERT. Bulletin 641G; from Contributions to Economic Geology, 1916, Part II, pp. 199-214; published November 17th.

Notes on Some Mining Districts in Eastern Nevada. JAMES M. HILL. Bulletin 648, 191 pp. Paper, 20 cents.

Barytes and Strontium in 1915. JAMES M. HILL. Separate from Mineral Resources of the United States, 1915, Part II; published October 6th. "The marketed production of crude barytes in the United States in 1915 was 108,547 short tons, valued at \$381,032. This is a notable increase over the production in 1914, which was 52,747 short tons valued at \$155,647. The increase was in large part due to the activity of the mines in Georgia, Kentucky, and Tennessee.

"The price paid for crude barytes in 1915 varied considerably in different States; thus, in Georgia the average price was \$4.13 a short ton; in Missouri the price was \$4.15 a short ton f. o. b. cars. These prices are higher than in 1914, but the average price did not advance as much as might have been expected, one factor in keeping it down appearing to be the opening of many deposits which have been idle for some time and whose output increased the supply in 1915. It is reported, however, that the demand for crude barytes by the manufacturers of lithopone, ground barytes, and barium chemicals has been very brisk. These augmented uses for domestic material have had a marked influence on prices, and it is understood that there has been a further increase in the price of crude barytes in 1916.

"No strontium bearing ores of domestic origin were reported

sold during the year 1915, and so far as the Survey has learned none of the American deposits were exploited. During the year some interest in domestic deposits has been manifested. It is understood that the manufacturers of red fire, both for signal and display purposes, and the beet-sugar interests have been looking into the question of obtaining strontium from home sources. It would seem that in view of the increased price of sugar it might be profitable for the beet-sugar makers to use the more effective *strontia* method rather than the one now in use. However, the substitution of the strontia process will require some time to bring about, and it depends on a number of economic factors concerning which the Survey has no information. Commercial strontium ores should contain at least 95 per cent strontium sulfate. At present English celestine is largely used on the eastern seaboard, where the strontium salts are made, and is laid down at the works at approximately \$12 a ton.

"According to the reports of the Bureau of Foreign and Domestic Commerce, Department of Commerce, the imports of strontium oxide, protoxide of strontium, and the strontianite or mineral carbonate of strontium were valued at \$1,016 in 1914, and \$6,411 in 1915. Imports of the strontium salts are free from duty. No figures are available for imports of celestine (strontium sulfate), used by manufacturers of strontium salts, this material being classed with all other chemicals not specially provided for in the present tariff."

This report also includes interesting discussions on the following subjects: Mining and preparation of crude barytes for market; geology of the barytes deposits of the United States; the manufacture of ground barytes; the manufacture of lithopone; the manufacture of barium chemicals; use of barium products; uses of strontium salts.

Phosphate Rock in 1915. W. C. PHALEN. With Sample Tests for Phosphate. W. B. HICKS. Separate from Mineral Resources of the United States, 1915, Part II; published October 6th. "The phosphate rock marketed in the United States in 1915 amounted to 1,835,667 long tons, valued at \$5,413,449. Compared with the production of 1914, which was 2,734,043 long tons, valued at \$6,668,041, this was a decrease of 898,376 long tons, or nearly 33 per cent, and in value of \$1,254,592, or nearly 44 per cent.

"The phosphate rock industry during 1915 was in the same bad condition, especially in Florida, that prevailed in 1914. Soon after the outbreak of the war in Europe the phosphate-mining companies of Florida, including not only those that produce the higher grade rock for export, but also those that supply the domestic trade, either curtailed production very materially or suspended mining.

"Shipments of phosphate rock to Germany, hitherto a large consumer, have almost entirely ceased, and those to other European countries have been seriously interrupted. Business has been greatly retarded by lack of freights and by increased freight rates, and there seems to be little likelihood of improvement till peace has been declared.

"The great demand for sulfates sold, especially toward the end of 1915, has also been a factor in curtailing the production of domestic phosphate rock. And prices have soared so high that the manufacture of good phosphate has shown a tendency to decline.

"The fertilizer materials imported into the United States in 1915 include many compounds containing phosphorus, nitrogen, and potash. Those containing phosphorus include bone ash, guano, bone slag, and crude phosphate rock. The potash fertilizers include various potash salts, kainite, manure salts, and

double manure salts. The nitrogen compounds are chiefly cyanamid, nitrates, and ammonium salts.

FERTILIZERS IMPORTED AND ENTERED FOR CONSUMPTION IN THE UNITED STATES IN 1915

FERTILIZER	Quantity (Long tons)	Value
Apatite.....
Bone dust or animal carbon, and bone ash, fit only for fertilizing.....	21,538	\$ 543,243
Calcium cyanamid or lime nitrogen.....	30,043	1,322,195
Guano.....	9,874	220,768
Kainite.....	6,674	95,440
Manure salts, including double manure salts.....	13,753	200,584
Phosphates, crude.....	5,359	50,606
Slag, basic, ground or unground.....	76	1,343
All other substances used only for manure.....	72,848	1,535,860
TOTAL.....	160,165	3,970,039

MATERIALS ENTERING LARGELY INTO THE FERTILIZER INDUSTRY IMPORTED FOR CONSUMPTION IN THE UNITED STATES IN 1915

	Quantity (Long tons)	Value
Fertilizers.....	160,165	\$ 3,970,039
Potassium chloride.....	57,741	2,296,606
Potassium sulfate.....	11,346	664,484
Sodium nitrate.....	770,628	22,844,746
TOTAL.....	999,880	\$29,775,875

This report has a particularly interesting discussion of the conservation of phosphate rock including under this heading notes on the influence of location of deposits, production and exportation, conservation of phosphate rock, mechanical methods of conservation, chemical methods of conserving phosphate rock, substitutes, phosphate reserves, and available foreign reserves. The processes for making soluble phosphates and a number of simple tests for phosphates (by W. C. HICKS) are also included.

Mineral Waters in 1915. RICHARD B. DONE. Separate from Mineral Resources of the United States, 1915, Part II; published October 31st. "The number of active mineral springs was smaller and the production was less though the value was greater in 1915 than in 1914. The decrease in production was 2,244,963 gal., or 4 per cent. The increase in value of medicinal waters was \$60,506 and in value of table waters was \$185,960; thus the total increase in value of sales was \$246,466, or 5 per cent. The increase in business is slightly less than the decrease in imports of foreign waters, and this, coupled with the increase of price per gal. from 9 to 10 cents, indicates increased sales of moderately high-priced domestic waters that have become valuable substitutes for waters previously imported. Production was reported from 45 springs for the first time in 1915."

In addition to a discussion of the mineral water trade in each State there is in this circular a general discussion of the output, value, price, uses, exports, imports, and the condition of trade in mineral waters.

Gold, Silver, Copper, Lead, and Zinc in California and Oregon in 1915. (Mines Report.) CHARLES G. YALE. Separate from Mineral Resources of the United States, 1915, Part I; published October 4th. This and the three succeeding separates give detailed information regarding these metals from the localities under discussion. For general information covering the whole United States the consolidated report which is presented in another separate each year should be consulted.

Gold, Silver, Copper, and Lead in South Dakota and Wyoming in 1915. (Mines Report.) CHARLES W. HENDERSON. Separate from Mineral Resources of the United States, 1915, Part I; published November 3rd.

Gold, Silver, Copper, Lead, and Zinc in New Mexico and Texas in 1915. (Mines Report.) CHARLES W. HENDERSON. Separate from Mineral Resources of the United States, 1915, Part I; published November 23rd.

Gold, Silver, Copper, Lead and Zinc in Utah in 1915. (Mines Report.) V. C. HEIKES. Separate from Mineral Resources of the United States, 1915, Part I; published November 24th.

Iron Ore, Pig Iron and Steel in 1915. ERNEST F. BURCHARD. Separate from Mineral Resources of the United States, 1915, Part I; published October 30th. "The iron ore mined in the

United States in 1915 amounted to 55,526,490 gross tons, as compared with 41,439,761 gross tons mined in 1914, an increase of 14,086,729 gross tons, or 34 per cent. Beneficiated ore instead of crude ore mined is included if the ore is treated in any way. The quantity of iron ore shipped from the mines in the United States in 1915 amounted to 55,493,100 gross tons, valued at \$101,288,984, as compared with 39,714,280 gross tons, valued at \$71,905,079, shipped in 1914. This represents an increase in quantity of 15,778,820 gross tons, or 40 per cent, and in value of \$29,383,905, or 41 per cent. The average price of ore per ton for the whole country in 1915 was \$1.83, as compared with \$1.81 in 1914. These quantities of ore, both mined and shipped, include the iron ore used for fluxing other metallic ores at smelters in the Western States, but the shipments do not include the iron ore sold for the manufacture of paint. The quantity of iron ore sold for the manufacture of paint in 1915 amounted to 20,760 gross tons, valued at \$48,760. In Arkansas one producer shipped 10 tons of loadstone, averaging 72 per cent of metallic iron, which was sold at a high price. This shipment is not included in the tabulated statistics of iron ore. The ore reported as sold for fluxing other than in the manufacture of pig iron amounted to 17,213 gross tons, valued at \$27,456, in 1915, as compared with 42,677 gross tons, valued at \$114,985, in 1914. The domestic iron ore actually sold for the manufacture of pig iron amounted in 1915 to 55,475,887 gross tons, valued at \$101,261,528, as compared with 39,671,603 gross tons, valued at \$71,790,094, in 1914."

IRON ORE MINED IN THE UNITED STATES, BY MINING DISTRICTS AND VARIETIES, IN 1915, IN GROSS TONS

DISTRICT	Hematite	Brown ore	Magnetite	Carbonate	Total	% Increase in 1915
Lake Superior(a)	46,944,254	46,944,254	+40
Birmingham.....	4,213,597	535,332	4,748,929	+11
Chattanooga.....	340,481	198,543	539,024	+25
Adirondack.....	699,213	699,213	+28
Northern N. J. & Southeastern N. Y.....	(b)	644,493(b)	644,493	+19
Other districts.....	728,992	754,000	464,130	3,455	1,950,577	+7
	52,227,324	1,488,709	1,807,002	3,455	55,526,490	+34

(a) Includes only those mines in Wisconsin which are in the true Lake Superior district.

(b) Brown ore included in magnetite.

One of the most interesting sections of this report relates to beneficiation of iron ores which is reported on by EDMUND NEWTON and HARLAN H. BRADT.

"The Bureau of Statistics of the American Iron and Steel Institute reports the production in 1915 of all kinds of pig iron, including such ferroalloys as spiegeleisen, ferromanganese, ferrosilicon, and ferrophosphorus, produced in blast furnaces, as well as some that were electrically produced, as 29,916,213 gross tons, compared with 23,332,244 tons produced in 1914, an increase of 6,583,969 or 28 per cent.

"According to reports to the United States Geological Survey by the manufacturers, the shipments of pig iron, exclusive of ferroalloys, in 1915, amounted to 30,384,486 gross tons, valued f. o. b. at the furnaces at \$401,409,604, as compared with 22,263,263 tons, valued at \$298,777,429, in 1914, an increase in quantity of 8,121,223 tons, or 36 per cent, and in value of \$102,632,175, or 34 per cent. The average price per ton in 1915 was \$13.21, and in 1914 it was \$13.42, a decrease in 1915 of \$0.21 a ton. These values represent the approximate price per ton f. o. b., at the furnaces; this approximate price eliminates freight costs, selling commissions, and other items, which are included in the market prices of certain grades of pig iron as published in the trade journals."

Detailed information as to the prices in different districts, the number of blast furnaces in operation, the monthly production, the production by grades and in accordance with fuels used, and import, export and foreign trade statistics are included.

"The quantity of ferroalloys reported is small, amounting to only about 1.28 per cent of the total marketed production of pig iron during 1915, but the value per ton is so much greater as to have an important influence on the apparent average value of the pig iron, if included with it, making it \$13.61 a ton instead of \$13.21.

"The shipments of ferroalloys in 1915, as reported to the United States Geological Survey, were 388,644 gross tons, valued at \$17,450,385, as compared with 255,524 gross tons, valued at \$9,350,245, in 1914. Of the shipments in 1915, 147,822 gross tons, valued at \$11,452,577, were made from imported ores derived from Australia, Cuba, India, Japan, Russia, South America, and Spain. The ferrovanadium, ferromolybdenum, ferromanganese, spiegeleisen, and ferrotungsten were made in part or wholly from imported ore. The quantity reported falls far short of the real production quantities as data concerning the sales of considerable quantities of electrically produced ferroalloys could not be obtained by the Survey."

FERROALLOYS OF DOMESTIC MANUFACTURE SOLD IN 1915

ALLOY	Quantity (Gross tons)	Value
Ferromanganese.....	144,260	\$ 9,253,443
Spiegeleisen.....	114,556	2,403,550
Ferrosilicon.....	128,263	2,595,265
Ferrophosphorus.....		
Ferromolybdenum.....		
Ferrotitanium (a) (10 to 20 per cent titanium).....	1,565	3,198,127
Ferrovandium.....		
Ferrotungsten (50 per cent or above, tungsten).....		
TOTAL.....	388,644	\$17,450,385

(a) No ferrotitanium reported in 1915.

DEPARTMENT OF AGRICULTURE

Manual of Procedure for Guidance of State Health, Food, and Drug Officials. J. S. ABBOTT and H. S. BAILEY. Unnumbered pamphlet.

Important Insecticides, Directions for Their Preparation and Use. C. L. MARLATT. Farmers' Bulletin 127, 48 pp. Paper, 5 cents.

The Intrinsic Values of Grain, Cottonseed, Flour, and Similar Products, Based on the Dry-Matter Content. E. G. BOERNER. Bulletin 374, 32 pp. Paper, 5 cents. This report shows the percentage of water contained in various grains, flours, and cottonseed, and explains the benefits derived by drying said products before marketing same.

Hemp Hurds as Paper-Making Material. LYSSTER H. DEWEY and JASON L. MERRILL. Department Bulletin 404, 26 pp. Paper, 5 cents. This report should be useful to all persons who are interested in the economic phase of papermaking, especially to print and book paper manufacturers. It also should be of interest to scientific investigators and chemists.

The Recovery of Potash from Alunite. W. H. WAGGAMAN and J. A. CULLEN. Contribution from the Bureau of Soils. Department Bulletin 415, 14 pp. Paper, 5 cents. "Describes location and extent of the Utah deposits of alunite, and the method of extracting the potash."

Cooling Hot-Bottled Pasteurized Milk by Forced Air. S. HENRY AYERS, JOHN T. BOWEN and W. T. JOHNSON. Department Bulletin 420, 38 pp. Paper, 10 cents.

The Action of Manganese under Acid and Neutral Soil Conditions. J. J. SKINNER and F. R. REID. Bulletin 441, 12 pp. Paper, 5 cents. "The results given in the bulletin throw further light on the effect of this catalytic fertilizer under various soil conditions. That its effect is dependent on the reaction of the soil is demonstrated. The bulletin is of interest to scientific investigators, to manufacturers of catalytic fertilizers, and to those growers whose technical training induces them to experiment with new substances, to increase or control crop production."

A Study of the Electrolytic Method of Silver Cleaning. H. L. LANG and C. F. WALTON, JR. Bulletin 449, 10 pp. Paper, 5 cents. Contains information regarding the advantages and limitations of the electrolytic method of cleaning silver and the conditions under which it is most efficient.

Improved Apparatus for Determining the Test Weight of Grain, with a Standard Method of Making the Test. E. G. BOERNER. Bulletin 472, 15 pp. Paper, 5 cents. Of interest to grain dealers and grain inspectors.

The following articles from Volumes 6 and 7 of the *Journal of Agricultural Research* are of chemical interest:

Influence of Barnyard Manure and Water upon Bacterial Activities of Soil. J. E. GREAVES and E. G. CARTER.

Alpha Crotonic Acid as a Soil Constituent. E. H. WATERS and LOUIS E. WISE.

Formation of Hematoporphyrin in Ox Muscle during Autolysis. RALPH HOAGLAND.

Comparison of the Nitrifying Powers of Some Humid and Some Arid Soils. C. P. LIPMAN, P. S. BURGESS and M. A. KLEIN.

Immobiity of Iron in the Plant. P. L. GILE and J. O. CARRERO.

Effects of Nicotine as an Insecticide. N. E. McINDOO
Acidity and Adsorption in Soils as Measured by the Hydrogen Electrode. L. T. SHARP and D. R. HOAGLAND.

Growth of Parasitic Fungi in Concentrated Solutions. LON. A. HAWKINS.

Freezing-Point Lowering of the Leaf Sap of the Horticultural Types of *Persea Americana*. J. A. HARRIS and WILSON POPHNOE.

Chemical Composition, Digestibility, and Feeding Value of Vegetable-Ivory Meal. C. L. BEALS and J. B. LINDSEY.

Use of Two Indirect Methods for the Determination of the Hygroscopic Coefficients of Soils. F. J. ALWAY and V. L. CLARK.

Energy Values of Red-Clover Hay and Maize Meal. H. P. ARMSBY, J. A. FRIES and W. W. BRAMAN.

Effect of Sodium Salts in Water Cultures on the Absorption of Plant Food by Wheat Seedlings. J. F. BREAZEALE.

BUREAU OF STANDARDS

Determination of the Degree of Uniformity of Bars for Magnetic Standards. RAYMOND L. SANFORD. Scientific Paper 295, 14 pp. "This paper (1) describes a method for determining the degree of magnetic uniformity along the length of a straight bar, (2) indicates the magnitude of the effect of nonuniformities on the accuracy of magnetic measurements, and (3) gives a criterion for the degree of uniformity of magnetic standards."

The Failure of Brass. I.—Microstructure and Initial Stress in Wrought Brasses of the Type, 60 Per cent Copper and 40 Per cent Zinc. P. D. MERICA and R. W. WOODWARD. Technological Paper 82, 52 pp. The paper gives an account of an investigation of the cause of failure of a number of articles, particularly bolts, of wrought brass of the type 60-40, of such material as naval brass and magnesium brass, with particular reference to the microstructure of the material and the presence in it of initial stress. In the course of this investigation the physical properties, microstructure, and the initial stress distribution have been studied in some 250 material, some of which had been in service in the Cornell Applied construction in the Electric Plant of the city of Milwaukee, in the U. S. Navy Department, and in the Pacific Coast construction and some of which were new material, still having their factory finish and free from any treatment. It was found that the initial stresses in brass could be measured on annealing for 24 hours at 100° C. (212° F.), and at 400° C. (752° F.) which the physical measurements and microscopy showed approximately confirmed.

2. The Effect of Corrosion on the Ductility and Strength of Brass. Part II. Microstructure. Technological Paper 82, 11 pp. The yield-point of a brass specimen, being drawn from stress, after the specimen has been annealed for 24 hours, is measured by the length of a brass wire. The measured yield-point is measured by a sufficient test specimen the test specimen is of brass.

On the other hand, the measured yield-point of the specimen of strength and ductility of brass, when measured with a test specimen, is measured by a sufficient test specimen the test specimen is of brass.

will vary in value, being greatest at the bottom of furrows and depressions and least, almost zero indeed, at the tops of the ridges. The *e. m. f.* will, therefore, other things being equal, be greater (*i. e.*, more electropositive) at the bottoms of the furrows than elsewhere; corrosion will set in here most rapidly, forming a crack which will grow narrower and sharper, its rate of growth being greater the sharper it is. In time the cross-section of such a bar is so reduced by these cracks that fracture occurs, the brass exhibiting only slight elongation (ductility) and failing at a stress value apparently less than the ultimate strength. This explanation is borne out by the examination of a number of brass failures which have occurred under such conditions."

3.—Initial Stress Produced by the "Burning-in" of Manganese Bronze. PAUL D. MERICA AND C. P. KARR. *Technologic Paper 84*, 7 pp. "In connection with the failure, by cracking, of a number of manganese bronze valve castings in the Catskill Aqueduct at or near areas repaired by "burning-in," an investigation has been made of the initial stress produced in a manganese bronze double bar casting by the burning-in of a constrained portion. The stresses measured were in each case about 8000 to 10,000 lbs. per sq. in. (*i. e.*, the true elastic limit of the material) and the material within the burned-in area was of course in tension. The microstructure of the portion adjacent to the burned-in metal was not altered; the burned-in metal was in all cases of finer grain than that of the casting.

"The conclusion is reached that, although distortion of a burned-in casting may partially relieve the initial stresses set up by this operation, such castings will, in all probability, generally contain local stresses of dangerous magnitude, *i. e.*, near the elastic limit of the material. Castings repaired in this manner should either be thoroughly preheated or subsequently annealed in order to eliminate these stresses."

Specifications and Tolerances for Weights and Measures and Weighing and Measuring Devices. Circular No. 61. These are the specifications and tolerances as adopted by the eleventh annual conference on the weights and measures of the United States, held at the Bureau of Standards, Washington, D. C., May 23 to 26, 1916, and recommended by the Bureau of Standards for adoption by the several states.

COMMERCE REPORTS—NOVEMBER, 1916

The first coal mine in the Malay Peninsula has just been opened. (P. 455.)

The output of **quinine** in Madras, India, shows a large increase, most of it is consumed locally, being issued to the natives by the Government. (P. 487.)

Efforts are being made to develop **electric iron** smelters in New Zealand, especially to use the titaniferous iron sands of the Jaranaki region. (P. 581.)

Over 100 **dyes** are now being made in Switzerland and available for export to the United States. (Pp. 583-8.)

Russia now supplies the bulk of the **sugar beet seed** used in the United States, which was formerly mostly obtained from Germany. (P. 596.)

The **peanut industry** of Madras, is increasing; much of the product is exported, and the rest is extracted in India for native use. (P. 600.)

Japan is now exporting considerable **paper pulp** to the United States. (P. 638.)

The present production of **platinum** in the Urals is only about one-third normal. (P. 661.)

The **cement** production of Spain shows a marked increase, 9 plants now being in operation. (P. 680.)

Plans are being made to reopen the **antimony** mines in New Brunswick. (P. 709.)

All the capital has been subscribed for the "British Dyes Limited," the government subsidized company for manufacturing dyes. (P. 724.)

Efforts are being made by the United States Bureau of Fisheries

to utilize the large deposits of **bones** in the Pribilof Islands. They are probably the largest known deposits of bones, representing accumulations of a century or more. (P. 726.)

New **antimony** deposits are being opened in South Africa. (P. 727.)

A company has been formed in Argentina for the manufacture of "Algarrobin," a brownish dye, obtained from the wood of the carob tree. It is being used especially for dyeing khaki cloth. (P. 731.)

The production of **flax for fiber** in Canada is steadily increasing. The export of **flaxseed** (linseed) has, however, decreased. (P. 733.)

Exports of **nitrate** from Chile show a large increase. (P. 740.)

The British minister of munitions has ordered a census of all **coal-tar products** in the United Kingdom. (P. 740.)

Efforts are being made to install **detinning plants** for old tin in various English towns. Formerly most of this scrap tin was exported to Germany. (P. 763.)

China and Japan are experiencing a great shortage of "**lacquer-varnish**," used in the lacquer-ware industry. The material is obtained from the juice of the *Rhus vernicifera*, or lacquer-varnish tree, the cultivation of which has fallen off. (P. 771.)

The Philippine Bureau of Science is taking steps to modernize the **Philippine sugar industry**. By present crude methods the yield is only 60 to 70 per cent, while in modern "centrals" a yield of 94 to 98 per cent is obtained. (P. 774.)

Geological studies are being made in Brazil of possible "pipes" of "Kumherlite," or **diamond matrix**. Thus far all the Brazilian diamonds have been obtained from placers. Recently discoveries of "mother lodes" have been reported. (P. 798.)

Considerable **scheelite** is now being mined in New Zealand. (P. 813.)

Annual exports of **platinum** from Columbia, now amount to over 11,000 troy ounces. (Supplement 42a.)

SUPPLEMENTS ISSUED IN NOVEMBER, 1916

NORWAY—106	CHINA, TSINGTAU—57h
SPAIN—15e	CHINA, MANCHURIA—52i
FRENCH WEST INDIES—28g	STRATTS SETTLEMENTS AND FED-
HAITI—30b	ERATED MALAY STATES—56a
PANAMA—35a	SIAM—58b
CHILE—41b	BRITISH WEST AFRICA—67a
COLOMBIA—42a and b	EGYPT—68a
BRITISH INDIA—50c	FRENCH WEST AFRICA—69a
CEYLON—51d	PORTUGUESE WEST AFRICA—77a

STATISTICS OF EXPORTS TO THE UNITED STATES

SWITZERLAND—583	SPAIN—Sup. 15c	HAITI—Sup. 30b
Vegetable alkaloids	Beeswax	Hides
Saccharin	Glycerin	Logwood
Acid potassium tar-	(56d)	Wax
trate	Saffron	Fustic
Boric acid	Argols	Bones
Phosphoric acid	Iron ore	
Sodium	Olive oil	CEYLON—Sup. 51a
Tanning extracts	Hides	Citronella oil
Glycerin		Coconut oil
Glue	SANTO DOMINGO—	Papain
Logwood extracts	(56d)	Graphite
Aniline dyes	Beeswax	Rubber
Indigo	Copper ore	
NORWAY—Sup. 106	Hides	MANCHURIA—Sup. 52i
Chemicals	Logwood	Soya bean oil
Cod liver oil	Sugar	Talcum
Fertilizers	COLOMBIA—Sup. 42a	
Hides	and b	SINGAPORE—Sup. 56a
Matches	Dividivi	Benzene
Paper	Gold	Cutch
Wood pulp	Hides	Gambier
Aluminum	Indigo	Gumcopal
Platinum ore	Ipecac	Gundamar
CHILE—Sup. 41b	Platinum	Guttajolalong
Antimony ore	Rubber	Gutta-percha
Argols	Silver	Hides
Beeswax	Tanning extract	Mangrove bark
Cascarina		Coconut oil
Cocaine	INDIA—Sup. 50c	Resin
Copper	IRON—	Rubber
Gold	Hides	Tin
Glue	Manganese ore	SIAM—Sup. 58a
Hides	Mica	Hides
Iodine	Saltpeper	Tungsten ore
Lead	Shellac	
Silver	Nux vomica	EGYPT—Sup. 68a
Nitrate	Senna	Beeswax
Potash	Indigo	Glue stock
Quilay bark	Turmeric	Gum arabic
Rubber	Lemon-grass oil	Hides
Tin	Coconut oil	Iron ore
Tungsten	Castor seeds	Rags
Zinc	Rubiac	Senna

NEW PUBLICATIONS

By IRENE DeMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

Analysis: A Textbook of Quantitative Chemical Analysis. J. C. OLSEN. 5th Ed., Revised and Enlarged. Svo. 555 pp. Price, \$3.50. D. Van Nostrand Co., New York.

Analysis: General Instruction and Methods of Analysis and Chemical Control; for Use in Factories of the Cuban-American Sugar Company. G. L. SPENCER. 3rd Ed. Svo. 39 pp. Price, \$1.00. Cuban-American Sugar Co., New York.

Bituminous Materials. Laboratory Manual. PREVOST HUBBARD. 8vo. 153 pp. Price, \$1.50. John Wiley & Sons, New York.

Cellulose: An Outline of the Chemistry of the Structural Elements of Plants. C. F. CROSS AND OTHERS. New Ed. Svo. 328 pp. Price, \$1.50. Longmans, Green & Co., New York.

Chemistry: A Laboratory Outline of College Chemistry. ALEXANDER SMITH. 12mo. 206 pp. Price, \$0.90. The Century Co., New York.

Chemistry: Manuel de chimie. B. GAUTHIER-ÉCHARD. 16mo. 335 pp. Deslis frères et Cie, Tours.

Chemistry of the Farm and Home. W. E. TOTTINGHAM AND J. W. INCE. 12mo. 434 pp. Price, \$1.25. Webb Publishing Co., St. Paul, Minn.

Civil Engineering Types and Devices; a Classified Index of Plant Constructions, Machines and Materials. T. W. BARBER. 8vo. 245 pp. Price, \$3.00. D. Appleton & Co., New York.

Construction: Modern Electrical Construction. H. C. HORSTMANN AND V. H. TOUSLEY. 5th Ed. 16mo. 439 pp. Price, \$1.00. Frederick J. Drake & Co., Chicago.

Cost Data: Estimating the Cost of Work. W. B. FERGUSON. 12mo. 169 pp. Price, \$1.00. Engineering Magazine Co., New York.

Cotton: Measurements Showing Cubical Contents and Density per Foot of Low Density Compressed Cotton. DENNIS MULLANE. 8vo. 25 pp. Price, \$1.50. Dealy-Adey-Elgin Co., Houston, Tex.

Cotton Calculator and Density Tables. W. H. LOWE. Svo. 47 pp. Price, \$4.00. The Author, Atlanta, Ga.

Engineering Chemistry. T. B. STILLMAN. 8vo. 760 pp. Price, \$5.00. Chemical Publishing Co., Easton, Pa.

Engines: The Design of Marine Engines and Auxiliaries. E. M. BRAGO. 8vo. 183 pp. Price, \$3.00. D. Van Nostrand Co., New York.

Gases of the Atmosphere. SIR WILLIAM RAMSAY. 4th Ed. 12mo. 306 pp. Price, \$2.25. The Macmillan Co., New York.

Industrial Arithmetic. C. G. WHITE AND P. P. COLOGROVE. 12mo. 285 pp. Price, \$0.80. Webb Publishing Co., St. Paul, Minn.

Inorganic Chemistry. L. C. NEWELL. Rev. Ed. 12mo. 595 pp. Price, \$2.00. D. C. Heath & Co., New York.

Lubricating Engineers' Handbook. J. R. BATTLE. 8vo. 333 pp. Price, \$4.00. J. B. Lippincott Co., Philadelphia.

Mechanical Engineering: Aide-Mémoire de l'ingénieur mécanicien. I. IZART. 8vo. 868 pp. Deslis frères et Cie, Tours.

Mechanical Equipment of Buildings. Vol. I. L. A. HARDING AND A. C. WILLARD. To be in 3 Vols. 8vo. 615 pp. Price, \$4.00. John Wiley & Sons, New York.

Metallurgy of Steel. J. F. W. HARBORD AND J. W. HALL. 2 Vols. 5th Ed. 8vo. 933 pp. Price, \$12.50. J. B. Lippincott Co., Philadelphia.

Milk: The Pasteurization of Milk; a Handbook Relating to the Installation, Operation and Control of Pasteurizing Plants. C. H. KILBOURNE. 16mo. 248 pp. Price, \$1.25. John Wiley & Sons, New York.

Municipal Engineering Practice. A. P. FOLWELL. 8vo. 422 pp. Price, \$3.50. John Wiley & Sons, New York.

Organic Chemistry: A Laboratory Manual of Organic Chemistry. MATTHEW STRELL. 8vo. 201 pp. Price, \$1.25. John Wiley & Sons, New York.

Organic Chemistry for the Laboratory. W. A. NOYES. 3rd Ed. Svo. 291 pp. Price, \$2.00. Chemical Publishing Co., Easton, Pa.

Oxy-acetylene Welding. S. W. MILLER. Svo. 287 pp. Price, \$2.40. Industrial Press, New York.

Pattern Making. JAMES RITCHIE. Rev. Ed. 12mo. 292 pp. Price, \$1.50. American Technical Society, Chicago.

Power Stations: Large Electric Power Stations; Their Design and Construction. G. KILGENBERG. Svo. 260 pp. Price, \$3.00. D. Van Nostrand Co., New York.

Refrigeration: The Elements of Refrigeration for Students, Engineers and Warehousemen. A. M. GREENE. Svo. 422 pp. Price, \$4.00. John Wiley & Sons, New York.

Rock Excavation: Handbook of Rock Excavation, Methods and Costs. H. P. GILLETTER. 2nd Ed. 12mo. 835 pp. Price, \$5.00. John Wiley & Sons, New York.

Steel: L'industrie de l'acier en France. A. TREPOD. 12mo. 520 pp. Price, \$4.00. Ch. Herissey, France.

Steel Square: A Practical Treatise on the Application of the Steel Square. S. A. HOFFMAN. 2 Vol. 12mo. Price, \$2.00. McGraw-Hill, New York.

Steel Square: A Practical Treatise on the Application of the Steel Square. S. A. HOFFMAN. 2 Vol. 12mo. Price, \$2.00. McGraw-Hill, New York.

Steel Square: A Practical Treatise on the Application of the Steel Square. S. A. HOFFMAN. 2 Vol. 12mo. Price, \$2.00. McGraw-Hill, New York.

Steel Square: A Practical Treatise on the Application of the Steel Square. S. A. HOFFMAN. 2 Vol. 12mo. Price, \$2.00. McGraw-Hill, New York.

Steel Square: A Practical Treatise on the Application of the Steel Square. S. A. HOFFMAN. 2 Vol. 12mo. Price, \$2.00. McGraw-Hill, New York.

Steel Square: A Practical Treatise on the Application of the Steel Square. S. A. HOFFMAN. 2 Vol. 12mo. Price, \$2.00. McGraw-Hill, New York.

Weights and Measures: Quick Calculator. R. KLEIN. Comp. 12mo. 13 pp. Price, \$0.80. E. P. Dutton & Co., New York.

Welding: Automobile Welding with the Oxy-acetylene Flame. M. K. DUNHAM. 167 pp. Price, \$1.00. Norman W. Henley Publishing Co., New York.

RECENT JOURNAL ARTICLES

Air Delivery Factors of Blowing. W. TRANKS. *Blast Furnace and Steel Plant*, Vol. 50 (1916), No. 12, pp. 551-553.

Analysis of Tank Resistance in Electrolytic Refining. LAWRENCE ADAMS. *Metallurgical and Chemical Engineering*, Vol. 15 (1916), No. 10, pp. 560-570.

Bisulfite Process. ANONYMOUS. *Engineering and Mining Journal*, Vol. 102 (1916), No. 21, pp. 895-898.

Black Sand of the Pacific Coast. HERBERT LANG. *Mining and Scientific Press*, Vol. 113 (1916), No. 23, pp. 811-813.

Carbon: Determining Carbon in Steel by Combustion. J. W. BARBER. *Iron Age*, Vol. 98 (1916), No. 19, pp. 1052-1055.

Carbonization of Wrought Iron in Gases. F. W. HARBORD. *Blast Furnace and Steel Plant*, Vol. 50 (1916), No. 12, pp. 556-557.

Cleaning the Ammonia Charge at the End of the Season. F. W. FRERICHS. *Power*, Vol. 44 (1916), No. 22, pp. 752-753.

Compression from a Mechanical Point of View. F. R. LOW. *Power*, Vol. 44 (1916), No. 20, pp. 674-676.

Condensation Pump: An Improved Form of High Vacuum Pump. IRVING LANGMUIR. *General Electric Review*, Vol. 19 (1916), No. 12, pp. 1060-1071.

Corrosion: Preventing the Corrosion of Pipe. F. N. SPERLEN. *Iron Trade Review*, Vol. 59 (1916), No. 22, pp. 1098-1101.

Crystals: On the Formation of Columnar and of Free Crystals during Solidification. H. M. HOWE. *Metallurgical and Chemical Engineering*, Vol. 15 (1916), No. 11, pp. 623-624.

Fuel: Excess Air in Fuel Combustion. M. B. SMITH. *Power*, Vol. 44 (1916), No. 20, pp. 680-682.

Heat Treatment for Special Alloy Steels. R. R. ABBOTT. *Steel and Iron*, Vol. 50 (1916), No. 11, pp. 345-348.

Industrial Organization. H. N. STROUCK. *Manufacturing and Chemical Engineering*, Vol. 15 (1916), No. 10, pp. 579-583.

Internal-Combustion Turbine. A. W. H. GRIFFIN. *Power*, Vol. 44 (1916), No. 23, pp. 785-787.

Iron: Conservation of Iron Ore Resources. C. K. LARTH. *Iron Trade Review*, Vol. 59 (1916), No. 21, pp. 1045-1046.

Iron and Steel Export Shipments. F. A. KELLY. *Iron Trade Review*, Vol. 98 (1916), No. 20, pp. 1132-1134.

Kelp Industry of the Pacific Coast. A. H. WRIGHT. *Iron Trade Review*, Vol. 45 (1916), No. 11, pp. 31-33.

Laboratory Efficiency. H. M. JOHNSON. *Engineering and Mining Journal*, Vol. 102 (1916), No. 22, pp. 945-946.

Lubricants: Roll-Neck Lubricants; Their Reclamation. W. M. DAVIS. *Blast Furnace and Steel Plant*, Vol. 50 (1916), No. 12, pp. 564-565.

Magnesian: A Sedimentary Magnesian Deposit. J. A. ELMER. *Metallurgical and Chemical Engineering*, Vol. 15 (1916), No. 20, pp. 999-1007.

Measuring the Flow of Compressed Air. F. A. KELLY. *Iron Trade Review*, Vol. 98 (1916), No. 19, pp. 1052-1055.

Oil Engine: A Unique American Oil Engine. J. C. FERRISS. *Iron Trade Review*, Vol. 58 (1916), No. 11, pp. 15-17.

Petroleum: Problems Connected with the Recovery of Petroleum from Unconsolidated Sands. W. H. KILPATRICK. *Iron Trade Review*, Vol. 59 (1916), No. 21, pp. 1045-1046.

Potassium Chlorate: Manufacture. A. H. BREWER. *Metallurgical and Chemical Engineering*, Vol. 15 (1916), No. 11, pp. 623-624.

Pressure Tests of Welded Boiler Tube Vessel. R. H. GILBERT. *Power*, Vol. 44 (1916), No. 20, pp. 674-676.

Pulp: Testing Pulp for Color and Strength. R. B. WILSON. *Power*, Vol. 44 (1916), No. 20, pp. 674-676.

Recrystallization after Deformation. H. M. JOHNSON. *The Iron Trade Review*, Vol. 59 (1916), No. 21, pp. 1045-1046.

Rubber: Local Growth of Rubber and Gutta-percha Plants. R. C. JOHNSON. *Metallurgical and Chemical Engineering*, Vol. 15 (1916), No. 11, pp. 623-624.

Schroeder: New Schroeder Process. W. H. JOHNSON. *Metallurgical and Chemical Engineering*, Vol. 15 (1916), No. 11, pp. 623-624.

Silica: The Importance of Efficient Sampling. J. W. AVERY. *Metallurgical and Chemical Engineering*, Vol. 15 (1916), No. 11, pp. 623-624.

Steam: Pump Water Heat for Generating Steam. A. C. BOYCE. *Iron Trade Review*, Vol. 59 (1916), No. 20, pp. 1045-1046.

Steam: Needed by Perfect Engine. J. H. SELL. *Power*, Vol. 44 (1916), No. 20, pp. 674-676.

Steam: Needed by Perfect Engine. J. H. SELL. *Power*, Vol. 44 (1916), No. 20, pp. 674-676.

Steam: Needed by Perfect Engine. J. H. SELL. *Power*, Vol. 44 (1916), No. 20, pp. 674-676.

Steam: Needed by Perfect Engine. J. H. SELL. *Power*, Vol. 44 (1916), No. 20, pp. 674-676.

Steam: Needed by Perfect Engine. J. H. SELL. *Power*, Vol. 44 (1916), No. 20, pp. 674-676.

Steam: Needed by Perfect Engine. J. H. SELL. *Power*, Vol. 44 (1916), No. 20, pp. 674-676.

MARKET REPORT—DECEMBER, 1916

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON DECEMBER 15

INORGANIC CHEMICALS

Acetate of Lime.....	100 Lbs.	3.50	@	3.60
Alum. lump ammonia.....	100 Lbs.	4 1/4	@	4 1/4
Aluminum Sulfate, high-grade.....	Ton	70.00	@	90.00
Ammonium Carbonate, domestic.....	Lb.	13 1/4	@	14
Ammonium Chloride, gray.....	Lb.	10 1/4	@	11
Aqua Ammonium, 26°, drums.....	Lb.	5 1/4	@	6
Arsenic, white.....	Lb.	7 1/2	@	7 1/2
Barium Chloride.....	Ton	95.00	@	100.00
Barium Nitrate.....	Ton	11	@	12
Barytes, prime white, foreign.....	Ton	—	@	—
Bleaching Powder, 35 per cent.....	100 Lbs.	4.50	@	4.75
Blue Vitriol.....	Lb.	12 1/4	@	13
Borax, crystals, in bags.....	Lb.	8	@	8 1/4
Boric Acid, powdered crystals.....	Lb.	12	@	12 1/4
Brimstone, crude, domestic.....	Long Ton	35.00		
Bromine, technical, bulk.....	Lb.	1.40	@	1.50
Calcium Chloride, lump, 70 to 75% fused.....	Ton	23.00	@	26.00
Calcium Chloride, granulated.....	Ton	39.00	@	—
Caustic Soda, 76 per cent.....	Lb.	4 1/4	@	4 1/4
Chalk, light precipitated.....	Lb.	4 1/4	@	—
China Clay, imported.....	Ton	18.00	@	30.00
Feldspar.....	Ton	8.00	@	15.00
Fuller's Earth, foreign, powdered.....	Ton	35.00	@	—
Glauber's Salt, in bbls.....	100 Lbs.	57	@	60
Green Vitriol, bulk.....	100 Lbs.	1.00	@	1.05
Hydrochloric Acid, commercial, 18°.....	Lb.	1 1/4	@	1 1/4
Hydrochloric Acid, C. P., conc., 22°.....	100 Lbs.	1 1/4	@	1 1/4
Iodine, resublimed.....	Lb.	4.25	@	4.30
Lead Acetate, white crystals.....	Lb.	13	@	13 1/4
Lead Nitrate.....	Lb.	16	@	16 1/4
Litharge, American.....	Lb.	10	@	11
Lithium Carbonate.....	Lb.	1.02	@	1.05
Magnesium Carbonate.....	Lb.	21	@	22
Magnesite, "Calced".....	Ton	6.00	@	7.00
Nitric Acid, 36°.....	Lb.	4 1/4	@	4 1/4
Nitric Acid 42°.....	Lb.	6	@	6 1/2
Phosphoric Acid, sp. gr. 1.750.....	Lb.	36	@	38
Phosphorus yellow.....	Lb.	1.00	@	1.10
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, casks.....	Lb.	41	@	42
Potassium Bromide (granular).....	100 Lbs.	1.30	@	1.35
Potassium Carbonate, calcined, 80 @ 85%.....	Lb.	35	@	40
Potassium Chlorate, crystals, spot.....	Lb.	65	@	67
Potassium Cyanide, bulk, 98-99 per cent.....	Mixture	1.40	@	1.60
Potassium Hydroxide.....	Lb.	80	@	85
Potassium Iodide, bulk.....	Lb.	3.45	@	—
Potassium Nitrate.....	Lb.	32	@	33
Potassium Permanganate, bulk.....	Lb.	2.75	@	3.00
Quicksilver, 8ask, 75 lbs.....	Lb.	80.00	@	—
Red Lead, American, dry.....	Lb.	9 1/4	@	10 1/4
Salt Cake, glass makers'.....	Ton	13.00	@	14.00
Silver Nitrate.....	Oz.	43 1/4	@	—
Soapstone in bags.....	Ton	8.00	@	12.00
Soda Ash, 58%.....	100 Lbs.	3.00	@	3.05
Sodium Acetate.....	Lb.	10	@	11
Sodium Bicarbonate, domestic.....	100 Lbs.	1.65	@	1.70
Sodium Bicarbonate, English.....	Lb.	3 1/4	@	3 1/4
Sodium Bichromate.....	Lb.	19	@	21
Sodium Chlorate.....	Lb.	24	@	26
Sodium Fluoride, commercial.....	Lb.	—	@	—
Sodium Hyposulfite.....	100 Lbs.	1.25	@	1.30
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	3.00	@	3.10
Sodium Silicate, liquid.....	100 Lbs.	1.50	@	3.40
Sodium Sulfide, 30%, crystals, in bbls.....	Lb.	1 1/4	@	2
Sodium Bisulfite, powdered.....	Lb.	5 1/4	@	5 1/2
Strontium Nitrate.....	Lb.	28	@	30
Sulfur, flowers, sublimed.....	100 Lbs.	2.30	@	2.70
Sulfur, roll.....	100 Lbs.	1.95	@	2.05
Sulfuric Acid, chamber, 66° Bé.....	Ton	26.00	@	28.00
Sulfuric Acid, oleum (fuming).....	Ton	40.00	@	45.00
Talc, American white.....	Ton	9.00	@	12.00
Terra Alba, American, No. 1.....	100 Lbs.	85	@	90
Tin Bichloride, 50°.....	Lb.	15.00	@	—
Tin Oxide.....	Lb.	50	@	52
White Lead, American, dry.....	Lb.	25	@	26
Zinc Carbonate.....	Lb.	13	@	14
Zinc Chloride, commercial.....	Lb.	9 1/4	@	9 1/4
Zinc Oxide, American process XX.....	Lb.	6 1/4	@	7 1/4

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	48	@	50
Acetic Acid, 56 per cent, in bbls.....	Lb.	8	@	8 1/2
Acetic Acid, glacial, 99 1/2%, in carboys.....	Lb.	32	@	34
Acetone, drums.....	Lb.	22	@	23

Alcohol, denatured, 180 proof.....	Gal.	60	@	62
Alcohol, grain, 188 proof.....	Gal.	2.65	@	2.70
Alcohol, wood, 95 per cent, refined.....	Gal.	80	@	82
Amyl Acetate.....	Gal.	4.00	@	4.50
Aniline Oil.....	Lb.	24	@	25
Benzoin Acid, ex-toluol.....	Lb.	9.00	@	10.00
Benzol, 90 per cent.....	Gal.	58	@	60
Camphor, refined in bulk, bbls.....	Lb.	85	@	86
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	52	@	55
Carbous Bisulfide.....	Lb.	6 1/4	@	6 1/2
Carbon Tetrachloride, drums, 100 gals.....	Lb.	17	@	18
Chloroform.....	Lb.	55	@	56
Citric Acid, domestic, crystals.....	Lb.	65	@	67
Cresol, U. S. P.....	Gal.	1.25	@	1.30
Dextrine, corn (carloads, bags).....	100 Lbs.	3.95	@	4.00
Dextrine, imported potato.....	Lb.	16 1/2	@	17
Ether, U. S. P., 1900.....	Lb.	15	@	20
Formaldehyde, 40 per cent.....	Lb.	11 1/4	@	12
Glycerine, dynamite, drums included.....	Lb.	55	@	55 1/2
Oxalic Acid, in casks.....	Lb.	47	@	50
Pyrogallie Acid, resublimed bulk.....	Lb.	3.25	@	—
Salicylic Acid.....	Lb.	1.15	@	1.20
Starch, cassava.....	Lb.	—	@	—
Starch, corn (carloads, bags) pearl.....	100 Lbs.	2.90	@	2.95
Starch, potato.....	Lb.	9 1/4	@	11
Starch, rice.....	Lb.	10	@	11
Starch, sago.....	Lb.	4.15	@	4.25
Starch, wheat.....	Lb.	8	@	9 1/4
Tannic Acid, commercial.....	Lb.	60	@	70
Tartaric Acid, crystals.....	Lb.	66	@	68

OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	37	@	38
Black Mineral Oil, 29 gravity.....	Gal.	13 1/4	@	14
Castor Oil, No. 3.....	Lb.	16	@	20
Ceresin, yellow.....	Lb.	16	@	20
Corn Oil, crude.....	100 Lbs.	12.50	@	13.00
Cottonseed Oil, crude, f. o. b. mill.....	Gal.	85	@	86
Cottonseed Oil, p. s. y.....	Lb.	12 1/4	@	13
Cresosote, beechwood.....	Lb.	2.00	@	2.25
Menhaden Oil, crude (southern).....	Gal.	68	@	70
Neat's-foot Oil, 20°.....	Gal.	1.20	@	1.10
Paraffine, crude, 120 m. p.....	Lb.	3 1/4	@	3 1/2
Paraffine Oil, high viscosity.....	Gal.	29 1/4	@	30
Rosin, "P" Grade, 280 lbs.....	Bbl.	6.85	@	—
Rosin Oil, first run.....	Gal.	38	@	—
Shellac, T. N.....	Lb.	39	@	40
Spermaceti, cake.....	Lb.	25	@	30
Sperm Oil, bleached winter, 38°.....	Gal.	92	@	93
Spindle Oil, No. 200.....	Gal.	24	@	25
Stearic Acid, double-pressed.....	Lb.	13	@	13 1/4
Tallow, acidless.....	Gal.	1.05	@	1.06
Tar Oil, distilled.....	Gal.	34	@	36
Turpentine, spirits of.....	Gal.	49 1/2	@	—

METALS

Aluminum, No. 1, ingots.....	Lb.	63	@	65
Antimony, ordinary.....	Lb.	14 1/4	@	14 1/2
Bismuth, N. Y.....	Lb.	3.05	@	3.10
Copper, electrolytic.....	Lb.	33 1/2	@	—
Copper, lake.....	Lb.	33 1/2	@	—
Lead, N. Y.....	100 Lbs.	7.62 1/2	@	7.65
Nickel, electrolytic.....	Lb.	50	@	55
Platinum, refined.....	Oz.	100.00	@	—
Silver.....	Oz.	76 1/4	@	—
Tin.....	Lb.	42	@	42 1/2
Tungsten (Wol).....	Per Unit.	20.00	@	—
Zinc, N. Y.....	100 Lbs.	11.25	@	11.50

FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	4.20	@	4.25
Blood, dried F O B Chicago.....	Unit	3.80	@	—
Bone, 4 and 50, ground, raw.....	Ton	28.50	@	30.00
Calcium Cyanamid.....	Unit of Ammonia	2.75	@	—
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	4.50	@	10
Phosphate, acid 16%.....	Ton	12.00	@	—
Phosphate rock; f. o. b. mine.....	Ton	2.75	@	3.00
Florida land pebble, 68 per cent.....	Ton	5.00	@	5.50
Tennessee, 78-80 per cent.....	Ton	450.00	@	475.00
Potassium "muriate" basis 80 per cent.....	Unit	15 1/4	@	16
Pyrites, furnace size, imported.....	Ton	3.80	@	10
Tankage, high-grade; f. o. b. Chicago.....	Unit	3.80	@	10

AT EASTON, PA.

No. 2

Advertising Manager: M. A. WILLIAMSON

H. E. BARNARD, H. K. BENSON, F. K. CAMERON, B. C. HESSE, A. D. LITTLE, A. V. H. MORY, M. C. WHITAKER

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879

35 East 41st Street, New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY EASTON, PA.

EDITORIALS:

Life and Personality of Dr. Stieglitz. W. D. Harkins . . .	118
The Niagara Situation and the Efficiency of a Democracy	120
"Neither Fish, nor Flesh, nor Good Red Herring" . . .	121
Intellect Conquers Appetite	121
A Noteworthy Contribution	122
In Search of One's Own	122
An Institute for Analytical Research	122

ORIGINAL PAPERS

Corrosion of Ingot Iron Containing Cobalt, Nickel, or Copper. Herbert T. Kaimus and K. B. Blake	137
Notes upon Oil Testing. Augustus H. Gill	138
Color Tests for Oils—Palm Oil. Augustus H. Gill	136
Wet Combustion in the Nitrosite Combustion Method for the Direct Determination of Rubber. L. G. Wesson and E. S. Knorr	139
Determination of Mineral Fillers in Rubber Aniline Method. Otto H. Klein, John H. Link and Frank Gottsch	140
The Free Carbon of Wood-Tar Pitches. H. K. Benson and L. L. Davis	141
The Determination of Gasoline Vapor in Air. R. P. Anderson	142
A New Qualitative Test and Colorimetric Method for the Estimation of Vanillin. Clarence Estes	142
Absorption of Tin by Proteins and Its Relation to the Solution of Tin by Canned Foods. R. C. Goss	144
The Utilization of Ammonium Chloride by Yeast Charles H. Hoffman	148
Syrups for Canning and Preserving. June B. McLean	144
Banana Stalks as a Source of Potash. H. E. Billings and A. W. Christie	145
The Relative Availability of Acid Phosphate and Raw Rock Phosphate in Indiana Field Experiments Conner	143
The Action of Calcium Carbonate on Acid Phosphate Egbert W. Magruder	145
A Contribution to the Theory of Emulsions. I. and on Pharmaceutical Practice. Leo Rosin and Walter F. Oesper	146

LABORATORY AND FIELD

Recent Developments in Chemical Engineering Equipment H. D. Miles 151
Emulsification of Mineral Lubricants: Col. A. J. G. H. 152
and Test Method F. H. Corbridge 153
The Sampling of Fertilizers F. J. L. 154
An Improved Tubular Arrangement for Chemical Reactors Clarence V. Heath 155

Appendix

Our Analytical Chemistry and Its Future. By J. H. Hillebrand. 1904. 100 pp. Price, \$1.00.

The First Report upon the Chemical Industries of the United States and Their Relation to National Progress. C. A. Brown.....	177
The Human Side of the Development of Chemical Industry. G. W. Thompson.....	181
The Chemist in the Canned Food Industry. W. D. Brown.....	185
Some Observations on the Present Status of the Subject of the Availability of Nitrogen in Fertilizers. Chas. B. Lippman.....	187

PERKIN MEDAL AWARD

Introductory Address.	Jerome Alexander	10:00
Presentation Address	C. F. Chamberlain	10:15
Address of Acceptance	Ernest Twitchell	10:30
The Twitchell Process	and the Glycerine Trade.	A. C. Langham
The Twitchell Process in the Soap and Candle Industry	Martin H. Ittner	10:45
An Appreciation of Dr. Twitchell	H. R. Schmidt	11:00

CURRENT INDUSTRIAL NEWS

[illegible]

American Institute of Higher Education	1997
University of California, Center for Investigation	2000

[illegible]

Presented by: Date: _____

UNIVERSITY OF TORONTO
 JOHN D. COOPER

From *Faraday's Annals*, Transactions of the Electrochemical Society of Chemical Society, The Association of London and Westminster, 1836.

1990-1991	1991-1992
1992-1993	1993-1994
1994-1995	1995-1996
1996-1997	1997-1998
1998-1999	1999-2000
2000-2001	2001-2002
2002-2003	2003-2004
2004-2005	2005-2006
2006-2007	2007-2008
2008-2009	2009-2010
2010-2011	2011-2012
2012-2013	2013-2014
2014-2015	2015-2016
2016-2017	2017-2018
2018-2019	2019-2020
2020-2021	2021-2022
2022-2023	2023-2024
2024-2025	2025-2026
2026-2027	2027-2028
2028-2029	2029-2030
2030-2031	2031-2032
2032-2033	2033-2034
2034-2035	2035-2036
2036-2037	2037-2038
2038-2039	2039-2040
2040-2041	2041-2042
2042-2043	2043-2044
2044-2045	2045-2046
2046-2047	2047-2048
2048-2049	2049-2050
2050-2051	2051-2052
2052-2053	2053-2054
2054-2055	2055-2056
2056-2057	2057-2058
2058-2059	2059-2060
2060-2061	2061-2062
2062-2063	2063-2064
2064-2065	2065-2066
2066-2067	2067-2068
2068-2069	2069-2070
2070-2071	2071-2072
2072-2073	2073-2074
2074-2075	2075-2076
2076-2077	2077-2078
2078-2079	2079-2080
2080-2081	2081-2082
2082-2083	2083-2084
2084-2085	2085-2086
2086-2087	2087-2088
2088-2089	2089-2090
2090-2091	2091-2092
2092-2093	2093-2094
2094-2095	2095-2096
2096-2097	2097-2098
2098-2099	2099-2100
2100-2101	2101-2102
2102-2103	2103-2104
2104-2105	2105-2106
2106-2107	2107-2108
2108-2109	2109-2110
2110-2111	2111-2112
2112-2113	2113-2114
2114-2115	2115-2116
2116-2117	2117-2118
2118-2119	2119-2120
2120-2121	2121-2122
2122-2123	2123-2124
2124-2125	2125-2126
2126-2127	2127-2128
2128-2129	2129-2130
2130-2131	2131-2132
2132-2133	2133-2134
2134-2135	2135-2136
2136-2137	2137-2138
2138-2139	2139-2140
2140-2141	2141-2142
2142-2143	2143-2144
2144-2145	2145-2146
2146-2147	2147-2148
2148-2149	2149-2150
2150-2151	2151-2152
2152-2153	2153-2154
2154-2155	2155-2156
2156-2157	2157-2158
2158-2159	2159-2160
2160-2161	2161-2162
2162-2163	2163-2164
2164-2165	2165-2166
2166-2167	2167-2168
2168-2169	2169-2170
2170-2171	2171-2172
2172-2173	2173-2174
2174-2175	2175-2176
2176-2177	2177-2178
2178-2179	2179-2180
2180-2181	2181-2182
2182-2183	2183-2184
2184-2185	2185-2186
2186-2187	2187-2188
2188-2189	2189-2190
2190-2191	2191-2192
2192-2193	2193-2194
2194-2195	2195-2196
2196-2197	2197-2198
2198-2199	2199-2200
2200-2201	2201-2202
2202-2203	2203-2204
2204-2205	2205-2206
2206-2207	2207-2208
2208-2209	2209-2210
2210-2211	

EDITORIALS

As the result of the annual ballot for officers of the American Chemical Society, the following elections have been recorded:

President: Professor Julius Stieglitz, of the University of Chicago.

Directors: Professor M. T. Bogert, of Columbia University, and Dr. A. D. Little, of A. D. Little, Inc., Boston, have been re-elected.

Councilors-at-Large: Dr. A. L. Day, of the Geophysical Laboratory, Washington, D. C., and Dr. C. L. Alsberg, of the Bureau of Chemistry, Washington, D. C., have been re-elected. Dr. M. C. Whitaker, of the United States Industrial Alcohol Company, New York City, and Dr. Irving Langmuir, of the Research Laboratories, General Electric Company, Schenectady, N. Y., were also elected.

An election is now being held by letter ballot of the Council for a director to fill the unexpired term of Dr. E. G. Love, the present Treasurer, who is *ex officio* a member of the Board of Directors.

LIFE AND PERSONALITY OF DR. STIEGLITZ

By W. D. HARKINS

Julius Stieglitz, the newly elected president of the American Chemical Society, is not only one of the most eminent organic chemists in the country, but is also one of its authorities on the application of physical chemistry in the teaching of analytical chemistry. For many years he has been very closely associated with the chemical society, as chairman of the Chicago Section, Councilor-at-Large, Associate Editor of the *JOURNAL*, and Chairman of the Chemical Section of the American Association for the Advancement of Science. He was a member of the committee on the revision of the constitution of the Society in 1912, and chairman of the committee which did such painstaking work last year in the settlement of the Allyn case, in which the question of pure food regulation was involved.

Dr. Stieglitz was born in Hoboken, New Jersey, May 26, 1867. When ready for college he took the entrance examinations for the College of the City of New York, but did not enter there. He went to Germany instead and was educated in Karlsruhe, and at the Universities of Berlin and Goettingen, where his work was done with A. W. Hofmann, Tiemann, and Victor Meyer. In his thesis he developed ideas which were quite new to Tiemann and found so many points in his work for which the explanations given at that time by chemists were unsatisfactory, that it has kept

him busy ever since to develop more satisfactory theories in regard to them. Thus his whole work has proceeded in logical sequence, and has grown somewhat as a tree grows, keeping every part properly correlated to the others. The fundamental subject on which his work has been done seems to be the mechanism of chemical reactions. While it is evident that organic chemistry is the best field in which to study such a subject, Dr. Stieglitz was one of the first of organic chemists to see that such endeavors as his must be futile if made without the aid of physical chemistry; hence, in pursuing his main idea, he was led to work on such subjects as catalysis, the solubility product, the theory of indicators and the relations between the carbon



JULIUS STIEGLITZ, PRESIDENT AMERICAN CHEMICAL SOCIETY

dioxide of the atmosphere and the purity of gypsum deposits as part of a study of climatic conditions of former ages. A great deal of his work has been on molecular rearrangement, and from such investigations he has obtained a vast fund of information bearing upon electron theories of valence. Unfortunately he has been either too busy or too modest to publish a considerable part of his material.

Dr. Stieglitz is a member of the National Academy of Sciences, the American Academy of Arts and Sciences, the Washington Academy of Sciences, and of

many other scientific societies. He has been elected president for 1917 of the Scientific Research Society, Sigma Xi.

In the University of Chicago, where he has worked for twenty-five years, Dr. Stieglitz has advanced from Docent to Chairman of the Department of Chemistry and Director of the Laboratories of the University. His ability as an administrator was particularly apparent in his influence upon the organization of the medical work, which was so helpful that President Harper, who considered this a turning point in the history of the University, stated that no one could estimate the value of his services. His reputation as a teacher is so widely recognized that Slosson, in his book on "Great American Universities," states: "Professor Stieglitz is one of those very rare individuals who have an equal mastery of the laboratory and of the lecture room, and who are able to direct research and elementary students at the same time without neglecting either." His tendency to sacrifice his own advantage for the general good, is illustrated by his acceptance of the heavy duties of Director of the Laboratories when already overburdened with executive work, because he saw that he could be of help in the development of the research facilities of all the laboratories by seeing that the funds available are used in the most efficient way. His acceptance of his first appointment in the university was characteristic of the man, for he came as docent at the request of Professor Nef on a salary of "nothing a year," because he recognized that the new university would be of the highest type and he saw the possibility of a career in science.

In beginning his work in the university he set before himself three things to be accomplished: first, to teach well; second, to do as much and as good research work as possible; and third, to be of some help in the general development of the university. The combination of these three aims has made his services of extreme value.

A very large part of his time is spent in looking after the welfare of the students, from freshmen up to men who took their Ph.D. ten or more years ago, to see that everyone is done justice, to make sure that the money available for helping students goes to the most deserving, to remove as much as possible the retarding effects of red tape in university administration upon the progress of the student, and to make sure that those who have left the university get as much advancement in their work as he is able to obtain for them. This personal interest the students recognized when they presented him with a memorial to show their appreciation of his work as leader of the movement in the faculty to modernize the curriculum, and to remove the prescription of books for all science students, which served as a bar to their progress. Last June, at the Quarter Centennial of the founding of the University of Chicago, the Division of Philosophy of the Department presented him with a loving cup in recognition of his great services to their behalf.

One of his cherished plans for his department just at present is the development in it of work in industrial chemistry, and the departmental faculty has recommended to the Trustees the establishment of a chair of industrial chemistry.

As President of the American Chemical Society, Dr. Stieglitz would like to encourage most strongly intimate relations of the universities and colleges with the industrial life of the nation, but with the settled purpose of protecting pure science in the universities. He believes that the industries are based upon pure science, and that to neglect the latter in America would be "to kill the goose that lays the golden egg." He is an ardent believer in preparedness, for he feels that all of our efforts in life must be in vain, so long as there is in the world no security for life. From the same standpoint he is very strongly in favor of very strenuous endeavor on the part of the human race in its warfare against disease—so he has always worked hard to get the university to undertake medical research on somewhat the plan of the Rockefeller Institute.

Perhaps it is his feeling in this connection which has made him one of the most active workers on the Council of Chemistry and Pharmacy of the American Medical Association. This Council has exposed many fraudulent patent remedies, and has caused even the leading manufacturers of medicines to conduct their business with much more regard to the health and life of those who take the medicines. Before the establishment of this Council the American public had absolutely no protection against the avarice of the manufacturers, or the ignorance of chemistry on the part of the average practitioner of medicine.

Professor Stieglitz's success in all of his work is probably due most of all to two characteristics: first, his great clarity of vision, and second, the intensity of his effort. He is very efficient, systematic, and an extremely hard worker.

For recreation he plays golf, which he enjoys, and he also recognizes that his output of work is increased by using a part of his time in this way. He is extremely fond of music and plays the cello.

One of his brothers is one of New York's best known physicians, and the other is a well-known artist who has received a medal for his photographs. One of Dr. Stieglitz's own hobbies is photography.

Among the thirty names that were listed on the list of the American Chemical Society under the heading of "men who have made a contribution to the progress of chemistry" in 1916, Dr. Stieglitz's name was listed. He is one of the few men who have made a contribution to the progress of chemistry in this way, and his name is listed on the list of the men who have made a contribution to the progress of chemistry in this way.

Dr. Stieglitz's name is on the American Chemical Society's list of the men who have made a contribution to the progress of chemistry in this way, and his name is listed on the list of the men who have made a contribution to the progress of chemistry in this way.

THE NIAGARA SITUATION AND THE EFFICIENCY OF A DEMOCRACY

On Friday, January 19th, President Wilson signed the measure giving temporary relief to the industries dependent on power derived from the Niagara River. The event has unusual significance. From time to time we are as a people somewhat prone to criticize the slowness of Congress in enacting much desired legislation. Especially during the past two years have we had striking illustration of the remarkable efficiency resulting from autocratic mandate or from orders-in-council. In such moods patriotic pride leads us to seek consolation in many other unrelated advantages which we enjoy under representative form of government; and so we strike the balance in our own favor; yet, after all, with a longing for greater speed in legislation.

Is the case really so bad? When a real emergency arises can we not enact needed legislation directly and quickly? Confidence in such national efficiency is gained by the recollection of the promptness with which Congress appropriated \$50,000,000 for defense at the outbreak of the war with Spain. Another emergency has recently arisen, and again Congress has proved to the country its ability to move rapidly in giving relief. During the past year constantly increasing quantities of the power developed by American capital on the Canadian side of the Niagara River have been taken over by the Canadian Hydro-Electric Commission for Canadian use. This, however, was at the expense of the important electrochemical industries on the American shore which had derived much of their needed power from the American development on the Canadian side of the river. Many plants were threatened with shut-downs for lack of current, and as the products of these plants, notably abrasives, carbon electrodes, automobile material, etc., were needed in factories throughout the country, the situation became acute.

Efforts for relief through the War Department failed, as the present Secretary of War ruled that he had no authority without specific legislation to issue permits for increased take-off of water on the American side. The matter was not subject to diplomatic adjustment, as no bad faith could be imputed to the Canadian authorities. Under the treaty of 1910 between the United States and Great Britain, the Canadian government had the right to take 36,000 cubic feet of water per second, the government of the United States 20,000 cubic feet. Pending the completion and proclamation of this treaty, the Burton law, originally enacted in 1906, to be effective for three years, was re-enacted for a further period of two years. Under this act the maximum take-off on the American side was 15,600 cubic feet per second. Expecting the passage of general legislation for control of water power use at Niagara this Burton law was again extended for a two-year period, expiring on March 4, 1913. Since that time nothing has been done in the matter of legislation.

With the aid of the War Department a resolution was recently drafted giving the Secretary of War

authority to grant temporary relief until July 1st, 1917, up to the maximum amount, 20,000 cubic feet, allowed by treaty. This joint resolution (S. J. Res. 186) was introduced in the Senate on December 19th, 1916, by Senator Wadsworth of New York, and immediately referred to the Committee on Foreign Relations. On the following day it was reported favorably by the Committee and promptly passed by the Senate. On December 22nd the resolution was discussed in the House, and amended on motion of Chairman Flood to restrict the authorization of the Secretary of War to March 4th, 1917, instead of to July 1st, 1917, as adopted by the Senate. The intervening holidays led to postponement of final action by the House. On January 4th the joint resolution was taken up by the House as the unfinished business, and was further amended, on motion of Representative Mann, fixing a penalty charge at the rate of \$100 per annum for each cubic foot of water diverted daily after the date set in the resolution for the termination of the permit. In this amended form the resolution was passed by the House. Conferees were named by both bodies and as a result of the conference the following joint resolution has been adopted by both the Senate and the House and has received the signature of the President:

"Resolved by the Senate and House of Representatives of the United States of America in Congress assembled, That the Secretary of War be, and he is hereby, authorized to issue permits, revocable at will, for the diversion of water in the United States from the Niagara River above the Falls for the creation of power to individuals, companies, or corporations which are now actually producing power from the waters of said river, in additional quantities which, with present diversions, shall in no case exceed the capacity of the generating machinery of the permittee and tenant companies now installed and ready for operation, nor an amount sufficient to enable the permittee to supply the now existing hydroelectric demands of the individuals, companies, or corporations which said permittee and tenant companies are now supplying, but not in excess of the capacity of power-using appliances of said consumers now installed and ready for operation: Provided, That in no event shall the total quantity of water diverted in the United States from said river above the Falls for power purposes exceed in the aggregate a daily diversion at the rate of twenty thousand cubic feet per second: And provided further, That this resolution shall remain in force until the first day of July, nineteen hundred and seventeen, and no longer, at the expiration of which time all permits granted hereunder shall terminate, unless sooner revoked; and nothing herein contained shall be held to confirm, establish, or confer in or upon any such permittee any right in or to the water which he is now diverting or which he may be authorized to divert hereunder. Any such permittee who without further authority of Congress diverts after the time herein named for the expiration of such permit any part of the additional amount of water authorized by Congress to be diverted for the first time under this resolution shall be guilty of a misdemeanor and be punished by a fine not exceeding \$2,000 nor less than \$500, or by imprisonment not exceeding one year nor less than thirty days, or both, in the discretion of the court; and each and every day on which such violation occurs or is committed shall be deemed a separate offense: Provided, That where such violation is charged against the company or corporate body, the offense shall be taken and deemed to be that of any director, officer, agent, or employee of such company or corporate body ordering, directing, or permitting the same."

"NEITHER FISH, NOR FLESH, NOR GOOD RED HERRING"

Some five years ago we suggested through the columns of *Science* the need of a readjustment of the policies of the American Association for the Advancement of Science. These suggestions proceeded from a loyal interest in the welfare of that organization and a deep-seated conviction of the important relation it bore to the advancement of the higher life of the Nation. Because of the rapidly increasing number of members of the various special scientific societies and of the constantly lengthening programs it was rapidly becoming a physical impossibility to conduct meetings of the Association along the enjoyable and thoroughly stimulative lines of earlier years. The Association was urged, therefore, to discontinue its Annual Meetings, to aid in all possible ways the up-building of the affiliated societies, and to hold, triennially, or quadrennially, meetings which should be truly great national gatherings of the scientists of America. At such meetings the usual program of disconnected reports of the results of researches would naturally be substituted by invited reports on noteworthy research and by symposiums on problems of fundamental and far-reaching importance, programs participated in by the very ablest men of the country. Such meetings "would be inspiring to all of us and would make a national impress."

About two years ago announcement was made by the officers of the Association that quadrennial general meetings would be held. The first of these was recently held in New York City. Has the idea of a general meeting been realized? We think not, and to confirm this judgment the same question has been asked of many who attended the meetings in the various Sections and the replies have been uniformly in the negative.

The limited registration of only 2,100, while published estimates indicate the attendance of approximately 8,000, suggests a greater interest in the meetings of the numerous affiliated societies meeting during Convocation Week than in those of the greater organization. The press accounts throughout the country leave clearly the conviction that no great impress has been made upon the body politic by this gathering of scientists. Some distinguished citizens of the city of the place of meeting attended some of the sessions. We sat near one. He did not snore, but he certainly had one of the best naps he has had since he was a boy. There was no great outpouring of wealth in this center of riches to support and endow the important researches being conducted by the members of the Association. Gifts for the research fund amounted to only \$1,500. Meanwhile the Council debated the question of the entrance fee of \$5.00 and, while admitting the fine results obtained during the past year by remitting the fee in case of members from affiliated societies, nevertheless, restricted the remission in the future to such as are "elected to membership in the American Association for the Advancement of Science within one year of the election to membership in an affiliated society."

It is evident from the program that some progress has been made toward a real general meeting; but, if a frank and friendly criticism may be made, that progress is slight. The officers of the Association have failed to grasp the full possibilities of such a meeting, the possibilities of stimulating the scientific mind of the country and of arousing the general public to the far-reaching importance of the work of its scientists.

We now have neither the former gathering of a limited number of congenial spirits, nor the character of program which the term "General Meeting" implies. We are "neither fish, nor flesh, nor good red herring."

The simple voting in the Council that once in four years a general meeting shall be held, does not create a general meeting in the sense which the times demand. That legislative act must be supplemented by the activities of a Program Committee in full sympathy with the new departure and blessed with an abounding spirit of originality.

Rouse yourselves, gentlemen of the Council; throw open wide the doors of the Association by the complete abolition of the entrance fee; trust the permanency of your membership to the attractiveness of your programs and the spirit of coöperation in scientific endeavor, rather than to the fictitious fear of renewed payment of this fee because of lapsed membership; impress upon your Program Committee the thought that times have changed and that if the American Association for the Advancement of Science is to continue that great usefulness which once characterized it, new policies must be adopted to meet the changed conditions (herein lies a direct responsibility for the meeting in Chicago four years hence); bring together all classes of scientific men who have each with the other some common ground of interest; and bring into full sympathetic touch with your efforts that great mass of thoughtful American citizens whose interest can be easily if correctly aroused and whose support will quickly dispel all of your financial cares and yield an endowment for research which will be whole-hearted and effective.

INTELLECT CONQUERS APPETITE

We have been present at many meetings where papers on chemical subjects were presented. We have often noted the look of weariness on the part of hearers as the dry, unessential and almost infinitesimal details of research were enumerated or the dreary monotone of almost interminable, continuous reading of microscopic processes. We have noticed the look of joy when the topic was recalled as a means to adjust a very different feature of the scientific life for the exact purpose of attending a highly localized game or festival. That is one side of the picture.

The other side was presented at the meeting of the Institute of Chemical Engineers at the Cathedral, Ohio, at the coming of January last, when Dr. J. E. Hirsch presented his paper on the nature of strychnine. No adverse advertisement of the fact of food has been promulgated. The audience was somewhat limited and the expressions in the press were consequently almost. A few minutes after Dr.

Bucher began speaking all realized that something out of the ordinary was happening. He used no notes, yet every sentence carried the conviction that the speaker could have expounded it into a full length lecture. The subject fairly oozed out of him through every figurative pore of his being. The audience drew nearer and compacted itself as near the speaker as chair space would admit. The address originally scheduled for thirty minutes proceeded for one hour. The Entertainment Committee rushed a notice to the Chairman that in the dining room above the coffee was getting cold, the foam on the beer was disappearing, the wiener wursts were shrinking and the ever present magician was longing to exhibit his art. The Chairman so announced. Instantly men, prominent in the chemical industries, rose to their feet in all parts of the hall and shouted, "No, we don't want to adjourn, we have never heard anything like this before." At the close of another hour the speaker finally stopped, in spite of his audience. Then all caught a good long breath, realizing that they had been participants in an unusual event.

All of this suggests that our universities, in addition to the training now given in the lecture room and in the research laboratory, could well lay more stress upon training in the method of oral presentation of the results of research.

A NOTEWORTHY CONTRIBUTION

It is hoped that every reader of THIS JOURNAL will deliberately take the time to read carefully the extremely interesting and important article in this issue by Dr. C. A. Browne, on *The First Report upon the Chemical Industries of the United States and Their Relation to National Preparedness*.

In his discovery of this document, now nearly one hundred years old, Dr. Browne has made an important contribution to present-day chemical economics. Read aloud it is difficult to decide in many passages whether it is the chemists of 1831 or those of 1917 who are pleading for the independence of this country along the lines of industrial chemistry.

We of the present have been obliged more or less to express opinions as to what may happen; the framers of the report of 1831, however, spoke from the vantage point of fact and history. Their findings, therefore, give added weight to our present-day contentions.

May this article find a wide reading, not only within, but outside the ranks of chemists!

IN SEARCH OF ONE'S OWN

The extreme paucity of exchanges with which we found THIS JOURNAL equipped led us on the afternoon of January the 12th (note the date) to make a cruise to three of the principal local centers of chemical literature. Our first port of call was the Chemists' Club Library—no, we shall wait until the next issue to narrate our discoveries there, for this is an important and serious matter.

Next on the schedule was the New York Public Library. Through the very courteous reception and guidance of Director Anderson and Mr. Gamble of the Technical Division, we were able to locate quickly

a wealth of chemical literature. The current numbers were all up to date, except in the case of the German chemical literature, of which, through some strange reasoning of the British war censors, we have all been deprived for some time. The journals, moreover, were readily available, with a seeming minimum of red tape. The visit was altogether delightful.

Our good ship next bore us to the library of the Chemistry Department of Columbia University. We glanced over the current journals on the shelves and found a somewhat limited but well selected group. There lay the *Journal of the American Chemical Society* in its New Year issue. Close by was the January 10th issue of *Chemical Abstracts*, fresh from the press. As we were traveling incognito we needed no modesty so we looked with a little tingle of pride (honest confession) for the January issue of our own and our only. It was not on the top of the pile. Good! that meant that some one was interested in reading it—but a hurried glance at the reading tables gave pride a little jolt, for the hypothesis was false. An inquiry of the pleasant librarian developed the fact that it had not yet arrived (this on the 12th, and oh, how we had worked to mail the issue on the 1st).

"Oh, no, this is quite customary; the date of its arrival varies from two to four weeks after the date of issue."

"Perhaps the box hasn't been opened yet." (We could not understand this "box" reference, for in case of loss we felt confident that the postmaster had duplicate keys.)

"Probably it has not yet been mailed." (Here was something definite to work on, though we knew how splendidly our publisher had cooperated with us in getting out the issue five days earlier than usual.)

"At any rate, if the explanation is wanted it should be sought at the University Library."

So thitherward we hurried. An inquiry in the serial room soon unraveled the mystery—there was no "box," no error on the part of the publisher. Matters were taking their normal course. The record showed that the subscription was not direct, not even through an agency. One of the professors turned his copy over to the library—"It is cheaper to get it that way and probably he has not yet finished reading his copy."

You know—we always thought of New York City as the home of high finance; we little realized what rigid institutional economy must sometimes be practiced to make ends meet.

AN INSTITUTE FOR ANALYTICAL RESEARCH

The suggestion of Dr. Hillebrand in his Chandler lecture, printed in this issue, as to the desirability of an "Institute of Analytical Research," should commend itself to most serious discussion by representative gatherings of chemists. He has clearly pointed out the need for such an institution and has offered valuable critical suggestions as to the ways in which the idea might be brought to fruition. Doubtless from the multitude of counselors there would be evolved that wisdom in procedure which would insure unqualified success.

ORIGINAL PAPERS

CORROSION OF INGOT IRON CONTAINING COBALT, NICKEL, OR COPPER^{1,2}

By HERBERT T. KALMUS AND K. B. BLAKE

There have been of late, in our technical journals, voluminous discussions as to the cause and prevention of the corrosion of iron and steel.

Dr. Walker³ says: "Corrosion is an electrolytic phenomenon and can be understood by electrical engineers on purely electrochemical grounds. It takes place at ordinary temperatures only in the presence of water through the reaction



This means that a metallic iron atom electrically neutral interacts with 2 hydrogen ions present in the water and which carry electrical charges; the result is the production of an iron ion which takes up the two electrical charges from the hydrogen ions and the deposition of the two atoms of hydrogen. Energy is lost to the surroundings and appears as electricity and heat."

In general, the electrolytic theory of corrosion is accepted, according to which the principal factors which influence corrosion are: (1) the number of hydrogen ions; (2) the intimacy of contact of the hydrogen ion with the iron; (3) the solution pressure of the iron; (4) the depolarizing action of oxygen; (5) the osmotic pressure of the iron ions. Nevertheless, with these general statements in mind, there is a certain amount of dissatisfaction with the application of the electrolytic theory, particularly as it bears on prediction and remedy. Taking the electrolytic theory without further consideration, one would conclude that homogeneity in the material insures protection from corrosion while heterogeneity enhances corrosion. While this is doubtless true as one term of the summation of causes which bring about corrosion, nevertheless, the other terms are of such importance as to make this conclusion frequently contrary to observation.

Accepting the electrolytic theory, it follows in the case of iron, other conditions being alike, that the approach to absolute freedom from impurities should add to its resistance to corrosion. It does not follow, however, that of the metals technically produced, those analyzing to have the least amount of impurities are the most non-corrosive, for other conditions are by no means always alike. Stresses or strains, even in a pure metal, produced by uneven cooling of a

casting or by rolling, whether hot or cold, provide unequal solution tension at various points in the metal, particularly on the surface, and would thus promote corrosion. Also in the preparation of metals of high chemical purity, the resistance to corrosion may be decreased by gas occlusion, or in other ways, in part due to the very attempt to attain the high degree of purity.

Stresses and strains are usually partially or entirely overcome by thoroughly annealing metals to be used for sheet roofing materials, or for other purposes where corrosion is of great importance. The effect of the occlusion of hydrogen in steel has been shown by a number of investigators to be very important, and, under certain conditions, the volume of this gas occluded will reach nearly 50 per cent of that of the metal itself.

It is common knowledge that two metals when alloyed often have greater resistance to corrosion than either component metal alone. The principle applies to any number of components. This is probably always due to the formation of some compound or compounds of the two metals, or under certain special conditions, it might be due to the combination of one alloying metal with the impurities of the other metal, in such a manner as to cause the solution tension of the resulting compounds to be about alike. The effect of alloying a second metal with iron or steel may also affect the corrosion of the original iron or steel by increasing or decreasing the amount of occluded hydrogen.

Another important effect of the introduction of the second metal may be to form an oxide, when corrosion commences, which is of such an adherent nature as to form a firm coating, inhibiting further corrosion or preventing an excess of oxygen. Or, conversely, initial rusting may render the underlying iron anodic and may accelerate corrosion, perhaps in a large measure due to the moisture held by the rust. Thus, a great deal would depend upon whether or not the rust was soft and spongy or hard and adherent.

We are inclined to agree with those who consider the phenomena of corrosion more complex than has been generally stated by enthusiastic adherents of the electrolytic theory. While this theory would seem sound as a guiding principle much additional data will be needed before it can be applied to actual cases. It is accepted by engineers and practical men in general, at least in those cases where it is applied to prediction.

SUMMARY OF INVESTIGATION

The investigation is primarily upon the corrosion of ingot iron and steels, having for its technical purpose the comparison of the relative behavior of these metals under various conditions of corrosion, and a series of tests have been made for the purpose of determining the relative resistance of these metals to corrosion. The results of this investigation are published in the *Journal of Industrial and Engineering Chemistry*, Vol. 9, No. 1, 1917, and are also published in the *Transactions of the American Institute of Chemical Engineers*, Vol. 15, 1917.

¹ Authors' abstract of report to the Canadian Department of Mines, published by permission of the Director of Mines, Ottawa, Ontario. This publication is one of a series on the rusting of iron and steel, published with reference to finding increased means for corrosion. It was published at Queen's University, Kingston, Ontario, for the Mines Canada, Canada Department of Mines. See also *Iron Corrosion*, 6 (1911), 367 and 131, 7 (1912), 6, 7, 1913, 129.

² This paper was presented January 10, 1917, at the 9th Annual Meeting of the American Institute of Chemical Engineers in printed form. In the abstract of the authors it was published by this journal. The examination extended comments and criticism of the paper were presented by Dr. Allerton S. Cushman. Opportunity will be given in the March issue of *THIS JOURNAL* for presentation of the views of Dr. Cushman and any reply the authors may desire to make. This feature.

³ *Transactions of the American Chemical Society*, 19 (1916), 435.

and carbon. We have particularly in mind the addition of small quantities of these elements to the very pure iron prepared by the open-hearth method for sheet roofing material. Our interest was stimulated by the positive nature of certain very early preliminary experiments described in the next paragraph.

PRELIMINARY EXPERIMENTS

Very early in the course of these investigations on cobalt and its alloys (in the autumn of 1912), a preliminary set of alloys was prepared by adding small percentages of both cobalt and nickel to very pure iron. These alloys were exposed for several months on the roof of Nicol Hall, Queens University, Kingston, Ontario. After this exposure they were removed, and the amount of corrosion determined. In every case it was found that the addition of small percentages of cobalt and nickel had decreased the corrosion of the pure iron.¹

Following this a second set of alloys was made with the same materials, in the same way, and exposed under the same conditions as the previous set, for a period from June 16, 1913, to October 16, 1913. At the end of this exposure of 122 days, the alloys were taken in, and the rate of corrosion in grams per sq. cm. of exposed surface per year was computed.

Unfortunately, two of the alloys of this set met with accident during the exposure, owing to dropping from the supports and coming in contact with the metal roof, so that the series is not sufficiently complete to warrant giving all the details. However, the results were in general accord with those of the previous set, which led us to believe that the addition of cobalt in proper proportions to pure iron might prove of benefit to its non-corrosive properties.

The general method of procedure with these preliminary experiments was the same as that described in detail for the complete set of experiments to be described below.

The two sets of experiments above described must be considered preliminary for a number of reasons, primarily because no heat treatment was given to the alloys.

CONCLUSIONS: 1—From these preliminary experiments, it appears that additions of small percentages of both cobalt and nickel to American Ingot Iron add to its non-corrosive properties.

2—Cobalt seemed to be more effective than nickel when used in like amount.

3—These results were such as to stimulate further interest, but were not sufficiently complete or satisfactory to warrant drawing definite conclusions, particularly as to the relative effects of nickel and cobalt.

EXPERIMENTS ON NON-CORROSIVE ALLOYS PREPARED BY ADDITIONS OF COBALT, NICKEL, AND COPPER TO AMERICAN INGOT IRON

Following are the data of three extended series of observations, from which our conclusions are drawn. The materials used for the preparation of the alloys of all three series, and likewise the general procedure,

were the same for all, and are given before the numerical corrosion values for the series.

MATERIALS FOR PREPARATION OF ALLOYS—The base of all the alloys was American Ingot Iron, furnished by Dr. Beck, American Rolling Mill Company, Middletown, Ohio, and analyzing as follows:

ANALYST	Fe	S	P	C	Mn	Cu	O	Si	Ni	Ca
Dr. Beck	99.9	0.023	0.004	0.010	0.031	0.028	0.035	Trace	None	None
Authors	99.9	0.027	0.0075	0.010	0.027	0.048	...	Trace	None	None

Inasmuch as there has been some discussion in recent literature as to the effect of copper in addition to the non-corrosive properties of American Ingot Iron and similar materials, we have made, in addition to the usual check analyses, additional analyses of the copper content. Checking our value of copper as 0.048, we have the following values from independent analyses: 0.046, 0.045, 0.050. These were made by two independent analysts.

A later analysis (by Dr. Beck) of American Ingot Iron rolled into sheets for roofing material and shipped to this laboratory by the American Rolling Mills, Middletown, Ohio, is as follows:

Sample No.	34175 (8' X 4')	S	P	C	Mn	Cu
American Ingot Iron Corrosion Sheet...		0.026	0.009	0.010	0.022	0.016

The cobalt, nickel and copper were of a correspondingly high degree of purity, analyzing, respectively, 99.7 per cent cobalt, 99.3 per cent nickel and 99.8 per cent copper. The cobalt was prepared in this laboratory by reduction of purified oxide,¹ and the copper and nickel were procured from reliable sources and analyzed in this laboratory as above stated.

METHOD OF PREPARATION OF ALLOYS

CRUCIBLE AND FURNACE—The alloys were all made in lined graphite crucibles obtained either from the Dixon Crucible Company or the Jonathan Bartley Crucible Company, and were either No. 3 or No. 5 size. These crucibles were lined with first-grade powdered magnesite, the magnesite being mixed with water to bind it until set. A Hoskins electric furnace of the carbon plate resistor type was used for melting these alloys.

MELTING AND CASTING—The components of the alloy to be prepared were weighed out and put into the crucible together. Often these went into a cold furnace to be melted without pre-heating, while some were pre-heated in the Monarch Oil furnace previous to putting them into the hot electric furnace.² The temperature of the inside of the furnace was measured from time to time, observations being made with a Wanner optical pyrometer.

After the melt had received what was considered a proper furnace treatment, powdered aluminum was added as a degasifier and it was then poured into an iron mold of variable depth which formed a cylindrical ingot about 1.25 in. in diameter. The alloys of Series I and II were cast in square molds of about the same volume. The casting usually weighed in the neighborhood of 2 lbs.

The alloy was not considered satisfactory unless the crucible lining remained intact throughout, and

¹ Canada Dept. of Mines, *Bull.* 209, 1913; *This Journal*, 6 (1914), 107.

² For a description of this furnace see Canada Dept. of Mines, *Bull.* 259, 1913.

¹ The "pure" iron was American Ingot Iron.

after the furnace treatment showed no evidence of having allowed the melt to come in contact with the crucible itself.

PREPARATION OF DISCS FOR CORROSION TESTS—The castings obtained were usually from 4 in. to 6 in. long, and about 1.25 in. in diameter. To obtain samples for corrosion tests, these bars were turned into discs and when satisfactory the discs were annealed in a Fletcher Russell muffle furnace.¹ For the small samples this was done by heating them at 780° C. for 2 hrs. and allowing them to cool with the furnace during a period of 6 hrs.

After turning off a skin to get rid of the outside layer, the disc was finished to a smooth surface in a lathe, the finishing chips being kept for analysis for carbon. After this operation the discs were carefully polished on the buffing lathe and measured for exposure.

MEASUREMENT TO DETERMINE CORROSION—Before exposure several careful measurements were made of the diameters and thicknesses of the discs, the average of the measurements being taken to compute the surface. In the first preliminary set of experiments the discs were then carefully weighed, washed in alcohol to remove any form of grease, and suspended by silk threads from pegs set in a large board. The board with samples was placed on the roof. In the second preliminary set of experiments and in Series I to III, instead of suspending the discs by silk cords, holes were drilled in one edge of them and vulcanized fiber pegs were tightly inserted. These were mounted on frames as shown in Fig. 1. This method of support was resorted to as the silk cords proved unreliable, and on several occasions, after particularly severe weather conditions, samples were ruined by falling to the metal roof.

After corroding a sufficient length of time, the samples were brought in and the rust removed with a 20 per cent solution of ammonium citrate. They were then carefully washed in alcohol, dried and weighed, and the loss in weight determined as shown in the tables to follow.

ABSORPTION OF CARBON MONOXIDE GAS Although



FIG. 1. METHOD OF EXPOSURE TO WEATHER

no carbon or carbon-containing material was added to the charge, it was always found that samples

of the alloy that the carbon content had increased, in one case from 0.010 per cent to 0.48 per cent. The conclusion seems to be that carbon was absorbed from the CO atmosphere within the furnace. The action did not seem to be uniform under the conditions that prevailed, and we did not determine the conditions which governed the rate of absorption of carbon by the metal. It was definitely observed that it was far more difficult to obtain low carbon castings of the cobalt-iron alloys than it was to obtain low carbon castings of either the nickel-iron or copper-iron alloys.

CORROSION TESTS—SERIES I (No Microphotographs)

Alloys H 196 to 216, described in Table I, were exposed as noted above. They were prepared as follows:

Furnace
Crucible
Soaking
Maximum Temperature
Degasser
Heat Treatment

Hoskins Resistor furnace Type F. C. No. 33
Graphite No. 3 magnesite lined.
Duration, 30 min. at 1500° C.
Reached by melt 1560° C.
Powdered aluminum 0.2 g.
None

The other alloys reported in Table I were made up under mill conditions by the American Rolling Mill Company and were given only the standard heating necessary in the rolling process and no special heat treatment. They, with the one sample of iron (No. 34,175), came to us in the form of partially rolled sheets, approximately 1/4 in. in thickness and 10 in. in width. The discs were cut directly from these sheets and after the proper measurements were exposed in the manner already described for Series I.

CONCLUSIONS: 1—Results with the set of alloys, Nos. 196 to 216, show that in every case the alloy formed by the addition of cobalt, nickel, or copper is less corroded in the atmosphere than is American Ingot Iron. These are unannealed samples.

2—The variations in the measurements are not so great but that Conclusion (1) is apparent, but they are sufficiently great that conclusions based upon a comparison of the alloys among themselves could not be drawn from this series alone.

3—The samples, Nos. 34,175 to 44,180, prepared by the American Rolling Mill Company, show such wide variations among the observations that no conclusions could be drawn from this series alone.

4—It is noticeable throughout this series that the rust on the cobalt samples is more tenacious than that of the other samples, and particularly that it is a dark, black color and does not come off so readily as the rust on the other samples. This is particularly noticeable on the American Ingot Iron.

CORROSION TESTS—SERIES II (No Microphotographs)

The alloys H 196 to H 216 used for Series II were identical with those used for Series I, but were made by the measurements for Series I the discs were again polished, reweighed, and measured for a second exposure. The American Rolling Mill sheet of iron that was used was again exposed, but in this case the samples showed the increased corrosion in the previous test, some samples being cut from the sheet and

¹ Samples I and II were not annealed, since III, IV and V were corroded.

TABLE I—RESULTS OF CORROSION TESTS—SERIES I
 Exposed, March 18, 1914, ten o'clock. Removed, August 31, 1914. Exposure, 3984 hours

Alloy Sample	Fe	Approximate Analysis Percentages	DIMENSIONS OF DISC BEFORE EXPOSURE			WEIGHT IN GRAMS BEFORE EXPOSURE	GRAMS REMOVED OF RUST	CORROSION OF DISC		NATURE OF RUST
			No.	Diam. Thickness Area				Total Corrosion X 10 ⁸	Loss in Weight in Grams per sq. cm.	
				Cm.	Sq. Cm.					
H 201	Fe	99.75 Ni 0.25	a	3.0053	0.5735	19.60	31.7343	31.1464	0.5879	752 Rust quite tenacious
			b	2.9353	0.4829	17.99	25.4387	24.9393	0.4994	696
H 202	Fe	99.5 Ni 0.50	a	2.9972	0.5167	18.98	28.3184	27.9340	0.3844	510 Rust quite tenacious
			b	2.6507	0.5299	15.45	27.7629	27.3216	0.4413	717
			c	2.4714	0.4335	12.96	15.9782	15.5042	0.4740	905
H 195	Fe	99.0 Ni 1.0	a	2.9129	0.6670	19.433	34.7888	34.2410	0.5478	694 Rust tenacious. Sample b had fallen off
			b	2.9126	0.6316	19.132	33.0043	32.2974	0.7069	928
H 196	Fe	98.0 Ni 2.0	a	2.9515	0.6293	19.520	33.6308	33.1004	0.5304	681 Rust removed somewhat easier than H 195
			b	2.9538	0.6741	19.960	36.0536	35.5070	0.5466	687
H 197	Fe	97.0 Ni 3.0	a	2.9939	0.5960	19.687	32.4942	32.0340	0.4642	589 Rust easily removed
			b	2.9756	0.4416	18.036	23.9081	23.4407	0.4674	652
H 200	Fe	99.75 Co 0.25	a	2.9068	0.3958	16.89	20.4681	20.0148	0.4533	673 Rust removed easier than H 200. Sample b had fallen off
			b	3.0148	0.3888	17.95	21.5157	20.9614	0.5543	775
H 209	Fe	99.5 Co 0.5	a	2.7903	0.5974	17.47	28.4904	27.9386	0.5518	793 Both samples off. Rust removed quite easily. Sample b had not rusted much on one side
			b	2.9556	0.5765	19.08	30.5810	30.2152	0.3658	478
H 198	Fe	99.0 Co 1.0	a	2.9825	0.6615	20.172	36.2452	35.6630	0.5822	722 Rust dark in color and more tenacious than H 197
			b	2.9629	0.6225	19.685	33.5751	33.0090	0.5661	720
H 199	Fe	98.0 Co 2.0	a	2.7545	0.6128	17.222	28.5496	28.0173	0.5323	774 Rust dark in color and tenacious
			b	2.9315	0.5527	18.590	29.2709	28.6635	0.5574	768 Rust dark in color and quite tenacious
H 200	Fe	97.0 Co 3.0	a	3.0368	0.5592	19.82	31.5005	31.1169	0.3835	482 Rust dark in color and quite tenacious
H 205	Fe	99.75 Cu 0.25	a	3.0178	0.5533	19.55	31.0141	30.5259	0.4882	627
			b	2.8759	0.5433	17.90	27.5937	27.0692	0.5245	738 Rust about the same as H 204
			c	2.8853	0.5895	18.42	30.1322	29.5943	0.5379	734
H 206	Fe	99.5 Cu 0.5	a	2.9472	0.5897	18.73	29.2433	28.6776	0.5677	761 Rust about the same as H 204
			b	2.9459	0.5579	18.81	29.6137	29.0536	0.5601	748
H 208	Fe	99.0 Cu 1.0	a	2.3835	0.7078	14.23	24.3692	23.9062	0.4630	816 Rust removed rather easily
			b	2.3772	0.6475	13.71	22.3719	21.9154	0.4656	835
H 216	Fe	100.0	a	3.6021	0.6731	26.73	44.8356	43.8024	1.0332	968 Rust quite easily removed. Sample a had fallen off
			b	3.7567	0.6153	29.43	53.3836	52.2870	1.0966	937
34175	S	0.027 P 0.0078 C 0.131	a	3.769	1.118	35.37	97.6351	96.7020	0.9331	664 Rust removed very easily
			b	3.683	1.118	34.18	95.2952	92.3370	0.9582	701 Rust removed very easily
34204	Co	0.22 Mn 0.036 Cu 0.020	a	3.718	1.047	33.95	89.1774	87.5760	1.6014	118 Rust more tenacious than 34175, but less tenacious than 34185
			b	3.698	1.049	33.32	88.3738	87.9770	0.3968	292
34196	Co	0.57 Mn 0.031 Cu 0.021	a	3.723	1.101	34.32	94.0772	93.2020	0.8752	640 Rust tenacious; not very different from 34204
			b	3.735	1.135	35.22	97.4638	96.5120	0.9518	678
34185	S	1.09 Mn 0.032 Cu 0.025	a	3.682	1.105	34.20	92.2378	91.1260	1.1118	823 Rust very tenacious
			b	3.712	1.091	34.22	92.5329	91.7200	0.8129	613 Rust very tenacious
44009	Ni	0.70 Mn 0.025 Cu 0.27	a	3.728	1.014	33.75	86.8718	85.8190	1.0528	783 Rust very tenacious, not unlike 34185
			b	3.739	1.063	34.50	91.4208	90.2970	1.1238	819

prepared for exposure in the manner described. The results appear in Table II.

CONCLUSIONS: 1—Results with the set of alloys, numbers 196 to 216, show that in every case the alloy formed by the addition of cobalt, nickel or copper is less corroded in the atmosphere than is American Ingot Iron. These are unannealed samples.

2—Conclusion (1) for Series II is in accord with the corresponding conclusions for Series I. Comparing the absolute amounts of corrosion (loss in weight in grams per sq. cm. of original surface per hour) we find that it is uniformly greater for Series I than for Series II, approximately in the ratio of 3 to 2. This may be in some measure accounted for by the fact that the exposure for Series I was largely in the summer time, whereas the exposure for Series II was both in summer and winter. It is more to be accounted for, however, by the fact that the exposure for Series II was of very nearly twice the duration that it was for Series I. After corrosion has continued for a certain period, especially with the more non-corrosive alloys, a hard, tenacious, dark-colored rust is formed which tends to protect the alloy against further corrosion.

3—The variations in the measurements are not so great but that Conclusions (1) and (2) are apparent, but the variations are sufficiently great that comparisons between the various alloys cannot be drawn without further confirming measurements to establish the law.

4—Samples Nos. 34,175 to 44,009, prepared by the American Rolling Mill Company, so far as this series alone is concerned, do not tend to bear out the

conclusions from the series prepared at the laboratory. From these samples alone it would seem that additions of small amounts of cobalt, up to one per cent, have very little effect on corrosion, and that the addition of nickel to about 0.7 per cent was harmful.

5—It is noticeable throughout this series, for the samples prepared at the laboratory, that additions of cobalt, nickel and copper all tend to make the rust more tenacious, darker in color, more uniform, and very much more difficultly removed by mechanical means than is the case with the pure American Ingot Iron. This fact is particularly noticeable with the cobalt samples.

CORROSION TESTS—SERIES III (*Microphotographs made*)

The samples of Series I and II received no heat treatment after casting. For further investigation Series III was prepared; a list of the alloys of this series with the method of preparation appears in Table IIIA, page 130.

FURNACE TREATMENT—In this series of alloys some of the charges were preheated in the Monarch Oil Furnace and some were introduced directly into the hot Hoskins Furnace. The data of preparation of two alloys by each treatment are given in detail. All samples of this series were prepared by one or the other of these methods as indicated. Any variation from these will be noted under the individual charge.

Samples were prepared from these alloys in the manner previously described and mounted for exposure on the roof of Nicol Building, Queens Uni-

TABLE II—RESULTS OF CORROSION TESTS—SERIES II
 Exposed, October 10, 1914. Removed, August 30, 1915. Period of Exposure, 7776 hours

Alloy Sample			APPROXIMATE ANALYSIS Percentages		DIMENSIONS OF DISC BEFORE EXPOSURE			WEIGHT IN Original Before Exposure	CORROSION OF DISC		NATURE OF RUST		
					No.	Diam. Cm.	Thickness Cm.		Area Sq. Cm.	Grams After Removal of Rust		Loss in Weight in Grams per sq. cm. $\times 10^6$	
H 204	Fe	99.75	Ni 0.25		a	2.984	0.540	17.59	28.9636	28.2924	0.6712	491	Difficult to remove. Dark mottled appearance
H 207	Fe	99.5	Ni 0.5		b	2.918	0.453	16.70	22.9425	22.3325	0.6100	470	Fairly tenacious
				a	2.980	0.487	18.49	26.1491	25.5458	0.6033	420		
				b	2.621	0.481	13.66	20.0225	19.5246	0.4979	470		
				c	2.480	0.401	12.76	14.3902	13.9915	0.3987	402		
H 195	Fe	99.0	Ni 1.0		a	2.898	0.600	18.25	30.0960	29.2932	0.7268	517	Rust tenacious, somewhat dark after removal of rust
				b	2.893	0.571	18.53	29.0754	28.4344	0.6410	445		
H 196	Fe	98.0	Ni 2.0		a	2.938	0.588	19.08	30.9354	30.2866	0.6488	437	Rust easily removed; light in color
H 197	Fe	97.0	Ni 3.0		b	2.940	0.641	19.43	33.7166	33.0554	0.6606	437	Rust easily removed; light in color
H 202	Fe	97.75	Co 0.25		b	2.982	0.561	19.18	30.2280	29.6297	0.5983	401	Rust dark, tenacious, and uniform over surface
				a	2.961	0.412	17.58	21.8434	21.2940	0.5494	402		
H 209	Fe	99.5	Co 0.5		a	2.885	0.371	16.43	18.7266	18.2327	0.4939	386	Rust medium dark in color
				b	2.759	0.550	16.72	25.5145	24.8650	0.6495	435		
H 198	Fe	99.0	Co 1.0		b	2.938	0.534	18.51	27.7878	27.1625	0.6253	500	Rust dark in color, fairly difficult to remove
				a	2.965	0.616	19.59	33.0186	32.2596	0.7590	478		
H 199	Fe	98.0	Co 2.0		b	2.940	0.590	19.03	30.5180	29.8162	0.7018	478	Rust dark in color
				a	2.730	0.584	16.74	26.4266	25.7902	0.6364	498		
H 200	Fe	97.0	Co 3.0		b	2.911	0.522	18.09	26.8364	26.1593	0.6771	482	Rust easily removed; metal underneath dark in color
				a	3.022	0.535	19.45	28.4286	27.8894	0.5392	356		
H 205	Fe	99.75	Cu 0.25		b	3.002	0.528	19.08	28.8106	28.2609	0.5997	371	Rust easily removed; metal underneath dark in color
				a	2.853	0.516	17.38	25.1354	24.5636	0.5718	414		
H 206	Fe	99.5	Cu 0.5		b	2.865	0.557	17.93	27.4168	26.8236	0.5932	415	Rust hard in spots, metal underneath dark in color
				a	2.918	0.515	18.07	26.6298	26.0090	0.6208	443		
H 208	Fe	99.0	Cu 1.0		b	2.918	0.520	18.12	26.8750	26.2528	0.6222	442	Rust light in color, metal underneath pitted
				a	2.353	0.673	13.65	21.3946	21.9834	0.4112	387		
H 216	Fe	100.0			b	2.350	0.616	13.20	20.4918	20.0884	0.4034	392	Rust very uniformly distributed and difficult to remove
				a	3.578	0.522	25.97	30.7980	30.5724	1.2256	608		
34175	S Mn	0.027 P	0.0078 C	0.131	b	3.732	0.584	28.66	49.7338	48.1793	1.5545	698	Rust easily removed
					a	2.897	0.769	20.12	36.7010	35.7888	0.9122	585	
34204	Co	0.22	Mn 0.036	Cu 0.020	a	2.561	0.768	16.42	30.5996	29.8434	0.7562	592	Rust light in color and fairly easily removed
					c	2.293	0.770	13.70	24.5528	23.9235	0.6293	591	
					d	2.050	0.766	11.47	19.3758	18.8358	0.5400	605	
					a	3.952	0.767	34.00	73.1770	71.6781	1.4989	567	
34196	Co	0.57	Mn 0.031	Cu 0.021	b	3.700	0.773	30.31	64.5962	63.1962	1.4000	594	Rust light in color and fairly easily removed
					c	3.430	0.768	26.73	55.1002	53.9060	1.1942	604	
					d	3.180	0.766	23.02	47.2278	46.1447	1.0831	567	
					a	2.930	0.769	20.50	40.2700	39.3239	0.9461	593	
34185	Co	1.09	Mn 0.032	Cu 0.025	b	2.672	0.766	17.56	33.1640	32.3249	0.8391	613	Rust light in color and fairly easily removed
					c	2.438	0.766	15.15	27.7012	26.9839	0.7173	609	
					d	2.171	0.763	12.53	21.7768	21.2004	0.5764	592	
					a	3.810	0.773	32.03	68.4924	67.1646	1.3278	584	
44009	Ni	0.700	Mn 0.025	Cu 0.270	b	3.553	0.774	28.48	59.6067	58.1286	1.4786	580	Rust light in color and fairly easily removed
					c	3.318	0.770	28.29	51.6070	50.5487	1.0583	539	
					d	3.068	0.769	22.14	44.1810	43.2005	0.9805	579	
					a	3.313	1.025	17.43	69.1338	68.0767	1.0574	574	
44009	S	0.020 P	0.0065 C	0.140	b	3.065	1.027	14.95	58.9434	58.0252	0.9182	788	Rust light in color and fairly easily removed
					c	2.812	1.032	12.64	49.8336	48.9872	0.8464	860	
					d	2.560	1.026	10.17	41.0208	40.3096	0.7199	883	
					a	3.313	1.025	17.43	69.1338	68.0767	1.0574	574	

versity, Kingston, Ontario. This series was mounted in the same way as Series II, and the duration of exposure was 253 days, 3 hours, beginning December 22, 1914, 1.15 P.M. to December 23, 1914, 4.30 P.M. time ending September 1, 1915, 4.15 P.M. to September 2, 1915, 7.30 P.M. Total hours, 6,075.

In addition to the samples prepared as above described, another set of samples was prepared from the American Rolling Mill Company alloys, and given a similar heat treatment.

After having been exposed the samples were brought in and carefully freed from rust and final measurements made as noted in Table III B. Microphotographs of this series are shown on pages 128, 129, 132 and 133.

ACCELERATED CORROSION TESTS—SERIES IV

A few accelerated corrosion tests were made on some of these alloys, the results of which may be instructive, although not conclusive. As to what would occur under service conditions in the atmosphere, the authors do not believe that much reliance can be placed upon conclusions drawn from accelerated

tests. These measurements are included with the rest for completeness.

Accelerated corrosion tests were made on the five heats of Ingot Iron alloys submitted by the American Rolling Mill Company, as follows:

No. 44175	No. 44196	No. 44185	No. 44009	No. 44009
Fe 0.026	Fe 0.004	Fe 0.006	Fe 0.006	Fe 0.006
P 0.009	P 0.006	P 0.006	P 0.006	P 0.006
C 0.010	C 0.015	C 0.010	C 0.010	C 0.010
Mn 0.017	Mn 0.017	Mn 0.017	Mn 0.017	Mn 0.017
Cu 0.016	Cu 0.028	Cu 0.028	Cu 0.028	Cu 0.028
Co 1.14	Co 0.60	Co 0.60	Co 0.60	Co 0.60

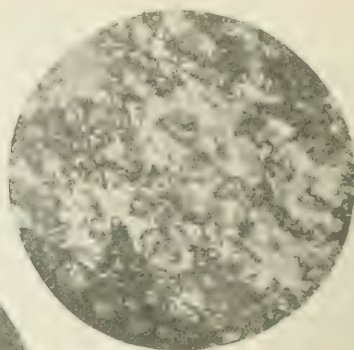
METHOD OF MAKING ACCELERATED CORROSION TESTS

These tests were made either by (a) immersing the samples in the form of spheres in a dilute solution and for a period of 1 hour and noting the loss in weight, or (b) subjecting them to the atmospheric action of dilute sulfuric acid and the atmosphere. The acid used for the tests was 10 per cent. H₂SO₄. Samples were used throughout in the form of spheres of approximately 1 cm. diameter.

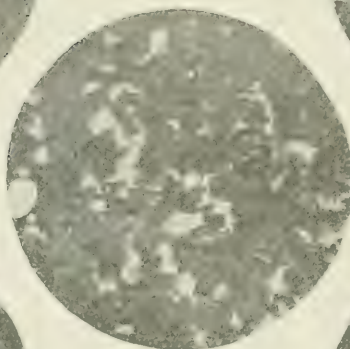
The immersion corrosion tests were made in accordance with the method in the following manner: One of a number of samples was placed in a beaker

MICROPHOTOGRAPHS
SERIES III

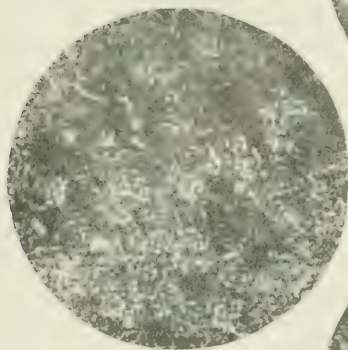
ALLOY S250
Co C Fe
0.25 0.083 99.6



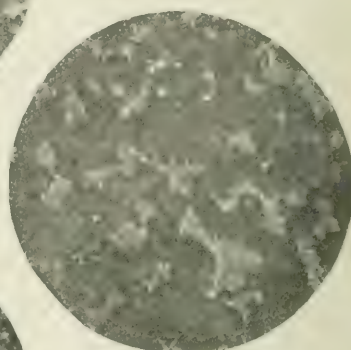
ALLOY S252
Co C Fe
0.50 0.31 99.1



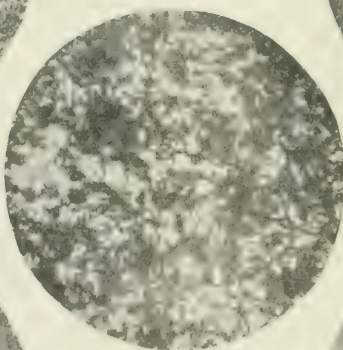
ALLOY S255
Co C Fe
0.35 0.21 99.4



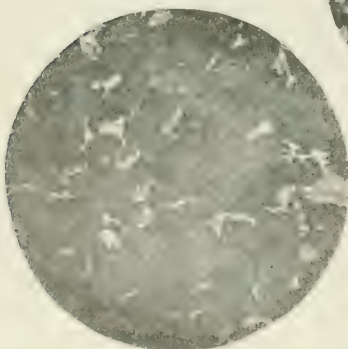
ALLOY S262
Co C Fe
1.0 0.62 98.3



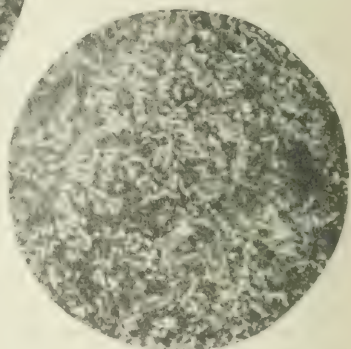
ALLOY S260
Co C Fe
0.75 0.17 99.1



ALLOY B209
Co C Fe
0.5 0.27 99.2

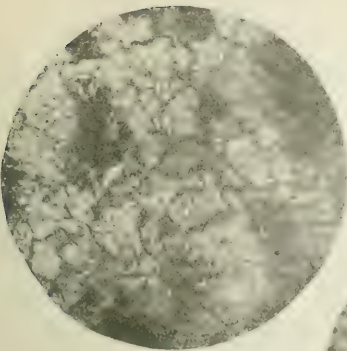


ALLOY B202
Co C Fe
0.25 0.18 99.5



ALLOY B198
Co C Fe
1.0 0.38 98.6

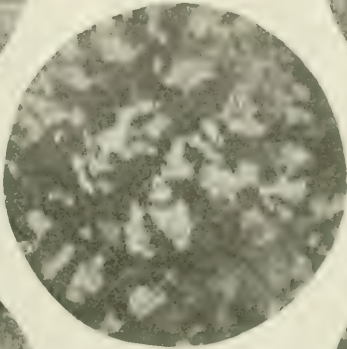
MICROPHOTOGRAPHS
SERIES III



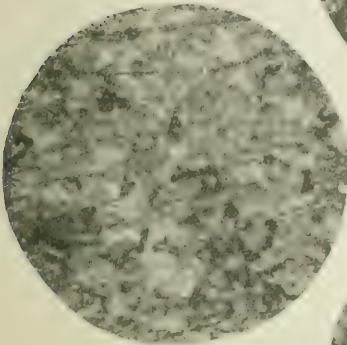
ALLOY B₂199
Co C Fe
2.0 0.16 97.8



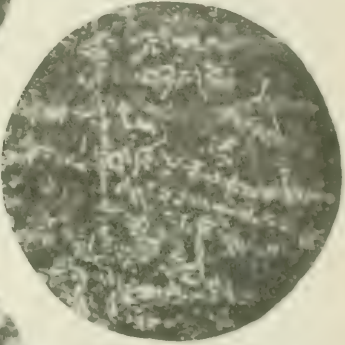
ALLOY S251
Ni C Fe
0.25 0.057 99.6



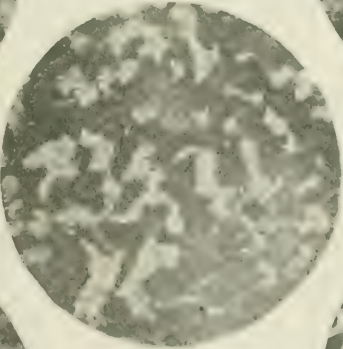
ALLOY C255
Co C Fe
0.35 0.49 99.2



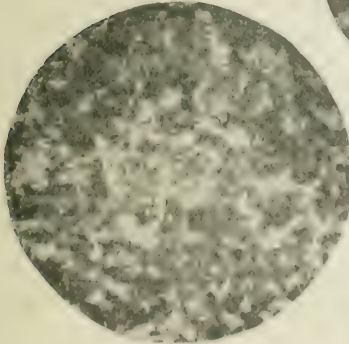
ALLOY B₂200
Co C Fe
3.0 0.17 96.8



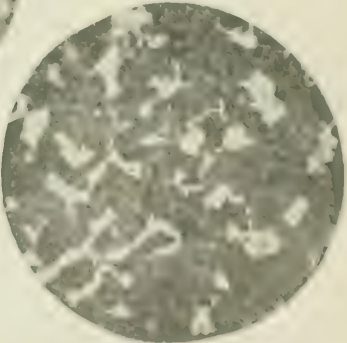
ALLOY S254
Ni C Fe
0.35 0.045 99.6



ALLOY B197
Co C Fe
0.46 0.40 97.5



ALLOY C202
Co C Fe
0.25 0.49 99.2



ALLOY S252
Ni C Fe
0.35 0.022 99.6

TABLE IIIA—COMPOSITION AND HEAT TREATMENTS OF ALLOYS—SERIES III

FURNACE: HOSKINS RESISTOR FURNACE, TYPE F. C. No. 105

CRUCIBLE: No. 3 GRAPHITE, MAGNESITE-LINED. DEGASIFIER: 0.2 G. POWDERED ALUMINUM

HEAT TREATMENT: ANNEALED BY HEATING IN GAS MUFFLE FURNACE AT 870° FOR 2 HRS., AND ALLOWING TO COOL SLOWLY WITH FURNACE

CHARGES (IN GRAMS) USED IN MAKING ALLOYS										Preheat		Temp. (°C.) of		Wt. of Casting Oz.	
										Oil Furn.	Soaking	Melt	ing		
										Min.	Min.	Max.	Max.		
										°C.	°C.	°C.	°C.		
										Alloy	Composition Percentages	Fe			
*Fe	—B 202—	1132	B 199	482	*Fe	—S 269—	566	B 202	Co 0.25 0.18	99.3	30	1570	1570 1570	20	
Co		2.85	Co	1.49	Ni	11.58	B 199	Co 2.0 0.16	97.8	30	30	1640	1700 1640	16	
S 262	B 199	603	B 30	255	C 204	—S 267—	326	S 250	Co 0.25 0.083	99.6	20	30	1560	1640 1560	19
Co		6.15	*Fe	255	*Fe	436	S 262	Co 1.0 0.62	98.3	30	30	1640	1700 1640	21	
—S 250—		778	Co	1.28	Ni	1.09	S 255(a)	Co 0.35 0.21	99.4	30	60	1640	1700 1640	21	
*Fe		1.95	Co		—C 255—		B 209	Co 0.50 0.27	99.2	20	30	1570	1570 1570	16	
Co		456	C 202	305	B 30	—S 268—	127	S 252	Co 0.50 0.31	99.1	30	30	1560	1640 1560	18
S 262		130	B 30	85	*Fe	467	S 256	Co 0.75 0.17	99.1	30	30	1640	1700 1640	21	
S 255		226	Alloy 32404	8.69	Ni	2.99	S 266(b)	Co 0.75 0.21	99.0	120	1640	1700 1640	17		
B 200		130	Co	0.65	B 207	—B 195—	B 200	Co 1.0 0.38	98.6	30	30	1570	1570 1570	24	
Pure Co		0.49	—B 199—	681	Ni	2.99	B 209	Co 3.0 0.17	96.8	30	30	1640	1700 1640	18	
—S 255—		375.5	B 198	0.65	Ni	4.04	C 202	Co 0.3 0.36	99.6	30	30	1570	1680 1570	16	
S 252		594	—B 199—	0.65	B 195	—B 196—	C 205	Co 0.35 0.49	99.2	30	30	1640	1700 1640	15	
*Fe		1.53	Pure Ni	2.85	Ni	6.95	B 204	Co 1.0 0.46	97.2	30	30	1570	1570 1570	21	
Co		467	*Fe	1132	Ni	—B 197—	S 251	Co 0.25 0.10	99.6	30	30	1570	1570 1570	20	
—S 265—		467	—S 251—	1.86	S 263	—B 197—	S 251	Ni 0.25 0.057	99.6	20	30	1560	1640 1560	20	
Alloy 32404		0.16	*Fe	743	Ni	3.68	S 254(c)	Ni 0.35 0.083	99.6	30	30	1640	1640 1640	16	
B 202	—B 209—	637	—S 254—	1.90	B 197	—B 197—	S 257(b)	Ni 0.35 0.060	99.6	20	30	1560	1640 1560	19	
Co		1.54	Ni	3.19	B 196	—B 197—	S 257	Ni 0.50 0.072	99.4	30	30	1640	1700 1640	21	
—S 252—		650	—S 257—	236	Ni	5.33	B 215	Ni 0.75 0.067	99.2	30	30	1640	1700 1640	21	
Co		1.55	S 254	495	*Fe	1.062	S 263(b)	Ni 1.0 0.065	98.9	30	30	1640	1700 1640	18	
—S 260—		576	—S 258—	935	Cu	2.66	S 269	Ni 2.0 0.085	97.9	30	60	1700	1700 1640	16	
B 200		192	—S 258—	935	*Fe	793	S 267	Ni 0.25 0.23	99.5	30	60	1700	1700 1640	24	
—S 266—		467	Ni	4.67	—B 205—	1.35	S 268	Ni 1.0 0.21	99.2	30	30	1640	1700 1640	22	
Alloy 32404		2.35	S 258	1.60	—B 206—	552	B 195	Ni 0.50 0.24	98.8	30	30	1570	1570 1570	20	
—B 198—		326	Ni	637	B 205	—B 206—	B 196	Ni 2.0 0.23	97.8	30	30	1570	1640 1570	22	
B 209		460	—B 195—	177	Cu	1.39	B 197	Ni 3.0 0.13	96.8	30	30	1640	1700 1640	8	
Co		4.80	S 261	177	Cu	1.23	B 205	Ni 0.50 0.17	99.3	30	30	1640	1700 1640	14	
—B 200—		340	—S 263—	637	—B 208—	318	B 208(a)	Cu 1.0 0.18	99.0	30	30	1640	1700 1640	14	
B 199		262	S 261	637	*Fe	279.5									
Co		11.63	Co	6.50	Cu	4.40									

(a) Cast 4 times before obtaining satisfactory sample.
(b) Cast 2 times before obtaining satisfactory sample.
(c) Cast 7 times before obtaining satisfactory sample.
(d) Cast 3 times before obtaining satisfactory sample.
(e) In this and the succeeding copper alloys the iron was first melted and the copper dropped into the molten iron through a small hole in a

*American Ingot Iron.

*American Ingot Iron.

(a) Cast 4 times before obtaining satisfactory sample.
 (b) Cast 2 times before obtaining satisfactory sample.
 (c) Cast 7 times before obtaining satisfactory sample.
 (d) Cast 3 times before obtaining satisfactory sample.
 (e) In this and the succeeding copper alloys the iron was first melted, and the copper dropped into the molten iron through a small hole in the furnace cover, the fall being directed by means of a tube of fused silica.

were covered and uncovered automatically by the tilting of this box over a knife edge pivot by the action of water from the water tap. The balls were held in place at one end of the box by pieces of glass rod.

The apparatus used for making these corrosion tests consisted of a wooden box 18 in. long and 12 in. wide, with sides about 3 in. high. This box was divided into 2 lengthwise compartments, one larger than the other, the large one being still further divided into 2 equal compartments; this division was across the narrow way of the box directly in the middle, the

dividing board extending well above the edge of the box. Across the outside of the bottom of the box in the middle a wooden knife edge was fastened.

The operation was somewhat as follows: The samples were placed in one end of the undivided lengthwise compartment, supported and held in place by glass rods, and covered with the corroding solutions. This unbalanced the box so that it inclined to one side keeping the samples under the solution until the box was tilted to the opposite side. This tilting was accomplished by opening the water tap above the

TABLE IIIB—RESULTS OF CORROSION TESTS ON ALLOYS—SERIES III

Alloy Sample	APPROXIMATE ANALYSIS Percentages				DIMENSIONS OF DISC BEFORE EXPOSURE			CORROSION OF DISC			NATURE OF RUST		
					No. (c)	Diam. Cm.	Thick. mm.	Area Sq. Cm.	Weight Original	Removal After Exposure		Loss in Weight Grams	
S 250	Fe 99.6	Co 0.25	C 0.083		a	2.898	0.303	16.78	15.4919	14.9704	0.5215	512	Rust light in color and fairly hard to remove
B 202	Fe 99.5	Co 0.25	C 0.18		b	2.787	0.473	16.25	22.2445	21.6166	0.6279	635	Rust fairly light in color and easily removed
C 202	Fe 99.2	Co 0.25	C 0.49		a	2.755	0.731	18.17	33.5618	32.8955	0.6663	604	
C 202	Fe 99.2	Co 0.25	C 0.49		b	2.690	0.415	14.83	18.1622	17.7127	0.4495	499	Rust medium dark in color and very tenacious
C 202	Fe 99.2	Co 0.25	C 0.49		c	2.480	0.430	12.97	16.0172	15.6219	0.3951	428	
S 255	Fe 99.4	Co 0.35	C 0.21		e	2.181	0.709	12.24	20.1774	19.8185	0.3589	484	
					a	2.022	0.363	17.72	17.4452	16.9153	0.5299	493	Rust light in color and fairly hard to remove
					b	2.988	0.368	17.42	17.8454	17.3428	0.5026	475	
					c	2.781	0.330	14.90	14.7667	14.2769	0.4898	542	
					e	2.940	0.463	17.80	24.0373	23.4600	0.5773	534	
S 265	Fe 99.3	Co 0.35	C 0.30		a	2.918	0.640	19.11	32.6708	31.9054	0.7654	659	Rust easily removed
					b	2.920	0.688	19.62	35.2712	34.5052	0.7660	643	
					c	2.747	0.660	15.95	33.7064	32.9352	0.7712	649	
					d	2.747	0.710	17.92	30.7998	30.1233	0.6765	622	
C 255	Fe 99.2	Co 0.35	C 0.49		i	2.655	0.526	15.40	21.8920	21.3656	0.5264	562	Rust difficult to remove
					b	2.478	0.309	11.98	11.2287	10.8213	0.4074	360	
					c	2.247	0.656	12.52	19.6978	19.2884	0.4094	585	
B 209	Fe 99.2	Co 0.50	C 0.27		a	2.873	0.550	17.75	27.1690	26.5160	0.6530	605	Rust hard to remove
					b	2.620	0.652	11.50	26.9648	26.3616	0.6032	863	
					c	2.810	0.425	11.42	19.8818	19.2750	0.6068	875	
S 252	Fe 99.1	Co 0.50	C 0.31		d	2.747	0.500	16.11	22.7015	22.3239	0.4686	479	Rust medium dark in color, tenacious
					e	2.692	0.440	15.07	19.2764	18.7810	0.4954	485	
					f	2.764	0.406	15.66	18.7750	18.3060	0.4690	493	
					g	2.881	0.510	17.59	25.7013	25.1668	0.5345	500	Rust dark in color and quite difficult to remove
					b	2.628	0.606	15.79	25.4463	24.9641	0.4822	502	
					c	2.854	0.364	18.51	27.7345	27.2048	0.5297	472	
					d	2.680	0.448	14.86	19.5841	19.1080	0.4761	527	
					e	2.582	0.553	14.92	22.0557	21.5971	0.4586	507	
					f	2.806	0.337	16.12	16.0904	15.6085	0.4819	492	

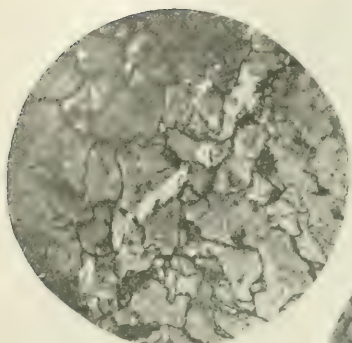
TABLE IIIB—RESULTS OF CORROSION TESTS ON ALLOYS—SERIES III—(Continued)

Alloy Sample	APPROXIMATE ANALYSIS Percentages	No. (c)	DIMENSIONS OF DISC BEFORE EXPOSURE		Area (sq. cm.)	WEIGHT IN GRAMS LOSS IN WEIGHT IN GRAMS		Total Corrosion per sq. cm. per 10 ³ hours	NATURE OF RUST	
			Diam. (in.)	Thick. (in.)		Original	After Removal of Rust			
S 266	Fe 99.0 Co 0.75 C 0.21	a	1.863	0.567	8.20	11.5887	11.3125	0.2762	555	Rust quite dark and difficult to remove
		b	2.705	0.580	16.35	25.4683	24.9446	0.4837	488	
		c	2.733	0.582	16.24	24.1817	23.6588	0.5229	530	
		d	2.720	0.564	16.35	25.1076	24.5862	0.5214	523	
B 198	Fe 98.6 Co 1.0 C 0.38	a	2.757	0.692	16.20	31.7021	31.0974	0.6047	615	Rust difficult to remove
		b	2.712	0.467	15.45	20.4550	19.9428	0.5122	545	
		c	2.703	0.547	16.04	23.9154	23.3908	0.5246	539	
		d	2.632	0.507	13.88	15.4269	15.0367	0.3902	463	Rust dark in color and hard to remove
S 262	Fe 98.3 Co 1.0 C 0.62	e	2.859	0.403	15.11	20.8344	20.3625	0.4719	514	
B ₁ 199	Fe 97.8 Co 2.0 C 0.16	b	2.597	0.930	16.44	45.6640	44.9795	0.6845	686	Rust coarse-grained, easily removed
B 199	Fe 97.5 Co 2.0 C 0.46	e	2.780	0.672	17.94	29.9907	29.4516	0.5391	495	
		a	2.857	0.662	16.56	32.6886	32.1677	0.6629	659	Rust fairly difficult to remove
		b	2.655	0.686	16.53	28.3872	27.8941	0.4931	441	
		c	2.780	0.635	17.60	29.6310	29.1169	0.5141	482	
B ₁ 200	Fe 96.8 Co 3.0 C 0.17	a	1.473	0.786	8.29	10.1161	9.8990	0.2171	433	
		a	2.900	0.373	16.57	18.9260	18.4505	0.4755	473	Rust medium dark in color, fairly coarse grained
		b	2.880	0.530	17.77	24.0182	23.5044	0.5138	476	
		e	2.882	0.513	17.86	25.7456	25.2590	0.4866	448	
B 200	Fe 96.6 Co 3.0 C 0.36	d	2.354	0.764	14.27	25.6795	25.3117	0.3678	425	Rust dark in color, difficult to remove
		b	1.857	0.624	8.97	12.8862	12.6576	0.2286	420	Exposed 4896 hours
		e	2.386	0.564	13.10	19.1863	18.9033	0.2830	446	Rust very loose
		a	2.905	0.734	19.92	37.8434	37.1360	0.7074	585	
S 251	Fe 99.6 Ni 0.25 C 0.057	b	2.772	0.587	17.14	27.4977	26.8967	0.6010	578	
		c	2.893	0.782	20.15	39.7612	39.0367	0.7245	592	
		a	2.830	0.611	17.94	29.3386	28.7089	0.6297	578	Rust coarse grained, easily removed
		b	2.568	0.552	15.10	21.8389	21.3033	0.5356	585	
B 204	Fe 99.6 Ni 0.25 C 0.10	a	2.730	0.464	15.54	20.7134	20.1127	0.6007	637	Rust dark in color and difficult to remove
		d	2.750	0.329	14.67	14.9593	14.4270	0.5323	598	
		c	2.740	0.575	16.64	25.8113	25.2424	0.5689	563	
		d	2.702	0.110	10.64	23.1422	22.5993	0.5432	588	Rust dark in color and difficult to remove
C 204	Fe 99.5 Ni 0.25 C 0.43	a	2.763	0.446	15.82	18.0503	17.5485	0.5018	522	Rust fairly loose and light in color
		b	2.770	0.653	18.90	29.8952	29.3469	0.5483	502	
		c	2.850	0.667	18.62	32.3107	31.7437	0.5670	502	
		a	2.832	0.493	16.96	23.8922	23.3215	0.5707	555	Rust coarse-grained on surface but fine grained below
S 257	Fe 99.6 Ni 0.35 C 0.060	b	2.797	0.662	16.37	30.9796	30.3607	0.6189	623	
		e	2.820	0.633	16.39	30.1311	29.5109	0.6202	623	
		a	2.818	0.390	15.88	18.6770	18.1632	0.5138	533	Rust medium in color and quite tenacious
		b	2.820	0.421	16.18	20.1592	19.6374	0.5218	531	
S 258	Fe 99.4 Ni 0.50 C 0.072	c	2.905	0.362	16.50	18.5816	18.0294	0.4522	481	Rust very dark in color and removed with great difficulty
		a	2.885	0.543	17.92	27.1168	26.7670	0.4798	442	
		d	2.479	0.579	14.04	21.4394	21.0221	0.4113	489	Rust medium dark in color, coarse-grained, tenacious
		b	2.119	0.555	10.64	14.8062	14.4988	0.3074	476	Exposed 4896 hours
S 259	Fe 99.2 Ni 0.75 C 0.067	c	2.780	0.570	17.09	26.5809	26.1139	0.4670	557	Rust fairly loose and light in color
		b	2.905	0.532	18.02	27.2486	26.6656	0.5830	533	
		a	2.865	0.425	16.63	21.0132	20.4614	0.5518	547	
		c	2.949	0.344	16.81	18.0560	17.4776	0.5784	565	
S 263	Fe 98.9 Ni 1.0 C 0.065	d	2.780	0.464	16.13	21.6476	21.1233	0.5243	533	
		e	2.901	0.596	18.56	30.4007	29.8090	0.5917	525	
		a	2.939	0.337	16.56	17.5516	17.0942	0.4574	455	Rust dark and very hard to remove
		b	2.875	0.339	16.16	16.9031	16.4033	0.4998	509	Rust dark in color and hard to remove
B ₁ 195	Fe 98.9 Ni 1.00 C 0.089	c	2.882	0.637	17.67	30.3503	29.8193	0.5310	495	
		e	2.852	0.512	17.65	25.6145	25.0789	0.5356	500	
		b	2.710	0.449	14.84	19.9142	19.4903	0.4239	470	Rust very dark in color and difficult to remove
		e	2.820	0.585	17.57	28.2365	27.7448	0.4917	462	
S 269	Fe 97.9 Ni 2.0 C 0.085	d	2.920	0.345	16.51	17.6610	17.1717	0.4893	488	Rust dark in color, coarse-grained and hard to remove
		a	2.880	0.574	18.12	27.4780	26.9605	0.5175	470	
		e	2.924	0.583	18.72	29.1942	28.7006	0.4936	538	Exposed 4896 hours
		b	2.865	0.638	18.57	31.7648	31.2547	0.5101	452	Rust dark, fine grained and quite tenacious
B ₁ 196	Fe 97.8 Ni 2.0 C 0.23	d	2.810	0.720	18.69	34.5114	34.0049	0.5065	447	
		e	2.696	0.645	16.30	28.2857	27.8783	0.4074	495	
		a	2.938	0.361	16.78	18.3561	17.9187	0.4374	429	Rust very dark and fine grained, quite tenacious
		b	2.952	0.232	15.77	12.1361	11.7085	0.4276	446	
B 197	Fe 96.7 Ni 3.0 C 0.21	c	2.818	0.224	14.39	10.6776	10.2948	0.3840	438	
		a	2.733	0.621	16.94	28.0926	27.6833	0.4093	398	Rust very dark in color
		b	2.740	0.436	15.45	19.4972	19.1351	0.3621	386	
		c	2.679	0.508	15.93	24.5124	24.1458	0.3666	379	
B ₁ 205	Fe 99.7 Cu 0.25 C 0.045	d	2.520	0.497	13.94	17.0521	16.4935	0.5586	663	Rust very loose and light in color
		b	2.768	0.464	16.02	21.2016	20.5370	0.6646	683	
		c	2.757	0.283	14.33	12.9512	12.5301	0.4211	412	
		d	2.790	0.584	17.22	27.5268	26.7933	0.7333	701	
B 205	Fe 99.6 Cu 0.25 C 0.19	e	2.790	0.653	17.85	30.6414	30.1192	0.5222	487	Rust fairly dark in color and tenacious
		a	2.800	0.663	19.10	31.2587	30.1331	0.5256	418	Exposed 4896 hours
		b	2.783	0.565	17.05	26.4556	26.0039	0.4517	440	Rust light in color and difficult to remove
		c	2.777	0.538	16.85	25.8509	25.1009	0.7402	702	
B ₁ 206	Fe 99.3 Cu 0.50 C 0.17	d	2.665	0.674	16.73	29.0202	28.5702	0.4500	443	
		e	2.805	0.586	17.43	27.8350	27.3661	0.4689	445	
		a	2.833	0.573	17.89	29.0498	28.5345	0.5153	481	Rust light in color and loose
		b	2.833	0.734	18.94	38.4891	37.9060	0.5501	418	
B 208	Fe 99.0 Cu 0.75 C 0.18	c	2.940	0.697	19.92	46.1969	45.5140	0.5520	456	
		d	2.570	0.524	13.41	22.7248	22.2673	0.4575	311	Rust dark in color, coarse-grained and difficult to remove
		b	2.620	0.272	13.81	13.1644	12.9983	0.4160	440	
		c	2.960	0.537	18.54	37.8118	37.3639	0.5544	468	
AMERICAN ROLLING MILL SAMPLES										
34204	*Fe 99.6 Co 0.35 C 0.01	a	3.238	0.731	23.84	46.9.86	46.2113	0.6873	698	Rust light in color and fairly tenacious
		b	2.989	0.823	21.34	44.0585	43.5660	0.6672	615	Exposed 4896 hours
		c	3.017	0.816	21.95	44.446	43.661	0.7858	658	Rust light in color and fairly tenacious
		d	3.140	0.814	23.16	48.9096	48.2394	0.7568	635	Exposed 4896 hours
34196	*Fe 99.3 Co 0.60 C 0.01	a	3.008	1.004	23.60	53.6016	52.9003	0.7013	660	Rust light in color and fairly tenacious
		b	2.910	0.978	23.82	51.8816	51.1813	0.6412	612	
		c	3.105	0.978	23.84	55.0917	54.3904	0.7056	613	
		d	2.993	0.999	23.13	51.1600	50.4587	0.6991	706	
34185	*Fe 98.8 Co 1.18 C 0.01	e	3.003	0.998	23.13	51.1600	50.4587	0.6991	706	
		a	3.138	1.006	23.27	60.0644	59.3631	0.7016	571	Rust medium in color and fairly tenacious
		b	3.180	0.971	23.55	60.4130	59.7117	0.7020	581	Exposed 4896 hours
		c	3.171	1.000	23.00	61.0000	60.3000	0.7000	581	Rust light in color and fairly tenacious

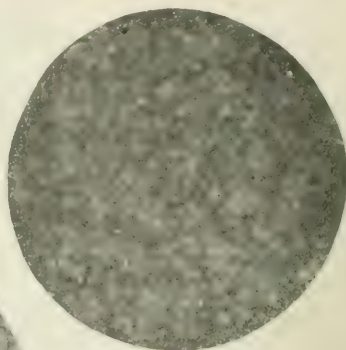
† These samples were mounted February 1, 1917, at 2.5 M.P.

American Iron and Steel Institute

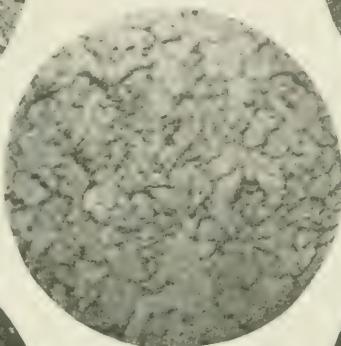
†† Etched for Microphotograph

MICROPHOTOGRAPHS
SERIES III

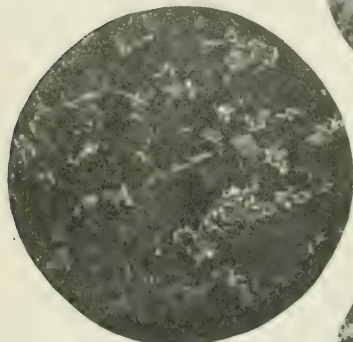
ALLOY S259
Ni C Fe
0.15 0.067 99.2



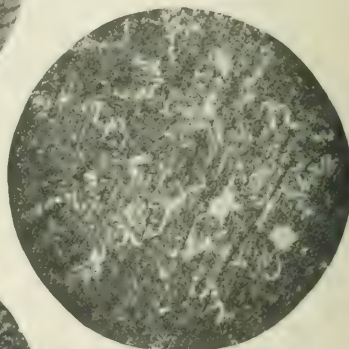
ALLOY B196
Ni C Fe
2.0 0.23 97.8



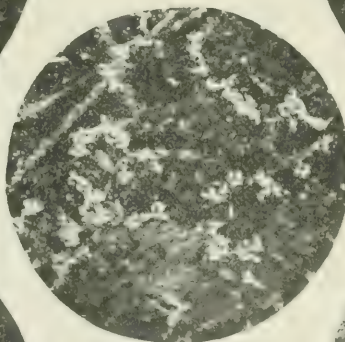
ALLOY S269
Ni C Fe
2.0 0.085 97.9



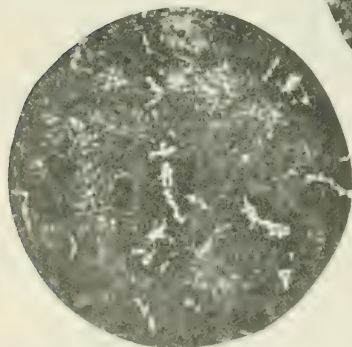
ALLOY B2195
Ni C Fe
1.0 0.089 98.9



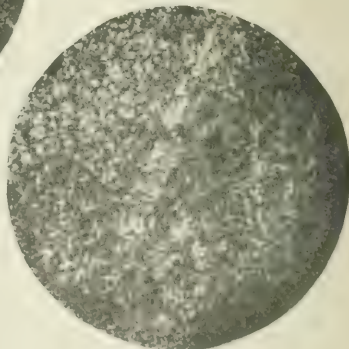
ALLOY B2197
Ni C Fe
3.0 0.13 96.8



ALLOY B195
Ni C Fe
1.0 0.24 98.8

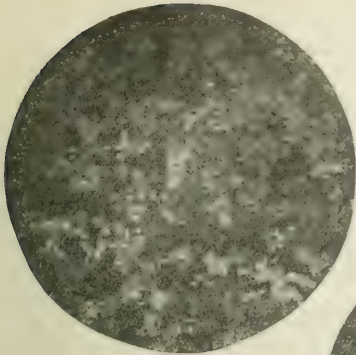


ALLOY S263
Ni C Fe
1.0 0.065 98.9

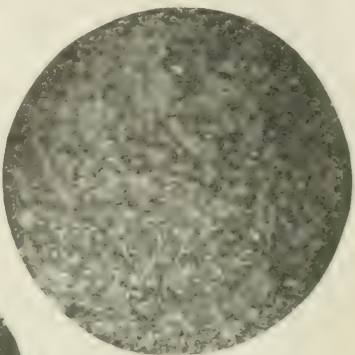


ALLOY B197
Ni C Fe
3.0 0.21 96.7

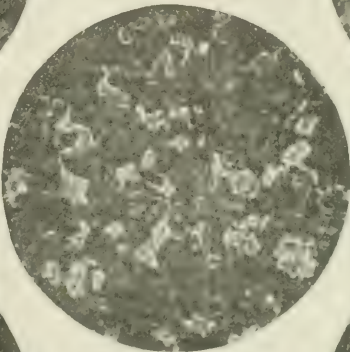
MICROPHOTOGRAPHS
SERIES III



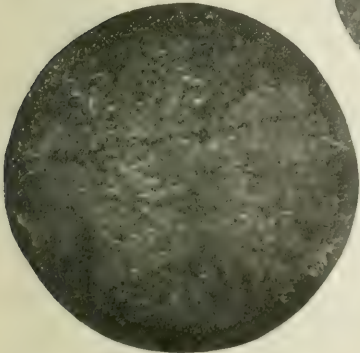
ALLOY C204
Ni C Fe
0.25 0.43 99.3



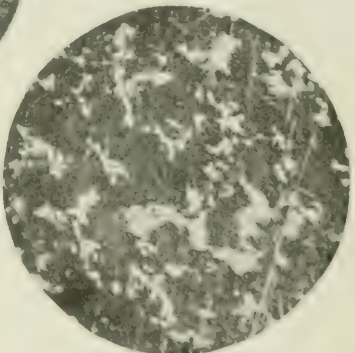
ALLOY B206
Cu C Fe
0.50 0.19 99.3



ALLOY B2206
Cu C Fe
0.50 0.17 99.3



ALLOY B2205
Cu C Fe
0.25 0.045 99.7



ALLOY B208
Cu C Fe
1.0 0.19 99.0

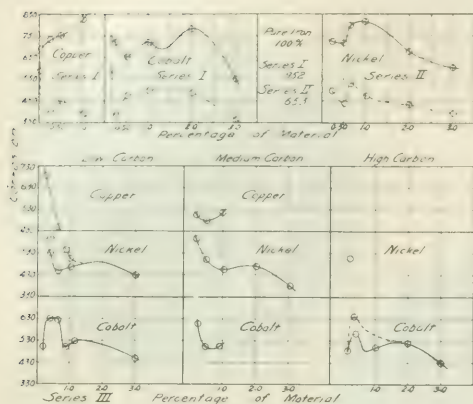
corrosion box, which allowed the stream of water to run into the high side of the large divided compartment, this being the end opposite to the one in which the samples were placed. As soon as this compartment was sufficiently full of water to overbalance the weight of the corroding solution and the samples, the box tilted, causing the solution to flow away from the samples and at the same time directing a stream of water from the tap, by means of the extended dividing board, into the other compartment, which again tended to overbalance the box and cause it to assume its original position.

In the end of each of the water compartments, just above the water line or the line to which it was necessary for the water to rise and overbalance the box, a hole was made which allowed the water to run out after it had been overbalanced. On account of the extra weight of the samples and glass rods it was necessary to have this water line fairly high, thus requiring an automatic device consisting of a glass

glass tube inserted into the hole and touching the bottom of the box, to drain completely. The action of the box was such as to tilt it according to one side at the water level, board a small trough, which carried away from the end of the water flowing over the top of the box. This compartment on the end of the box was filled by the water, which dripped through hole made in the trough for the purpose. The stream from the tap and from hole were so adjusted that a complete period of the box was about one half hour.

TABLE I. Results of Corrosion Tests (See Fig. 1)

Alloy	Time, hours	Weight loss, gms.	Area, sq. cm.	Corrosion rate, mm. per year
C204	10	0.0015	1.0	0.0015
B206	10	0.0015	1.0	0.0015
B2206	10	0.0015	1.0	0.0015
B2205	10	0.0015	1.0	0.0015
B208	10	0.0015	1.0	0.0015



laboratory for 5 hours and 5 minutes. Immersion and exposure were each divided into 12 approximately equal intervals, the twelve $4\frac{1}{2}$ -minute immersions with the corresponding twelve exposures constituting the corrosion test, which was repeated with the same set of spheres. It will be seen from Tables IV A and B

TABLE IVB—ACCELERATED CORROSION TEST, MAY 26, 1914

Sample No.	Surface sq. cm.	WEIGHT IN GRAMS			Corrosion per sq cm per hr.
		Original	Final	Loss	
34175	7.953	8.3199	8.3033	0.0166	0.00232
34185	7.808	7.8532	7.8352	0.0180	0.00256
34196	7.421	6.7530	6.7386	0.0144	0.00216
34204	7.376	6.6374	6.6222	0.0152	0.00229
44009	6.867	5.3483	5.3404	0.0079	0.00216

that the two sets of measurements agree very well among themselves and that the order of passivity of the alloys is as follows: 44,009; 34,196; 34,204; 34,175; 34,185.

For comparison with the above, the standard sulfuric acid accelerated corrosion test was run with the modified one just described. These tests were made by immersing the 5 samples above described in 20 per cent sulfuric acid continuously for 54 minutes. Table IVC gives the results of the test which was repeated with the same set of samples.

TABLE IVC—STANDARD ACID ACCELERATED CORROSION TESTS

Sample No.	WEIGHT IN GRAMS				CORROSION		
	Before	After immersion		Grams Loss in weight		per sq. cm. per hr.	
	Im- mersion	1st	2nd	1st	2nd		
34175	8.3273	8.3235	8.3199	0.0038	0.0036	0.00053	0.00052
34185	7.8608	7.8569	7.8532	0.0039	0.0037	0.00054	0.00049
34196	6.7584	6.7557	6.7530	0.0027	0.0027	0.00040	0.00040
34204	6.6440	6.6406	6.6374	0.0034	0.0032	0.00051	0.00050
44009	5.3514	5.3498	5.3483	0.0016	0.0015	0.00026	0.00024

The two tests agree with one another and show the order of passivity of the alloys to be as follows: 44009; 34196; 34204; 34175; 34185.

CONCLUSION—If these accelerated corrosion tests could be relied upon as accurately reproducing atmospheric conditions, it would be clear that the addition of monel metal to American Ingot Iron to the extent of about 1 per cent produces a more non-corrosive alloy for sheet roofing materials than the addition of similar small percentages of cobalt.

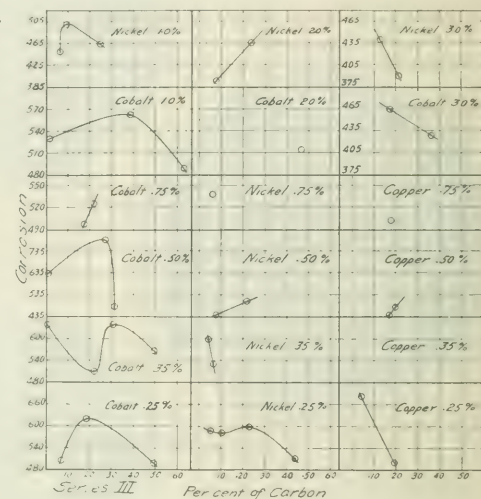
This type of corrosion test shows the alloy containing 0.06 per cent Co to be more non-corrosive than

either the one containing more (1.18 per cent) or the one containing less (0.35 per cent cobalt).

CORROSION TESTS, AMERICAN INGOT IRON ALLOYS IN THE FORM OF SHEET ROOFING MATERIALS—SERIES V

In addition to the numerous corrosion experiments on discs of the alloy above mentioned, there were atmospheric corrosion tests made on sheets of these alloys under service conditions.

Pure cobalt of the supply mentioned on page 124 was sent from this laboratory to the American Rolling Mill Company, Middletown, Ohio, early in 1913. It was arranged to make up charges in their 4-ton experimental furnace, such as could be rolled into full-sized roofing sheets to be subjected to the usual corrosion tests. Three such cobalt alloy sheets were sent to this laboratory, together with a run similarly prepared, using monel metal in place of cobalt and a

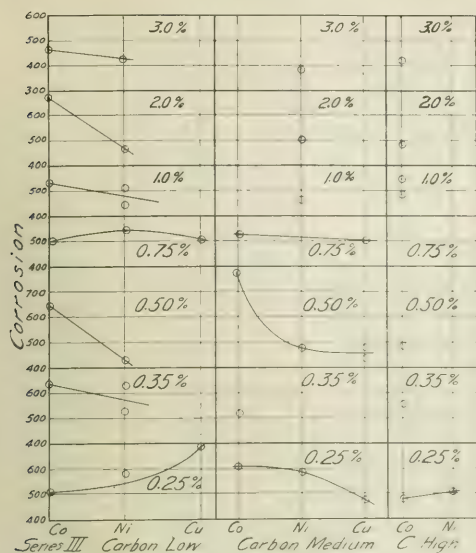


sheet of standard American Ingot Iron for comparison. These sheets were 30 in. by 96 in. in dimensions and No. 26 gauge (0.0188 in. in thickness). All of the sheets were received in duplicate and analyzed as follows:

American Ingot Iron	1 per cent Co Alloy	0.60 per cent Co Alloy	0.35 per cent Co Alloy	1 per cent Monel Metal
34175	34185	34196	34204	44009
S 0.026	S 0.034	S 0.040	S 0.022	S 0.025
P 0.009	P 0.006	P 0.008	P 0.009	P 0.008
C 0.010	C 0.015	C 0.010	C 0.010	C 0.010
Mn 0.022	Mn 0.017	Mn 0.020	Mn 0.020	Mn 0.015
Cu 0.016	Cu 0.028	Cu 0.024	Cu 0.020	Cu 0.24
	Co 1.18	Co 0.60	Co 0.35	Ni 0.75

The five sheets were mounted side by side on a wooden frame built to support them. They were exposed in a plane making 60° with a horizontal. They have been corroding since March 18, 1914, and since that time photographic and visual observations have been made at regular intervals.

It will take at least another year for these sheets to corrode through to destruction, before which time no



final conclusions can be drawn. Up to this time it would appear, however, that the loss of weight of the 1 per cent cobalt alloy and of the 0.60 per cent cobalt alloy was less than that of the others. Both of these have formed very hard, dense, tenacious, protective coatings.

While there may be some doubt as to which is the least corroded sheet of the three, the 1 per cent cobalt alloy, the 0.60 per cent cobalt alloy, or the 1 per cent monel metal alloy, there can be no doubt as to the fact that all of these three are far superior in non-corrosive action to the sheet of pure American Ingot Iron, or to the sheet containing 0.35 per cent cobalt alloy. The pure American Ingot Iron sheet is the most corroded to date.

The accompanying graphs were prepared for the purpose of visualizing the foregoing data.

GENERAL CONCLUSIONS

I—The corrosion, or loss of weight in grams per sq. cm. of original surface per hour is a function of the length of exposure, being less for the longer exposures. This is true because of the property of these alloys to form a self-protecting layer or coating.

II—The graphs representing Series I and II show remarkable similarity of form. These series were for independent corrosions of the same set of samples. Therefore such irregularities as appear in general are probably due, not to uncertainties of measurement, but to lack of control of the physical structure of the alloys in preparation.

III—The alloys formed by the addition of small percentages of copper, nickel and cobalt (from 0.25 per cent to 3.0 per cent) to American Ingot Iron, are more resistant to atmospheric corrosion than the pure American Ingot Iron, from which the alloys were prepared.

IV—Considering the data for alloys formed by adding various amounts of cobalt (from 0.25 per cent to 3.0 per cent) to American Ingot Iron, with very little, if any, carbon content, it is apparent that the corrosion is not a simple function of the percentage of cobalt content. In general, the corrosion of the alloys formed by the addition of 3 per cent of cobalt to American Ingot Iron is about 75 per cent as great as that of the alloys formed by the addition of 0.5 per cent of cobalt.

V—Alloys formed by the addition of 0.25 per cent to 3.0 per cent cobalt to American Ingot Iron, with very little, if any, carbon content, are corroded in the atmosphere to an extent varying between 50 per cent and 75 per cent of that of the pure American Ingot Iron from which the alloys were prepared.

VI—Conclusions (4) and (5) are approximately true for the corresponding nickel alloys as for the cobalt alloys. There seems to be very little choice between the use of nickel and cobalt to form alloys with American Ingot Iron containing between 0.25 per cent and 3.0 per cent of the added metal for the prevention of corrosion. This is true so far as the disc tests show, but with the exception noted in Conclusion VII.

VII—As corrosion progresses, all of the alloys prepared form self-protective coatings of oxides. It is noticeable throughout that the oxides formed by the cobalt are darker, denser, and more tenacious than those formed by the other alloys.

VIII—The preventive effect of the protective coating mentioned in Conclusion VII does not seem to have worked greatly to the advantage of cobalt alloys, in spite of its more satisfactory appearance, in the length of time that the above experiments were allowed to run.

IX—In order to establish finally the possible ultimate advantages of the cobalt alloy protective coating, as compared with the other sheets, all of the alloys should be allowed to corrode to destruction. The results of such tests, as discussed in the text above, will be published later.

X—The addition of copper to American Ingot Iron to an extent between 0.25 per cent and 0.75 per cent seems to be conducive to reducing the corrosion of American Ingot Iron under atmospheric conditions. It is difficult to say whether or not the addition of copper in these amounts has a greater effect than the corresponding amounts of nickel or cobalt. Additional experiments will be required to determine these facts, but there can be but little doubt that the addition of copper, as above reported, diminishes the corrosion of the pure American Ingot Iron.

XI—The amount of corrosion caused with the percentage of carbon in the alloy can be compared, and as may be seen best by reference to the graphs.

During the course of making the foregoing observations set forth in this paper, which extended over a period of several years, the authors were fortunate to time assisted by Mr. C. H. Harper, Research Laboratory, Queen's University, Kingston, Ont., and Professor, Moosejaw College, Saskatchewan; and Mr. W. L. Smith, Research Laboratory, Queen's University, Kingston, Ont.

University, Kingston, Ontario, now Metals Department, Deloro Mining & Reduction Company, Deloro, Ontario. The authors wish hereby to acknowledge their indebtedness to these gentlemen, and as well to Mr. R. C. Wilcox, Research Laboratory, Queens University, Kingston, Ont., now analyst, The Exolon Company Thorold, Ontario, by whom most of the analyses reported in this paper were made.

150 SOUTH STREET, CAMBRIDGE, MASSACHUSETTS

NOTES UPON OIL TESTING

By AUGUSTUS H. GILL

Received October 21, 1916

I—A TEST FOR OILS BY SALTING-OUT THEIR SOAPS

It is a well known fact to the commercial soap maker that different soap stocks require varying amounts of salt for the "salting out" process. It occurred to the writer that if this could be made quantitative, it would form an additional criterion by which to judge of the purity or genuineness of an oil.

Reference to the literature revealed the fact that this principle had already been made use of by Carpenter¹ for detecting the presence of cocoanut and palm oils in soaps. Soap from ordinary oils requires from 8 to 10 cc. of a saturated solution of salt, whereas that from cocoanut oil may require 50 cc.

The procedure is as follows: 2 g. of the oil are saponified with 5 cc. of 10 per cent caustic soda, adding alcohol if necessary. Evaporate to dryness on a water bath, dissolve the soap in warm water, cool, neutralize with hydrochloric acid, using phenolphthalein as an indicator, and make up to 50 cc. Titrate 10 cc. of this solution with salt solution (320 g. to the liter) in a bottle after the manner of the determination of hardness in water until the lather obtained just does *not* persist for five minutes. From the HCl used, and this titration with salt, calculate the grams of salt necessary to precipitate the soap found from 1 g. of oil. The following results were obtained:

TABLE I.—GRAMS NaCl PER GRAM OIL.

Oil	I	II	
Pure olive.....	2.2	2.1	
Olive Foots(?).....	10.6	11.6	Suspected sample
Cottonseed.....	8.0	8.6	
Linseed.....	14.6	12.9	
Oleomargarine.....	2.8	2.8	
Butter.....	1.4	1.2	
Cocoanut.....	No end point obtainable.		

That something was really wrong with the olive foots was evident from the fact that in making soap from them in a large way, it had to be "broken" twice and that nearly double the usual quantity of salt was required.

II—A TEST FOR GELATINOUS MATTER IN LINSEED OILS

In determining unsaponifiable matter in linseed oil, it was noticed that a white, cotton-like-looking cloud formed between the soap solution and the supernatant layer of gasoline. It was further noticed that the oils which showed the greatest amount of this cloud or sludge were slowest in drying and gave the roughest,

dullest and least elastic surfaces, particularly in patent leather finishes.

The procedure is as follows: Saponify 10 g. of the oil with 20 cc. 10 per cent caustic soda, by heating in a 6 in. porcelain dish over a low flame. Add warm water when necessary and boil until saponification is complete. Make up the soap solution to 225 cc. in a graduate with warm distilled water. Warm water should be used to prevent the hydrolysis of the soap. Pour out 25 cc. into a 6 in. test tube, seven-eighths to one inch in diameter, add 8 cc. of 86° gasoline (from Pennsylvania crude) and shake thoroughly. Whirl in a centrifuge at 1800 r. p. m. for 3 min. by the watch and observe the amount of sludge that forms between the layers.

Ordinary linseed oil gives a sludge nearly 10 mm. in thickness or more, while an artist's oil which had been thoroughly washed with water and allowed to stand and settle gave less than 5 mm. which is the smallest amount ever seen in a linseed oil.

The first linseed oil, on applying the "breaking" test, "broke" at about 295° C., while the artist's oil did not "break" below 300° C.

Attempts to remove all the sludge by centrifuging repeatedly (up to nine times in one instance) with fresh gasoline were unsuccessful. More sludge was found in the ninth than in the first centrifuging. The first time, however, gives comparative results. Attempts to make the test quantitative by collecting and weighing on a tared filter were also unsuccessful.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE

COLOR TESTS FOR OILS—PALM OIL

By AUGUSTUS H. GILL

Received October 21, 1916

The chemist uninitiated in this subject would infer that color tests for different oils rest upon the same firm basis as those for copper, iron or chromium—particularly after hearing testimony in certain legal cases. Palm oil is positively sworn to—not something giving reactions like palm oil—and this, on the strength of a single reaction lasting less than ten seconds!

Speaking from an experience of over thirty years, and from extensive and careful reading, this is not the case—color tests are merely circumstantial evidence. If a color test be obtained, there is a *probability* that a certain oil is present, but no *certainty*. Nor can any positive conclusions be drawn from any *one* test, save that of isolating unsaponifiable oil; one must have the evidence of several different tests, each confirming the other.

Nor can any other conclusion be possible. The oils are products of organic life, and this is dependent upon conditions of growth, in the case of a vegetable oil, as to whether the season be wet or dry, warm or cold, the fruit be underripe, fully ripe or overripe; and in the case of an animal oil, upon the feed. A hog fed on corn gives lard of a higher titer test and lower iodine value than one fed on mast. Similarly, cows fed upon cotton or sesame cake give milk, the fat of which responds to the same color tests as do.

¹ W. Lant Carpenter, Allen's "Commercial Organic Analysis," 2 (1910), 436.

cotton and sesame oil. To complicate further matters, we have the different varieties of the same fruit: *e. g.*, the olive, of which there are 300 different varieties in Italy alone, which yield oils which differ among themselves. Instead of wondering that the chemist cannot do more, the marvel is that he does as well as he does.

The color tests upon which some dependence may be placed are few, and are as follows:

Halphen test for Cottonseed Oil.

Becchi test for Cottonseed Oil.

Baudouin test for Sesame Oil.

Liebermann-Storch test for Rosin Oil.

Crampton-Simons test for Palm Oil (until recently).

THE HALPHEN TEST is probably the best test for cottonseed oil, and one of the more clearly marked and characteristic color tests. It is, however, also given by Kapok oil¹ (which comes from a related plant) which is used as an edible oil where the plant is grown—in China, East and West Indies, and in Africa. Baobab oil¹ also responds to it even more strongly than cottonseed. On the other hand, a negative Halphen test is no proof of the absence of cottonseed oil, as old rancid oil, one which has been heated to 200–220°, or has been blown, does not give the test.

Lewkowitsch says:² "It should be distinctly understood that color reactions taken by themselves should not be relied upon as giving a decisive answer. At best they can be used only as a preliminary test, or as a confirmatory test. The ease with which this test can be carried out, and its apparent reliability, have led to an overestimation of this very useful and important reaction; so much so that grave errors may be committed by those who assign to this test an exclusive or even a paramount importance. It is altogether unjustifiable to look upon this test, as has been done, as permitting of quantitative interpretation." It is not known what is the cause of the reaction.

THE BECCHI (OR SILVER NITRATE TEST)—Here the statements contained in the literature are very conflicting. Eminent authorities have pronounced both in favor of and against it. It is, however, to be noted that absolutely pure lard, tung and olive oil are not infrequently met with which give the test; consequently its indications cannot be considered as conclusive.

The substance which gives the reaction is supposed to be aldehydic in its nature—this receives some support from the fact that a body of a phenolic nature, Gossypol, has been discovered in the color from cottonseed hulls.

THE CAMDEN BAUDOUIN TEST is probably the most reliable of all the color tests. It should be noted, however, that it is also given by olive oil of Italy, Belgium and France but not by the fatty acids obtained from them. Furthermore, certain petroleum hydrocarbons respond to the test. Rancid sesame oil and some extracted by chloroform failed to respond. The oil

stance which gives the reaction seems to be a thick non-crystallizable oil free from nitrogen.¹

THE LIEBERMANN-STORCH TEST is a reliable test for rosin oil, but is not conclusive, as cholesterol gives the same color, which is fugitive. The substance which gives the reaction is unknown.

THE CRAMPTON-SIMONS TEST FOR PALM OIL—Lewkowitsch, in his last edition, says: "These color tests appear to the author to be very uncertain." The test was published in 1903³ and is carried out by the Department of Internal Revenue as follows:⁴ 9 cc. of the filtered fat are placed in a 15 cm. tube and 3 cc. of the subsequently described acetic anhydride reagent is added. The tube is then vigorously shaken for from 5 to 10 seconds. The color of the emulsion should be noted, as a bluish green color is indicative of the presence of palm oil. The tube is then placed into a centrifuge and whirled for from 5 to 10 seconds at about 1500 to 2000 r. p. m. It is then taken out and noticed that the tube has the appearance of two layers, the acetic anhydride in the bottom of the tube as it was before shaking, and the fats above. The color of the lower layer at this point should be noted. A light blue is indicative of the presence of palm oil. One drop of sulfuric acid, specific gravity 1.53, is added to the tube. Previous to the addition of the sulfuric acid at this point the analyst should place himself in the best light possible in the laboratory. An overhead light, such as a skylight, is the preferable sort of light in order to read the colors. After adding a drop of sulfuric acid the tube is inverted and immediately returned to its former position: as the drops of the acetic anhydride, which formed the lower layer, drop back, the color is noted. The acid has changed this acetic anhydride to a fairly deep blue. This is proof of the presence of palm oil.

It is to be noted in making this determination that several precautions are necessary: we must have experience, and the proper temperature of the fat, pure reagents and speedy manipulation, as the color changes so fast that the test has to be carried out from beginning to end in as short a time as possible.

The acetic anhydride reagent is made by adding to 50 cc. of C. P. acetic anhydride, one drop of sulfuric acid, specific gravity 1.53. Then the mixture is shaken and must stand 5 minutes before being used, as the reagent must not be used if it has stood over 10 minutes. Experience has taught us that the reagent is not sensitive for use before 30 minutes standing and is not sensitive for use after 30 minutes. The filtered fat previously described is brought to a temperature of about 45°. The point is very necessary because we have found by experience that temperatures below this do not work very satisfactorily, and very much above it.

The procedure involving the use of acetic anhydride has been modified by the Department of Internal Revenue (Circular Chemistry Division).⁵

¹ *Chemical and Technical Analysis*, 13, 1916, 20.

² *Lab. Manual*, 27, 1906.

³ *Chemical and Technical Analysis*, 13, 1916, 20.

⁴ *Department of Internal Revenue Circular Chemistry Division*, 1910, No. 100, 1913, 1, 8.

⁵ *Department of Internal Revenue*.

¹ *Michigan Chemical*, 130 (1903), 80.

² *Chemical Technology and Analysis of Fat, Oils, and Resins*, 2nd Ed., 2 (1914), 303.

"The test described is not satisfactory for the following reasons:

"(a) Other oils than palm oil give colors which are easily mistaken for the palm oil test.

"(b) The color produced is not permanent. It changes and fades so rapidly that it is very difficult to recognize it.

"(c) The test is not definite, as there is little difference in the color produced when palm oil is present and when it is absent.

"(d) The color produced is changed so much by slightly varying the amount or strength of the sulfuric acid used."

The authors state, and this has been substantiated by numerous others, that similar reactions are given by mustard and sesame oils, and that the latter can be washed out by alcohol.

A blue color obtained by the Revenue test, therefore, could equally well be due to the sesame oil, as no requirement of washing with alcohol is mentioned.

Further objections to the test are, that different chemists, skilled in the art, get different results and have difficulty in duplicating their own results. This was shown in a recent case which came to the writer's notice; numerous samples (up to 56 in some cases) were submitted to six different chemists, three technical men, one a former employee of the Revenue Bureau and another Doctor Crampton himself, three university professors, and there was practically no agreement among them. Certainly it has no claims to reliability or to be classed even with the Becchi test.

In addition to the interfering oils, mustard and sesame, it is interesting to note that the test is sometimes given by linseed oil, but not by rosin or rosin oils.

In trying to ascertain the cause of this test and of substances present in oleomargarine and likely to produce it, the statement was found in one of the quasi-scientific papers that the yellow color of butter and certain animal fats and oils was due to carotin;¹ this substance was prepared by the extraction of dried carrots with carbon bisulfide, and some of this solution added to cottonseed oil. The carbon bisulfide was evaporated off at a temperature below 70° and the resulting oil tested, when it was found to give the familiar blue color as if palm oil were present. Apparently then it was due to carotin and not exclusively to palm oil as supposed.

To substantiate this conclusion, a quantity of palm oil was saponified with alcoholic sodium hydroxide, leaving a slight excess of alkali; to ensure the absence of free palm oil, the alcohol was evaporated, and the residual soap dissolved in water and shaken out with carbon bisulfide; this assumed a deep red color. Both soap and extract were saved, the carbon bisulfide distilled off and the residue again treated with an excess of sodium hydroxide as before, to ensure the complete removal of any palm oil which might possibly have escaped saponification. The resulting soap solution was extracted with carbon bisulfide as before, with similar results. Some of this deep red carbon

bisulfide solution was added to cottonseed oil, the solvent evaporated below 70°, the oil tested, and it gave the characteristic blue color, although no palm oil was present. The fatty acids from palm oil soap solution which had been extracted with carbon bisulfide, on the other hand, did not give the usual blue color, showing that the substance producing it had been completely removed by the carbon bisulfide.

Carotin, according to Willstätter and Stoll,¹ has the formula $C_{40}H_{56}$, crystallizes either in rhombohedrons or plates, with a coppery or blue sheen. It melts at 174° (corr.), is difficultly soluble in methyl and ethyl alcohol, acetone and petroleum ether, but readily dissolves in benzol and carbon bisulfide. It is an unsaturable body (absorbing halogens) and auto oxidizable. This would account for the bleaching of palm oil by light. It dissolves in concentrated sulfuric acid with the formation of an indigo-blue color. It is further interesting from the fact that it is one of the few colored hydrocarbons.

That the substance extracted from palm oil was really carotin would seem to be shown by the following tests, being the same as employed by Palmer and Eckles in their work.²

1—By the absorption spectrum: Tested in the Krüss single-prism spectroscopie, according to the method of Formanek,³ the readings given below were obtained for the end towards the red of the absorption band between the E and F lines.

	In CS ₂ solution	In alcohol solution
Carotin from carrots.....	13.64	14.13
Carotin from palm oil.....	13.25	14.34
Carotin from grass.....	13.43	14.62

The solutions of carotin, from carrots, from palm oil and from grass, shut off the portion of the spectrum toward the violet end very sharply, as if a card had been placed between the instrument and the bottle containing the solution. The agreement, although somewhat divergent mathematically, is regarded as satisfactory. Phytosterol which might have been extracted at the same time gives no absorption spectrum.

2—It is not extracted from its petroleum ether solution by 80–90 per cent alcohol.

3—It absorbs bromine, as does carotin.

4—It is not adsorbed by precipitated chalk.

5—It gives a deep red color in carbon bisulfide solution.

6—It gives the same blue color in acetic acid when treated with sulfuric acid as does carotin from grass and carotin from carrots.

Samples of cottonseed oil which gave no test were treated with a carbon bisulfide solution of carotin obtained from palm oil, but containing no palm oil, and also with a solution of carotin from carrots. The portions of carbon bisulfide evaporated off below 70° and with palm oil were sent to two different chemists, and both reported them to contain palm oil.

The amount of carotin obtained was small, as may

¹ Willstätter and Stoll, "Untersuchungen über Chlorophyll," p. 241.

² J. Biol. Chem., 17 (1914), 190.

³ Spektral analytischer Nachweis künstlicher organischer Farbstoffe, 1900.

¹ This statement was undoubtedly based on the work of Palmer and Eckles

be judged from the fact that from 5000 kilos of fresh carrots (472 kilos dry) Willstätter and Escher¹ obtained only 125 g. of carotin. This is 2.5 parts in 100,000. Chemical tests for colors not infrequently have a delicacy of one part in one billion.

That carotin is contained in animal fats and oils was abundantly shown by the work of Palmer and Eckles² in the dairy laboratory of the University of Missouri, in cooperation with the U. S. Department of Agriculture.

They showed it to be contained in butter fat and the body fat obtained from cows, and further that it was not generated by the animal, but absorbed from the feed, particularly grass. Hence, it is easy to see why June butter is so highly colored. This work is confirmed by the Department of Internal Revenue³ in that the test similar to that given by palm oil would be given by an oleomargarine containing 20 per cent of butter or by oleo oils. This has been further substantiated by the work of other chemists.

In view of all these facts it would seem to be impossible to prove the presence of palm oil by this test alone in a mixture—oleomargarine, for example—in which butter (from 5–16 per cent) and oleo oil (45–50 per cent) were present, since all three contain the same substance—carotin, to which the characteristic blue color is due.

As a result of this work it would seem that the acetic anhydride or acetic acid-sulfuric acid test for palm oil, is no longer available for use in connection with oleomargarine for the following reasons:

I—Unreliability of this particular test, no two chemists agreeing upon its interpretation.

II—That the test is one for carotin rather than palm oil and may be given by butter, oleo oil or sesame oil—ingredients ordinarily found in oleomargarine.

III—As applied by the Revenue Department, it is untrustworthy, because interfering oils, as sesame, are not washed out.

This communication may be regarded as preliminary, as the subject is being further studied.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE

WET COMBUSTION IN THE NITROSITE COMBUSTION METHOD FOR THE DIRECT DETERMINATION OF RUBBER⁴

BY L. G. WISSON AND E. S. ENOCH

In order to make more feasible the possible use in technical laboratories of the nitrosite combustion for the direct determination of rubber in rubber goods, we have attempted the application of "combustion in the wet way" to this analytical procedure.

The "nitrosite combustion" method, as described in a previous publication,⁵ is based upon the formation of the "nitrosite" of rubber by the action of nitrogen oxide gases upon the caoutchouc of the sample. This is then separated from other substances (cellulose, and

burned in a specially constructed electrically heated combustion tube. The special apparatus and technique required was a decided obstacle to the general use of this method, even should its reliability be demonstrated, and we therefore turned to "wet combustion" as an escape from this difficulty.

In the course of our experiments, acetone-extracted crude rubber was first used. The nitrosite was formed in the flask used for the combustion, and after the complete expulsion of the rubber solvent (chloroform), the combustion followed in a manner quite similar to those later described. We obtained as dependable values 96.8, 97.0, 97.6, and 97.1 per cent $C_{10}H_{16}$, average 97.1 per cent; theoretical, 97.3 per cent $C_{10}H_{16}$.

In the regular analytical procedure this simple treatment of the nitrosite is not possible since the latter must be separated from the mineral matter and other impurities by the use of some solvent after filtration from the chloroform. We first used a solvent acetone, which was added to the dry nitrosite in the combustion flask. The acetone was first evaporated off, then the flask was heated $1\frac{1}{2}$ hrs. by a boiling water bath while a current of dry air passed slowly through the flask. The value now obtained (100.7 per cent) upon combustion, indicated a retention of acetone.

A repetition of this experiment with the use of only ethyl acetate as solvent gave 96.4, 97.1, and 97.0 per cent $C_{10}H_{16}$. These figures were more promising. Moreover, the ethyl acetate on evaporation left the residual nitrosite in a more porous, and thus more favorable, condition for rapid expulsion of the organic solvent than did the acetone. Ethyl acetate was therefore adopted as the solvent in all of the analyses of vulcanized rubber.

The use of acetic ester did not, however, eliminate our troubles with retained solvent, as we found when we next turned to the analysis of compounded rubber samples, instead of the raw gum. We believe that this difficulty explains most of the erratic results we had to the end of our work. We believe that we have now found the remedy for this retention of solvent in the addition of water, containing a drop of hydrochloric acid, to the nitrosite, and subsequent evaporation of this to dryness, after all solvent has been removed in the ordinary way.

In a sample compounded with 50 per cent Fine Para, using the method described we found 94.4, 94.6, 94.8, and 94.4 per cent $C_{10}H_{16}$, average 94.5 (theoretical, 34.4 per cent $C_{10}H_{16}$).

In a sample (C) compounded with 50 per cent plantation rubber, we found 95.0, 95.8, 95.6, and 95.1 per cent $C_{10}H_{16}$, average 95.4 per cent (theoretical, 34.4 per cent $C_{10}H_{16}$).

EXPERIMENT

PREPARATION OF THE NITROSITE FOR THE COMBUSTION.—When the rubber sample has been ground to a mesh of 100 or 200 mesh, 100 mg. (0.1 g.) of it is placed in a 100-ml. flask with acetone and $1\frac{1}{2}$ ml. of concentrated nitric acid, and allowed to stand

¹ Willstätter and Escher, *Untersuchungen über Chlorophyll*, p. 41.

² *Ind. Eng. Chem.*, **17** (1925), 190–191.

³ Evidence in court, 1915.

⁴ This article represents those work done by L. G. Wison in the course for the degree of Bachelor of Science in Chemistry at the Case School of Applied Science. Read at the 10th Meeting of the American Chemical Society, New York City, September 10, 1916.

⁵ L. G. Wison, *This Journal*, **9** (1917), 131.

to dissolve in, or thoroughly absorb, chloroform. A small Florence flask (75 cc.) is used, which may be about one-half full of the solvent. Nitrous oxide vapors, evolved from dilute nitric acid (sp. gr. 1.3) and arsenic trioxide, are then passed through the cooled chloroform until the deep green color becomes permanent for about 15 min., and the whole allowed to stand over night for completion of the action.

The chloroform is then decanted through a dry Gooch crucible and asbestos matte (the former rests in an ordinary 60° filter funnel) into the combustion flask, from which the chloroform is then evaporated by means of a boiling water bath and a dry air current.¹ Meanwhile the residue in the Florence flask has been similarly dried. The separation of fillers and nitrosite is now brought about in the following way: Small portions (5 cc.) of calcium chloride-dried ethyl acetate are added to the residue in the Florence flask, the latter warmed, and the liquid decanted through the Gooch crucible into the combustion flask, repeatedly, until the filtrate runs through entirely colorless. After evaporation of the acetate (recovery of the solvent as well), the residue is carefully freed from solvent by warming the containing flask in a boiling water bath for about 15 min., after which 15 cc. of water, containing 1 drop conc. HCl, is added, and quickly evaporated by the use of a boiling calcium chloride bath and brisk current of dry air. The heating is continued at least 1/2 hr. after the residue is again apparently dry.

THE COMBUSTION APPARATUS consists of a 200 cc. round-bottom distilling flask, which is provided with a dropping funnel (100 cc.) through a one-hole rubber stopper, and a series of U-tubes containing in order, (1) conc. H_2SO_4 - $\text{K}_2\text{Cr}_2\text{O}_7$, renewed every 1 or 2 combustions, (2) water containing a drop of the preceding, (3) granular zinc, (4) calcium chloride, (5) soda-lime (weighed), (6) soda-lime and calcium chloride (weighed).

THE COMBUSTION—The weighed soda-lime tubes in position, and the combustion flask cooled by water, a volume (20 cc.) of cooled concentrated sulfuric acid is run rapidly into the flask onto the nitrosite; then the cooled oxidizing solution of 10 g. pulverized $\text{K}_2\text{Cr}_2\text{O}_7$ in 75 cc. conc. H_2SO_4 in a very slow stream. The flask may now be gently warmed by a sand bath to obtain a moderately rapid evolution of gas.² This is done as long as gas continues to be evolved (about an hour), when a carbon dioxide-free current of air, the heating being maintained, is passed *via* the dropping funnel through the apparatus for at least 1/2 hr. to sweep all carbon dioxide into the soda-lime tubes. $\text{Wt. CO}_2 \times \frac{13.6}{44.0} \times 200$ gives percentage $\text{C}_{10}\text{H}_{16}$ in the sample.

We hope, in conclusion, that further study and im-

¹ Mr. J. F. Tuthill of the Bureau of Standards has found that the chloroform-soluble residue thus recovered may be very appreciable, and it is to his suggestion that this modification is due.

² That carbon monoxide is formed during the combustion can be shown by allowing the gases which have passed the absorption train to come in contact with heated copper oxide and then barium hydrosulfide solution. A precipitate ensues, but the amount is not appreciable for the results of the analysis.

provements of this method will eventually give a reliable and not too difficult procedure for the direct determination of rubber, not only in good quality compounds but also in factis and other inferior substitute-containing rubbers.

CASE SCHOOL OF APPLIED SCIENCE
CLEVELAND, OHIO

DETERMINATION OF MINERAL FILLERS IN RUBBER ANILINE METHOD

By OTTO H. KLEIN, JOHN H. LINK AND FRANK GOTTSCH

Received October 23, 1916

Although the use of aniline as a solvent for vulcanized rubber is not new, there is very little information to be found concerning such use in the literature. We have, therefore, thought that an account of the method as far as it has been worked out, together with some analyses of samples of known composition, would be of interest.

This report should be considered as a preliminary one, as the supply of rubber mixings at hand for our experiments was limited and other rubber fillers than those used are yet to be experimented with.

In making the determination it is essential that the sample be finely powdered (20 mesh). A 1-gram sample is extracted with acetone for 4 hours, dried at a low temperature, and then transferred to a weighed 100 cc. centrifuge tube. The residue is covered with 50 cc. of pure aniline, 5 cc. of nitrobenzene added, the mixture stirred, covered, and heated at 160° C. with occasional stirring until solution is complete.

It is our practice to heat the samples over night in a Freas oven. In most cases solution is complete by the next day. Sometimes the sample dissolves in 3 to 4 hours. If the rubber is not yet in solution, this can be seen by stirring with a glass rod. When solution is complete, there is nothing to be seen but fine pigment, free from rubbery appearance.¹ The tube is allowed to cool sufficiently, filled up with ether and well stirred. It is then centrifuged for 15 minutes at 1500 r. p. m.

The supernatant liquid is decanted, about 25 cc. of ether added and the pigment stirred up completely. It is centrifuged again and the decantate added to the first. Four such washings with ether are necessary. The tube is dried at 100° C., cooled and weighed. The united decantates are evaporated and then ignited in a weighed porcelain or silica dish; the weight of fillers found is added to that in the tube.

The percentage of fillers plus that of total acetone extract is subtracted from 100 per cent, and the difference recorded as *rubber gum*.

Aniline differs from other solvents in that rubber dissolved in it forms a thin solution which permits the mineral fillers to separate readily.

The small amount of nitrobenzene used, causes a more rapid solution. It was found that semicured compounds dissolve more slowly than thoroughly cured soft stocks or very hard ones. With undercured compounds a soft pasty mass is formed, which

¹ The chemist who makes the analysis for the first time may be uncertain of himself at this point, but after one or two determinations have been made he will at once recognize any undissolved rubber.

TABLE I—RESULTS ON SAMPLES OF KNOWN COMPOSITION: ANILINE METHOD FOR FILLERS

Sample Number:	O No. 1	O No. 2	H	I	J	U No 1	U No 3	G No 1	C	G No 14
COMPOSITION OF SAMPLES (Percentages)										
Pure Rubber (Fine).....	40.3	40.3	40.3	40.0	30.0	40.0	40.6	37.0	24.44	37.00
Sulfur.....	2.0	2.0	2.0	4.0	3.0	3.0	3.0	3.0	...	3.0
Zinc Oxide.....	18.9	18.9	18.9	...	30.0	14.0	56.4	30.0	...	30.0
White Lead (Dutch).....	18.9	18.9	18.9	15.0	11.11	...
Light Magnesia Carbonate.....	9.9	9.9	9.9	4.44	...
Hydrated Lime.....	2.0	2.0	2.0	6.67	...
Litharge.....	8.0	8.0	8.0	10.0	...	15.0	6.67	...
Whiting.....	26.0
Lithopone.....	20.0
Vermilion.....	15.0
Carbon Black.....	10.9	...
Golden Antimony.....	19.0	26.67	...
Magnesium Oxide.....	5.0
Aluminum Flake.....	17.0
Sublimed White Lead.....	38.0	20.0
Asbestos.....
Plumbago.....
Cure.....	20 X 40	90 X 40	100 X 250° F.	100 X 250° F.	100 X 250° F.	80 X 30	130 X 38	...	60' X 60 lbs
ANALYTICAL RESULTS (PERCENTAGES) BY ANILINE METHOD										
Fillers Found.....	58.76	59.36	58.72	55.00	67.03	58.60	57.56	90.05	74.11	60.44
Organic Acetone Extract.....	58.71	59.43	58.40	54.70	67.79	57.40	57.40
Free Sulfur.....	0.42	0.20	0.97	4.50	0.74	1.19	1.29	0.83	5.04	...
Rubber.....	39.75	39.17	39.44	39.34	29.60	39.53	39.33	36.86	24.79	33.04
Fillers in Dish.....	0.10	0.18	0.47	0.00	8.21	0.32	0.44	1.41	3.60	...
(a) Caucho Rubber.	0.00	0.36	0.82	0.09	5.51	0.32	0.44

is very slow to dissolve, while this does not occur if the material is properly vulcanized.

We found that in a few cases an additional digestion with half the quantity of solvent for 5 hours reduced the amount of mineral fillers about 0.5 per cent. In specification work it is advisable to make this second digestion after the ether has been expelled from the tube by heating.

In Table I, Samples O No. 1 and O No. 2 are the same, except that O No. 2 was purposely overcured. Sample H was prepared using the same recipe as for Samples O Nos. 1 and 2, but by another manufacturer. Samples H, I and J were unintentionally undercured. Sample C is a hard valve. Sample G No. 14 contains Caucho rubber.

Analysis of the fillers showed that the rubber as found by difference did not include all the sulfur of vulcanization.

It will be noted that the sum of the percentages of rubber found and of the organic acetone extract is slightly greater than the percentage of rubber used in the recipe.

The fillers during vulcanization and afterwards in the course of analysis have combined with sulfur to form new compounds. If this combination of fillers and sulfur is a substitution of sulfur for some other acid radical, the resultant product would usually weigh less than the sum of the ingredients entering the reaction and the rubber found by difference would be slightly greater thereby.

We expect to continue these experiments when other samples are available, and a final report will be made on the subject when we shall have all the data at hand.

BOARD OF EXAMINERS AND APPOINTMENTS
CENTRAL TESTING LABORATORY
150 E. Wacker Dr., New York City

THE FREE CARBON OF WOOD-TAR PITCHES

By H. R. BURGESS AND L. E. DAVIS

Received November 22, 1916

In the examination of wood tars it was found that the so-called "free carbon" of the residuum had an exceptionally high as determined by the method generally employed for this purpose. It was accordingly

considered worth while to ascertain whether the carbonaceous residue from carbon disulfide extraction really consisted of carbon or of probable hydrocarbons that are insoluble in carbon disulfide. Previous work had already shown a marked variation in the solubility of bitumens in the usual petroleum solvents, wood-tar pitch being almost completely insoluble in petroleum distillates or turpentine, and only slightly soluble in benzol.

The relative solubility of bitumens was therefore determined in carbon disulfide and acetone by the usual method. The resulting residue insoluble in a given solvent was in each case again extracted with the other solvent. The wood tars were obtained from the experimental wood distillation plant at the University of Washington, from a commercial plant in Oregon and from a hard wood distillation plant in Michigan. Commercial coal-tar pitches were taken from a local Barmen plant, the petroleum asphalt from a city paving plant and the Trinidad asphalt from a laboratory sample. The results are given in Table I.

TABLE I—RESPECTIVE SOLUBILITIES OF BITUMENS IN ACETONE AND CARBON DISULFIDE

SAMPLE	INSOLUBLE IN CARBON DISULFIDE		INSOLUBLE IN ACETONE		MEAN	PERCENT
	Per cent	In solution	Per cent	In solution		
Douglas fir pitch....	67.7	59.7%	57.7	57.8%	700	2.9
Douglas fir pitch....	62.5	30.1	31.6	31.1	185	1.0
Douglas fir pitch....	63.1	33.1	34.8	34.4	150	0.8
Douglas fir pitch....	60.2	22.0	21.5	21.5	130	0.1
Hard wood pitch....	50.7	1.2	1.2	1.2	100	0.1
Hard wood pitch....	48.0	1.2	1.2	1.2	100	0.1
Hard wood pitch....	41.8	0.4	0.4	0.4	100	0.1
Coal-tar pitch....	35.0	0.4	0.4	0.4	100	0.1
Coal-tar pitch....	35.0	0.4	0.4	0.4	100	0.1
Coal-tar pitch....	35.0	0.4	0.4	0.4	100	0.1
Coal-tar pitch....	35.0	0.4	0.4	0.4	100	0.1
Trinidad asphalt....	35.0	0.4	0.4	0.4	100	0.1
Trinidad asphalt....	35.0	0.4	0.4	0.4	100	0.1

NOTE: (a) 100° C.

1—The free carbon of wood-tar pitches cannot be determined by carbon disulfide.

2—Asphalts are supposed to be soluble in the usual petroleum solvents.

3—Coal-tar pitches may be mixed with the rubber and the resultant mixture for the determination of free carbon.

Submitted for November, 1916

Published by the American Chemical Society

THE DETERMINATION OF GASOLINE VAPOR IN AIR

By R. T. ANDERSON

Received November 10, 1916

One of the methods of determining gasoline vapor in air is to combust the mixture with oxygen in a combustion pipette according to the usual gas-analytical procedure. Assuming that the gasoline vapor contains only members of the paraffin series of compounds, the volume of gasoline vapor may be computed from the formula¹

$$V = \frac{2T.C. \cdot CO_2}{3}$$

in which V , $T.C.$, and CO_2 represent, respectively, the volume of gasoline vapor in the sample chosen for combustion, the contraction resulting from the combustion, and the amount of carbon dioxide that is formed. The chief objection to the method lies in the difficulty in obtaining complete combustion of the gasoline vapor, especially when the sample to be analyzed contains more than 5 or 6 per cent by volume. The attempt has been made by the author to develop a reliable procedure for the combustion of gasoline vapor, but up to the present time the results have not been entirely satisfactory.

In a recent article by Burrell and Robertson,² a comparison is made between the combustion method under discussion and a method involving the separation of the gasoline by condensation with liquid air, on a series of five samples of air containing gasoline vapor. The figures in Table II of their article show an excellent agreement between the results obtained by the two methods. This agreement is, however, as regards the mixtures containing high percentages of gasoline vapor, the result of the approximate method of calculation employed by Burrell and Robertson, since the results obtained by computing correctly the amounts of gasoline vapor from the combustion data are different from those given in the table.

	Cc.	1	2	3	4	5
COMBUSTION DATA						
Burrell & Robertson { Volume of Sample	50.60	46.80	34.58	28.89	40.96	
{ Contraction	2.15	4.95	4.27	10.58	25.10	
{ Carbon Dioxide	2.70	6.19	5.29	12.78	30.50	
PER CENT GASOLINE VAPOR (Burrell & Robertson):						
Approximate Calculation	1.07	2.65	3.07	8.86	14.83	
Liquid Air Separation	1.08	2.40	3.09	9.04	14.85	
GASOLINE VAPOR:						
Volume, $V = \frac{2T.C. \cdot CO_2}{3}$	0.53	1.24	1.08	2.79	6.57	
Per cent, $\frac{100V}{\text{Sample}}$	1.08	2.64	3.13	9.67	16.03	
Value of $n = \frac{CO_2}{V}$	5.06	5.01	4.88	4.58	4.65	

In the preceding table, the first five lines of figures are taken from Table II of the article by Burrell and Robertson. The approximate method of computation which they used is based upon the fact that the average composition of the gasoline vapor corresponds quite closely to the formula C_8H_{12} , and the volume of the vapor was found by dividing the volume of carbon dioxide that was obtained by 5. Lines 6 and 7 contain, respectively, the volumes of gasoline vapor obtained by computation from the combustion

¹ See de Voltaire and de Smet, *Z. anal. Chem.*, **49** (1910), 661, or Dennis' "Gas Analysis," p. 131, Table II.

² THIS JOURNAL, **7** (1915), 112. See also Burrell and Boyd, Bureau of Mines Technical Paper 115.

data, and the percentages of gasoline vapor in the samples. The agreement of the percentages in Line 7 with those given in Line 5 is good for the first 3 samples, but in the last 2 samples there is considerable difference due apparently to failure to burn completely the gasoline vapor in the combustion pipette. This idea is borne out by calculating the value of n in the hydrocarbon mixture C_nH_{2n+2} , for the different samples. This gives the apparent average number of carbon atoms per molecule (see Line 8). The decrease in the value of n with the increase in the percentage of gasoline vapor is a strong indication of the failure to get complete combustion with the richer mixtures, since the value of n presumably is actually the same in each case.

This note has been prepared for publication with the idea of correcting the impression that might be obtained from the article of Burrell and Robertson that the combustion method may successfully be used for the determination of gasoline vapor when it occurs in large amounts in air.

CORNELL UNIVERSITY
ITHACA, NEW YORK

A NEW QUALITATIVE TEST AND COLORIMETRIC METHOD FOR THE ESTIMATION OF VANILLIN

By CLARENCE ESTES

Received October 2, 1916

A colorimetric method for the estimation of vanillin in commercial vanilla extracts has been devised by Folin and Denis,¹ who employ phosphotungstic-phosphomolybdic acid reagent for development of the color. This method is somewhat tedious as it requires several reagents, two filtrations and special precautions in mixing. The author has devised a new colorimetric method, which is very simple, as it requires only one reagent and one filtration. This new method depends upon the reaction of vanillin and a solution of acid nitrate of mercury. The color produced in this reaction is violet to violet-red. This color reaction seems to be characteristic only of vanillin and the acid nitrate of mercury, as acid nitrates of many other metals were prepared in the same way as that of mercury, but in every case they failed to develop a color; also many other organic compounds containing a hydroxyl group and an aldehyde group have been substituted for vanillin in the reaction, but so far no color reaction was found which resembled that of vanillin. Some other organic compounds were found which gave a color reaction with the acid nitrate of mercury reagent; however, the colors produced could never be mistaken for that produced by vanillin.

REAGENT—ACID NITRATE OF MERCURY

Dissolving metallic mercury in twice its own weight of concentrated nitric acid (sp. gr. 1.42); after solution is complete dilute with 25 times its weight of water.

Other proportions of both mercury and nitric acid may be used instead of the one given above; however, it is necessary to have a slight excess of nitric acid as

¹ THIS JOURNAL, **4** (1912), 670.

the mercury must be in the mercuric and not in the mercurous condition.

PROCEDURE

The test is best carried out by dissolving the substance suspected of containing vanillin in about 5 cc. of water; to this solution is added about 0.5 cc. of the acid mercuric nitrate reagent. The solution is then heated in boiling water for about 5 minutes.¹ At the end of this time, if vanillin is present, a violet to violet-red color is produced. The intensity of this color produced is directly proportional to the quantity of vanillin present, as is shown later.

METHOD FOR THE COLORIMETRIC ESTIMATION OF VANILLIN

Since the color produced was directly proportional to the quantity of vanillin present and was characteristic only of vanillin, it appeared that it might be made the basis of a colorimetric method for the quantitative estimation of vanillin.

STANDARD VANILLIN SOLUTION

The standard vanillin solution is prepared by dissolving 1 g. of the purest vanillin in water and diluting to 100 cc.

The first work was to determine whether the intensity of color developed by the reaction between the acid nitrate of mercury and vanillin could be duplicated in solutions of equal strength of vanillin when the same quantity of the acid nitrate of mercury was used. The accuracy with which the color was developed is shown in Table I. Solutions A and B were treated in exactly the same way. The results show that the intensity of the color developed can be duplicated and that the color is directly proportional to the quantity of vanillin present if other conditions are kept the same.

TABLE I

All of the colorimetric determinations were made on the Duboseq colorimeter.

Solution A	Reading A	Solution B	Reading B
5 cc. Std.	20	5 cc. Std.	20.9
5 cc. Std.	20	5 cc. Std.	20.7
5 cc. Std.	20	10 cc. Std.	10.0

The next tests carried out were to determine the quantity of reagent to use. The results obtained from these determinations are recorded in Table II. All the solutions represented in this table were prepared at the same time, the only difference being in the quantity of reagent used.

TABLE II—EFFECT OF REAGENT ON THE COLOR

No.	U. S. Std. Vanillin Solution	Reagent	Time on Water Bath	Std. R.	U. K. R.
1	5 dl. to 50	0.1	5 min.	0 std.	
2	5 dl. to 50	0.2	5 min.	0 std.	11.3
3	5 dl. to 50	0.3	5 min.	50 std.	13
4	5 dl. to 50	0.4	5 min.	50 std.	23.8
5	5 dl. to 50	0.5	5 min.	50 std.	24.2
6	5 dl. to 50	1.0	5 min.	50 std.	color not same hue and much weaker
7	5 dl. to 50	2.0	5 min.	0 std.	color yellow

This table shows that the intensity of the color developed depends to some extent upon the quantity of reagent used. The full color was developed when 0.5 cc. of the reagent was added. When 1 cc. was

added the color developed did not have the same hue and was also much weaker in intensity. When 2 cc. of the reagent were added the violet-red color had entirely disappeared and in its place a lemon-yellow color appeared. Apparently the destruction of the violet-red color and the development of the lemon-yellow color are caused by too large a quantity of nitric acid, as the violet-red color is destroyed when a small quantity of nitric acid is added to the violet-red colored solution produced when 0.3 cc. of the reagent has been used.

The effect of time in boiling water on the intensity of color was next determined by developing the color in a number of solutions in exactly the same way, with the exception of the length of time in heating. The results, given in Table III, show that the color is almost completely developed in the first 10 minutes, as there is an increase of only 2.5 scale divisions in the next 15 minutes.

TABLE III—EFFECT OF TIME IN WATER BATH ON INTENSITY OF COLOR

No.	Cc. Std. Van. Sol.	Cc. Reagent	Time on Water Bath	Std. R.	U. K. R.
1	5 dl. to 50	0.5	5 min.	30 std.	
2	5 dl. to 50	0.5	10 min.	30 std.	20.0
3	5 dl. to 50	0.5	15 min.	30 std.	21.3
4	5 dl. to 50	0.5	25 min.	30 std.	22.5

The results given in Tables I, II and III complete the preliminary study on the colorimetric method for the estimation of vanillin in pure aqueous solutions. The method finally adopted from the results in Tables II and III for the development of the color in the standard solution is as follows: To 5 cc. of the standard vanillin solution in a 50 cc. graduated flask is added 0.5 cc. of the acid nitrate of mercury solution and the flask placed in boiling water and allowed to remain there for 10 minutes or longer. The flask is then taken out and cooled quickly. The color is developed in the unknown solution in exactly the same way.

ANALYSIS OF COMMERCIAL EXTRACTS

Owing to the fact that the acid nitrate of mercury reagent when added to a vanilla extract causes a precipitation of the resins, coloring matter, etc., it was found necessary to modify the quantity of reagent to be added so as to have an excess to react with the vanillin. After a few preliminary tests on vanilla extracts, both alcoholic and non-alcoholic extracts, the two following methods of procedure were adopted:

ALCOHOLIC EXTRACTS—To 5 cc. of the vanilla extract in a 50 cc. graduated flask are added 5 cc. of water and 1.5 cc. of the acid nitrate of mercury reagent. The standard is made up at the same time with 5 cc. of the standard vanillin solution, 0.5 cc. of the reagent and 5 cc. of water. The two flasks are now placed in boiling water for 10 minutes. At the end of this time the contents are cooled and compared, made up to the same volume, filtered and the colors compared.

NON-ALCOHOLIC EXTRACTS—The standard is prepared just the same as in the case of the alcoholic extracts. The only change in the preparation of the unknown is in the quantity of reagent to be added, as it was found that 1 cc. instead of 1.5 cc. gave the maximum intensity of color.

¹ The color is produced slowly at the ordinary temperature.

TABLE IV. ANALYSIS OF VANILLA EXTRACTS BY THE ABOVE METHODS

EXTRACTS Sample Number	ALCOHOLIC				NON-ALCOHOLIC	
	1	2	3	4	5	6
PER CENT VANILLIN:						
Gravimetric method.....	0.26	0.26	0.14	0.11	0.80	0.29
Colorimetric method.....	0.24	0.26	0.14	0.08	0.77	0.22

The results in the above table represent single determinations, both by the gravimetric and colorimetric method; these were the only samples of vanilla analyzed and do not represent selected results from a larger number of analyses.

CONCLUSION

I—A new qualitative test for vanillin has been devised.

II—The results obtained by this new colorimetric method on commercial vanilla extracts agree very closely with those obtained by the gravimetric method.

UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

ADSORPTION OF TIN BY PROTEINS AND ITS RELATION TO THE SOLUTION OF TIN BY CANNED FOODS

By B. C. Goss

Received November 16, 1916

The presence of tin in foods which have been packed in tin cans has long been known and a great amount of work has been done on this subject, especially since 1878, when Menke published an article on "Tin in Canned Foods."¹ This work has, however, been almost entirely concerned with the mere presence of tin, determination of total tin present and with methods for recovering it.^{2,14} The general procedure is to destroy first the organic matter. This is done by wet or dry oxidation or a combination of the two.

In the dry oxidation, the food is evaporated and the dry mass charred and oxidized in a muffle furnace, a small amount of potassium nitrate or nitric acid assisting in the operation. The tin is left in an insoluble form as stannic oxide. It is then rendered soluble by fusion with sodium carbonate and sulfur or with caustic potash, giving, respectively, sodium sulfostannate or potassium stannate. Also the stannic oxide may be reduced to metallic tin by a stream of hydrogen gas at red heat or fused with potassium cyanide and the metal dissolved in hydrochloric acid.

The moist incineration processes involve oxidation of organic matter by nitric acid, hydrochloric acid and potassium chlorate, sulfuric acid and potassium sulfate or by a mixture of nitric and sulfuric acids. In the latter two cases the tin is left in soluble form, as stannic sulfate, without any volatile compounds being formed which might cause a loss of part of the

tin. Having destroyed the organic matter and having the tin in solution, the amount may be determined either gravimetrically or by one of several volumetric methods, all of which depend upon the conversion of stannous to stannic salts. We have adopted, for the purpose of this investigation, the method worked out by H. A. Baker, now of the American Can Company,¹ and used with slight variations by the Bureau of Chemistry, American Can Company and the National Canners' Association.

A new method may be mentioned here which was tried for determining the tin in our solutions. We have found that the organic matter may be easily and quickly destroyed by perchloric acid at its boiling point where the approximate composition² is $\text{HClO}_4 \cdot 2\text{H}_2\text{O}$, or, especially by a mixture of perchloric and nitric acids from which the nitric acid may then be easily driven off. The salts of perchloric acid are perfectly stable, readily soluble and not reduced by electrolysis so it was thought that the tin might be very accurately determined by electrolysis of this perchloric acid solution. We found that by using a mercury surface of 200 cm^2 , as the cathode, with which the tin is easily amalgamated while the over-voltage of the hydrogen is at a maximum, tin ions could be completely and quickly removed from large volumes of dilute solution. In the removal of the mercury by distillation, however, difficulties were encountered, owing to the tendency of the tin to oxidize and stick to the walls of the flask. We expect to do more work along this line.

Little or no exact information has been obtained regarding the mechanism of the solution of the tin by the canned food nor the condition in which it is present. Bigelow and Bacon³ compared the acidity of a large number of canned foods with the total tin present, and there appears to be little relation between the two. For example, beets packed in plain tin cans were found, 6 months after packing, to contain 72.8 mg. of tin per 100 mg. of acid, while cherries contained only 1.5 mg. of tin per 100 of acid. J. P. Atkinson noticed that if tin salts were added to meats, only a third to a half of the tin could be recovered by electrolysis even after an artificial gastric digestion.⁴ We have noticed that in the electrolysis of a pulped food sample over a mercury cathode only a part of the tin was deposited, even after a much longer time than is usually necessary. Evidently the tin is not entirely in solution. Some evidence on this point was found in the experiments of Unger and Bodlander, confirmed by Buchanan and Schryver, in which the food was roughly separated into liquid and solid portions by a sieve and each analyzed separately for tin.^{5,6} The solid portion, of course, still contained large amounts of liquid but the results showed an unequal distribution of tin between the liquid and solid portions.

¹ Chem. News, **38**, 5.

² Analyst, **1880**, p. 218.

³ Chem. News, **48**, 357.

⁴ Chem. Ztg., **24**, 263.

⁵ Z. Nahr. Genussm., **3**, 246.

⁶ Chem. Ztg., **23**, 854.

⁷ Von. Hyg., **45**.

⁸ Z. Nahr. Genussm., **7**, 676.

⁹ U. S. Dept. Agr., Bureau of Chemistry, Bull. **107**, 61.

¹⁰ Report No. 7, Local Government Board, Gt. Britain (1908).

¹¹ U. S. Dept. Agr., Bureau of Chemistry, Bull. **137**.

¹² Ibid., **67**.

¹³ THIS JOURNAL, **5** (1913), 3.

¹⁴ 8th Intern. Congr. Appl. Chem., **18**, 35.

¹ 8th Intern. Cong. Appl. Chem., **18**, 35.

² J. Am. Chem. Soc., **34** (1912), 1480.

³ THIS JOURNAL, **3** (1911), 842.

⁴ J. P. Atkinson, Bureau of Health, New York (unpublished).

⁵ Beckurts, *Jahresber.*, **45**.

⁶ Report No. 7, Local Government Board, Gt. Britain (1908).

It is obvious from this brief review of the situation that the first question to be settled is exactly the one of how much tin is in true solution in the various kinds of canned foods as well as the total amount of tin present.

EXPERIMENTAL

We have succeeded in making a satisfactory separation of the tin which is in true solution from the combined tin by means of dialysis. Owing to the ease with which tin salts hydrolyze, precautions had to be taken to avoid hydrolysis during the dialysis. The following scheme was adopted. The bottom was cut off from a wide, two-liter bottle and replaced by a film of collodion which was made by pouring out the collodion upon a dish of mercury and before entirely hard, pressing it upon the glass.¹ This makes a membrane which is very strong and capable of being used for several determinations before requiring replacement and, therefore, owing to ease of preparation, strength, and the short time required for dialysis, it was chosen in preference to gold-beaters' skin and thin parchment which were also tried. The acidity of the sample of food was determined directly on removal from the can by titrating 20 cc. of the filtered juice, using phenolphthalein as indicator, against $N/10$ sodium hydroxide. If the juice was too darkly colored, azolitmin on a spot plate was used.² Information regarding the character of the acid was obtained in most cases from the work of Bigelow and Dunbar, "Acid Content of Fruit Juices."³ In most berries the acidity is due chiefly to citric acid while in the stone fruits, such as cherries, plums, peaches, apples, apricots and most pears, the predominating acid is malic.

One liter of an acid solution of the same kind and strength as that of the liquid of the canned food was placed in a high crystallizing dish and the dialyzer suspended in this solution. A weighed sample of the pulped fruit was placed inside and constantly stirred so as to present a fresh surface to the membrane. A battery of 8 dialyzers was stirred from a central revolving shaft. It was found that in about 48 hours the equilibrium was established, although in some cases a longer time was allowed, and after this interval the dialyzer was raised and the volume of the contents inside and out measured. The large volume of the solution outside the membrane was evaporated and transferred to a Kjeldahl flask and the residue of pulp inside to another: 100 cc. of concentrated nitric acid were added to each and the mixtures let stand. If the food sample contained much sugar, rapid oxidation began almost at once and the flasks were left until brown fumes ceased to come off when 20 cc. of concentrated sulfuric acid were added and heat applied, thus avoiding too violent action. After heating until dense fumes of sulfuric acid appeared, the flasks were cooled and in case the solution was not colorless, small portions of nitric acid were added successively and heating repeated. The finally

clear solution, from which all nitric acid had been expelled, was cooled, diluted with water and the acid neutralized with concentrated ammonia, testing with litmus paper and then the solution was acidified slightly with hydrochloric acid, heated to boiling and hydrogen sulfide passed in until the tin was all precipitated. The precipitates were allowed to settle and filtered in pairs, by suction, through asbestos, using false bottom Gooch crucibles. The precipitates were washed with hot water which had been saturated with hydrogen sulfide. The tin sulfide was dissolved in Erlenmeyer flasks by boiling with concentrated hydrochloric acid, to which successive small portions of potassium chlorate were added and the chlorine expelled at the end of the addition of a gram of aluminum foil. The flasks, four at a time, were placed upon a hot plate and attached to a carbon dioxide generator. After all the air had been displaced by carbon dioxide, the tin was reduced to the stannous condition by the addition of about 2 g. of aluminum foil. The solutions were boiled for a few minutes after the aluminum disappeared and then cooled in ice-water, still in an atmosphere of carbon dioxide, removed one at a time, tubes and stoppers washed down with air-free water and titrated with $N/100$ iodine solution, using starch as indicator. Each time a series of titrations was made the iodine was standardized against a tin solution, 1 cc. of which contained 1 mg. of tin. Knowing the amount of tin in the solution outside the membrane, from the relative volumes of the acid solution and of the food pulp, the total amount of tin which was in true solution was calculated and, by difference, the tin which was in an insoluble form. The determinations were carried out in pairs and the average of results given. In some cases, as that of rhubarb, the agreement was exceptionally close, the pair yielding, respectively, 8.9 and 9.17 mg. of insoluble tin in a 75-g. sample. Where a large percentage of the tin was in an insoluble form, however, the agreement was not so close, due partly at least to the impossibility of getting two samples having just the same proportions of liquid and solid, and therefore in which the insoluble tin compound was equally distributed. A determination of the total tin in the samples of food used was also made in the usual way.

It will be noticed that in Table I the foods examined are arranged in the order of their increasing acidity as shown in column 6. It is thought that without the total tin nor the tin which is in solution are directly proportional to the acidity and it is evident that the amount of tin which is removed from the sample is dependent upon many other factors. In tabulating the amount of tin in solution in the pulp from the known relative of its residue to the amount of tin dialyzed and the volume of the pulp it was assumed that the tin in original solution was free to diffuse throughout the whole volume of the pulp, that is, that the amount needed for the solid portions of the food did not become the reserve over which the dialyzer could draw. In order to eliminate the maximum possibility which might arise from this source, the

¹ Bigelow and Gamberling, *Ann. Chem. Soc.*, **39** (1917), 1176.

² Bigelow and Dunbar, "Acid Content of Fruits," unpublished.

TABLE I

No.	Food Sample Used	Age Years	Time of Sample Hours	Vol. of Dialy- sate Cc.	Vol. of Acid Cc.	Vol. of Pulp Cc.	Mg. Tin in		Acidity (Per cent) by Titration	Mg. Tin per Kg.		Per cent of Tin In- soluble		
							Solution	Pulp		Total	In Solution		Insoluble	
1	Beets (Bur. Chem. F 21644)	5	100	72	970	205	45.6	37.7	Citric.....	0.074	833	552	281	33.9
2	Beets (enamel) (New York State)	1	100	72	970	205	45.6	37.7	Citric.....	0.080	11			
3	Pumpkin (Bur. Chem. F 21040)	5	100	56	905	235	3.6	59.0	Citric.....	0.085	836	310	526	63.0
4	String beans (Maryland)	1	50	168	1010	140	1.8	5.9	Citric.....	0.090	154	42	114	73.5
5	Squash (Bur. Chem. F 22642)	3	100	72	995	270	5.2	24.8	Citric.....	0.112	300	66	234	78.0
6	Tomatoes (N. Y. State)	1	100	53	975	170	3.78	3.24	Citric.....	0.39	70	44	26	37.1
7	Black cherries (enamel)	5	100	56	970	200	1.8	5.8	Malic.....	0.51	90	18	72	83.3
8	Pickled peaches (N. Y. State)	1	100	56	970	200	1.8	5.8	Malic.....	0.52	90	18	72	83.3
9	White cherries (N. Y. State)	1	75	120	950	198	4.68	5.7	Malic.....	0.58	138	74.7	62.7	45.7
10	White cherries (N. Y. State)	1	75	144	940	150	4.9	5.4	Malic.....	0.58	138	74.7	61.4	44.9
11	Strawberries (Bur. Chem. F 22617)	5	100	50	970	265	14.5	27.1	Citric.....	0.70	416	185	231	55.5
12	Red cherries (Bur. Chem. F 22614)	5	100	58	950	230	5.9	16.3	Malic.....	0.71	222	73	149	67.2
13	Raspberries (Bur. Chem. F 21623)	5	100	72	935	240	2.6	15.4	Citric.....	0.71	316			
14	Raspberries (enamel) (Bur. Chem. F 21626)	5	100	72	935	240	2.6	15.4	Citric.....	0.75	180	32.7	147	81.6
15	Gooseberries (Maryland)	1	50	48	980	150	4.0	6.56	Citric.....	1.2	212	92	118	56.2
16	Rhubarb (Bur. Chem. F 22634)	5	75	72	745	190	103	35.4	Citric & oxalic.....	1.5	1847	1725	122.2	6.62
17	Rhubarb (Bur. Chem. F 22634)	5	75	144	900	190	109	29.5	Citric & oxalic.....	1.5	1847	1741	118.7	6.38
18	Currents (enamel) (N. Y. State)	3	100	72	935	240	2.6	15.4	Citric.....	2.2	110			

volume of the solids was determined in the case of two of the foods which contained the highest percentage of tin in solution, for it would be in such foods that the error must be greatest. A weighed sample of rhubarb, similar to the one used in the dialysis, was sucked dry of liquid in a Buchner funnel and the solid residue immersed in a measured amount of water, noting the increase in volume. This was found to be only 0.3 cc. so that the volume of the pulp inside the membrane through which tin could diffuse was 189.7 instead of 190.0 cc. Calculating the amount of tin in solution, on this basis, in the pulp we found 26.22 instead of 26.26 mg., a difference of 0.04 mg., which is negligible. Next to rhubarb, beets contain the highest percentage of tin in solution, and the difference found in the amount of tin in solution in the pulp, when the volume of the solid in the pulp was taken into consideration, was 0.02 mg. out of a total of 9.63 mg. From these results we have concluded that the volume actually occupied by the solid in the pulp may be neglected and the tin in the solution in the pulp calculated as if it were equally distributed over the total volume inside the membrane.

It will be observed from Table I that rhubarb, which was the first of the fruits examined, showed a small percentage of tin in an insoluble form, while pumpkin, squash, string beans and other foods high in proteins, contained a large amount of tin which was no longer in solution. We expected then that in the case of the berries, which are rather strongly acid and contain almost no protein matter, the greater part of the tin would be found in solution as was determined for rhubarb. When we came to examine raspberries, however, we were much surprised to find so high a percentage of the tin, about 81 per cent, in an insoluble form. The same was true in varying degrees for other similar fruits, strawberries, gooseberries, currants, cherries, etc. Since there appeared to be some relation between the amount of protein matter and the part of the tin which was insoluble, and since the only proteins in berries are in the nuclei of the seeds, some of these seeds were analyzed for tin.

The whole raspberries, containing 180 mg. of tin per kg., were pulped and pressed through cloth, the seeds being removed from the solid residue by washing and decantation in a large crystallizing dish. In this

way perfectly clean seeds, free from pulp, were obtained. These were then washed with boiling water, dried in air and the tin determined in the usual way. The tin in the seeds ran 805 mg. per kg. In other words, most of the tin which is in an insoluble form was found in the seeds. In strawberries, this retention of tin is even more marked. The seeds of strawberries were found to contain, roughly, six times as much tin, weight for weight, as the whole fruit—the seeds gave 2630 mg. per kg. as compared to 416 for the whole fruit. The fact that the larger part of the tin in the berries mentioned is combined and insoluble in the seeds is of fundamental importance in determining the physiological action of tin in canned foods, for the seeds, and with them the adsorbed tin will be eliminated, to a large extent at least, directly in the feces.

On the basis of these experiments, it would appear that the amount of soluble tin salts, rather than the total tin present in a can of food, should be limited, since it is the part of the tin adsorbed which determines the physiological action. A few typical determinations on fruit seeds appear in Table II.

TABLE II—ABSORPTION OF TIN BY SEEDS OF FRUITS

No.	Food Sample	Age Yrs.	Acidity Per cent	Total Tin Mg. per Kg.	Per cent Insoluble	Seeds Mg. per Kg.
1	Red cherries.....	5	Malic 0.70	222.0	67.2	448.0
2	Black cherries (enamel).....	5	Malic 0.51	90.0	83.3	321.0
3	Red raspberries (enamel).....	5	Citric 0.71	180.0	81.6	805.6
4	Strawberries.....	5	Citric 0.70	416.0	55.5	2630.0
5	Tomatoes.....	1	Citric 0.39	70.0	37.1	106.5

We have already mentioned the fact that beets and rhubarb, the first of the foods examined, contain almost no protein and that in these foods we found large amounts of tin in solution. The foods high in proteins, such as string beans, squash and pumpkin, next to be investigated, showed a high percentage of tin in an insoluble form. In berries, we found that the greater part of the tin was concentrated, with the protein, in the seeds. It seemed from these results that there was some connection between the amount of protein in the food and the percentage of tin in solution as well as the total amount of tin removed from the inner surface of the can.

In order to get further evidence on the part played by proteins in determining the action of canned foods on the tin can, the following experiments were car-

ried out: Coagulated globulins, prepared by heating the 10 per cent sodium chloride extract from dried, pulverized pea beans (soup beans), were washed and suspended in water in contact with tin plate of 392 sq. cm. surface and the tubes sealed. After two weeks, an average of 0.6 mg. of tin was found combined with the protein. Also, it was found that proteins, sealed with dilute acid solutions in contact with tin, greatly increase the amounts of tin going into solution (Table III). In these experiments a coil of tin plate, having

TABLE III—INFLUENCE OF AGAR JELL, PROTEINS, ETC., ON SOLUTION OF TIN BY CITRIC ACID

	Time (Mo.)	Mg. Tin Dissolved
Citric Acid (5%).....	2	17.9
	7	20.5
Citric Acid (5%) + Agar Jell.....	2	18.3
	7	25.0
	7	25.3
Citric Acid (5%) + Proteins.....	4	32.7
	4	34.6
Citric Acid (2%).....	7	11.7
Citric Acid (2%) + Agar Jell.....	7	16.9
Citric Acid (2%) + Crushed Peas.....	7	35.5
Citric Acid (2%) + String Beans.....	7	32.5

a surface of 392 sq. cm., was sealed in contact with a constant volume of citric acid solution (100 cc.), a part of the tubes containing citric acid alone, the others having coagulated proteins, agar jell, etc., added. All were kept at the same temperature.

The simple first reaction of the acid in the can of food is complicated by the presence of large amounts of colloidal proteins which undoubtedly affect the solution of tin. Albumins, globulins and other proteins are negative colloids and are precipitated by an ion of opposite charge. This is especially true of the heavy metal ions, of which tin is an example, and this precipitation is irreversible. It is known that when a sol is thus precipitated, the precipitating ion is firmly adsorbed and carried down with it. Linder and Picton first observed this in the case of arsenious sulfide sol and barium chloride.¹ In such cases the solution remaining is found to be strongly acid and in the same degree in which the precipitate contains the metal ion. These precipitates hold the metal ion very firmly and no amount of washing will remove it. In some respects they appear to be true chemical compounds, but the composition is too variable to admit of this view. For example, precipitates formed by the action of copper salts on albumins contain all the way from 1.4 to 20 per cent of copper oxide.²

These facts observed for other heavy metals agree closely with the facts observed in the combination of tin with food materials. After a small amount of tin has been dissolved from the surface of the can, adsorption and precipitation take place. When the tin ion is removed from solution by the proteins, the acid ion is liberated and more tin dissolved. In this way the tin would be constantly removed from solution and a small concentration of acid could ultimately dissolve a very large amount of tin. If the cell walls surrounding the colloidal proteins were unbroken, the proteins could not diffuse out into the solution, but the tin could enter and adsorption take place. Since practically all of the action of the food on the container takes place after processing, which involves

heating to a rather high temperature, most of our proteins have been coagulated, but this seems to have little or no effect on the removal of tin from solution, and coagulated proteins were found to take up large quantities of tin. Beans were pulverized with sand, extracted first with water, obtaining a solution of proteoses and albumins, and then with a 10 per cent sodium chloride solution which removed large quantities of globulins. These solutions and egg albumen were used for the following tests: Small volumes of each of the above solutions were added to an excess of 2.5 and 5 per cent stannic chloride and stannic ammonium chloride solutions and the precipitate which was formed filtered, washed several times in boiling water, dried at 110° C. and the percentage of tin in a weighed sample determined gravimetrically. Parts of the same protein solutions were coagulated by heat and the coagulated proteins suspended in the same tin solutions for two days. The results show a varying percentage of tin which, however, is uniformly high. It was also noticed that if the precipitate was filtered and washed and one part of it dried and the percentage of tin determined, while the other part was put back in the solution and let stand, it continued to adsorb more tin. For example, 40 cc. of dilute globulin solution in 10 per cent NaCl were added to 400 cc. of 5 per cent stannic ammonium chloride; a white precipitate formed which was warmed to complete the coagulation and let stand for a day, then filtered, washed and dried; 0.409 g. gave on analysis 0.227 g. of tin or about 55.5 per cent. A part of the same precipitate was left in contact with the solution for a week before filtering, when 0.777 g. showed 0.441 g. of tin or 60.6 per cent. Using a 5 per cent stannic chloride solution the percentage of tin in one case ran to 69.2. As might be expected, the percentage of tin increases with the concentration of the solution. This is shown in Table IV.

TABLE IV—ABSORPTION OF TIN BY COAGULATED PROTEINS

	Original concentration of Tin as stannic chloride per cent	Final concentration of Tin in solution per cent	Per cent of Tin in Precipitate
A.....	0.001680	0.000680	59.5
B.....	0.001680	0.000680	59.5
C.....	0.001680	0.000680	59.5
D.....	0.004680	0.001600	65.60

Stannic chloride solutions, of varying concentrations, were made up and concentrated hydrochloric acid added to each to prevent hydrolysis. A constant weight of coagulated protein, 1.5 g., was suspended in 500 cc. of each solution and left for a week, after which a portion of the clear liquid was withdrawn with a pipette and analyzed for tin, and the protein was filtered off, washed with several portions of boiling water, dried at 110° C., and the percentage of tin determined. It will be noticed that in each case tin was left in solution.

Experiments were made with the stannic tin compounds from several of the standard food brands. Although the highly acid contents were abundant in tin and it was found that from 100 to 1000 mg. were easily found. However, it is most accurate if the samples of stannic water had been poured in to the can

¹ *Chem. Soc. Trans.* 67, 1895, 63.

² W. W. Taylor, "Chemistry of Colloids," p. 118.

and contained 300 mg. of tin per kg., were boiled for about 5 hours with water and the three protein solvents, 10 per cent NaCl solution, 70 per cent alcohol and 2 per cent HCl, and filtered through hardened filters. In the first three cases—water, alcohol and salt solutions—only 32.5, 32.8 and 35.8 per cent, respectively, of the tin was found in solution. The hydrochloric acid seems to break up the tin compound slowly on boiling and after 5 hours 25.4 per cent of the tin was still found combined with the solid residue. The question as to whether the tin which is adsorbed by these proteins passes through the processes of digestion without being absorbed is of first importance. We have mentioned this point in regard to the tin which was found combined in the seeds of berries and in addition have performed the following experiments to obtain further information.

Artificial gastric digestions were carried out upon the solid residue obtained by boiling canned squash, which contained 300 mg. of tin per kg. with water and filtering. This solid residue contained about 67 per cent of the total tin in the squash sample. The gastric juice, pepsin in 0.35 per cent HCl, was added to the squash and the mixture kept in a thermostat at 36° C. for 24 hrs., after which it was transferred to a dialyzer and the tin in solution determined in the usual way. Less than 10 per cent of the tin was found in solution. Both gastric and tryptic digestions were kindly carried out for us by Dr. E. N. Harvey, of the Biology Department, on the tin protein complex, prepared by allowing the freshly coagulated protein to stand in contact with tin solutions, after it had been allowed to dry, and in each case only a trace of tin was found in solution. It appears from the above results that the tin protein combination which is formed is very stable, and in most of the foods containing the larger amounts of tin, the greater part is in an insoluble form. The possibility suggests itself that the part of the tin which is so firmly adsorbed will be eliminated directly in the actual digestive processes and not figure in the physiological action as determined for soluble tin salts.

The work of J. P. Atkinson on the electrolysis of metallic salt solutions to which chipped beef had been added is of interest in this connection. A known amount of the metal in the form of a soluble salt was added to finely divided beef and then submitted to artificial gastric digestion for 24 hrs. at 37° after which the solution was electrolyzed for 45 to 50 hrs. A few typical results follow:

METAL	Added Gram	Recovered Gram	Difference Gram	Per cent Recovered
Mercury.....	0.0500	0.0121	-0.0379	24.1
Mercury.....	0.0500	0.0217	-0.0283	43.4
Tin.....	0.0330	0.0051	-0.0279	15.5
Tin.....	0.0330	0.0063	-0.0267	19.1
Zinc.....	0.0500	0.0561	+0.0061	100.0
Nickel.....	0.0492	0.0497	+0.0005	100.0
Iron.....	0.0500	0.0497	-0.0003	99.7

It appears that the metals of relatively low toxicity are least firmly bound and he suggests that this may offer an explanation of the relative toxicity of metals, in that they interfere with the metabolism of the cell. Iron, being so easily separated, adds to this view. It was found that the toxicity of mercury as the bichloride

was greatly diminished by adding it to chopped meat and submitting it to an artificial gastric digestion. One mg. of mercury as bichloride will kill a 250-g. guinea pig in 4 hrs. if injected subcutaneously, toxic symptoms beginning in a few minutes. The same quantity of mercury, after combining it with tissue as described above, produced no toxic symptoms and death did not follow until the fifth day. Rabbits also were injected without apparent harmful effects.

RÉSUMÉ AND CONCLUSIONS

It has been shown that the solution of tin by canned foods is neither dependent upon, nor proportional to, the acidity alone and, also, that in the foods of relatively slight acidity which dissolve large amounts of tin, the greater part of the tin is in the form of an insoluble and stable complex. The explanation which agrees most closely with the observed facts is that we are dealing here with adsorption phenomena; that the tin, after being dissolved from the lining of the can, is being constantly removed from solution by the proteins, carbohydrates and other highly porous solid phases in contact with the solution. Whether we regard this as an adsorption of tin ions, or whether we consider the tin salt to be first hydrolyzed and the resulting stannous hydroxide adsorbed, in either case the acid would be regenerated and able to attack more tin. The former explanation seems to be the more probable; i. e., the tin ions are adsorbed, since tin is taken up equally well by proteins even from concentrated acid solution. It will be seen from the above results that while in several respects the observed phenomena appear to be true adsorptions, in one important respect they differ. While a true adsorption is an equilibrium and can be approached from either side, being reversible, this removal of tin is not a reversible action, for if the tin protein complex is transferred to an aqueous solution containing no tin, it does not lose tin to the liquid phase. A number of cases similar to this are known and have been called by W. W. Taylor, "Pseudo-adsorptions."¹ The removal of heavy metal salts from solution by charcoal is an example of this type of action; the first stage may be an adsorption, since the salts of heavy metals are strongly adsorbable, but a secondary reaction must have taken place and the final state cannot be put down to adsorption alone.

The author wishes to express his appreciation and thanks for the very valuable assistance and advice given by Dr. G. A. Hulett in connection with this work.

LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON, N. J.
AND BUREAU OF CHEMISTRY, WASHINGTON, D. C.

THE UTILIZATION OF AMMONIUM CHLORIDE BY YEAST

By CHARLES H. HOFFMAN
Received January 6, 1917

The economy resulting from the use of certain mineral salts, especially calcium and ammonium salts, as yeast foods in baking, has been shown in a previous paper² by Dr. H. A. Kohman and the writer. It was

¹ W. W. Taylor, "Chemistry of Colloids," p. 252.

² This JOURNAL, 8 (1916), 781.

there shown that the use of ammonium chloride or other ammonium salts, $\frac{1}{2}$ lb. per 1,000 lbs. flour used with the water in the dough batch, produces a saving of 30 per cent of the usual quantity of yeast and at the same time decidedly improves the quality of the bread. When calcium sulfate and potassium bromate are used in addition to the ammonium chloride a saving of 50 per cent in yeast results. It was also stated, in this paper, that the ammonium chloride disappeared during the fermentation and that it could not be recovered as ammonia from the bread. The present work substantiates our previous finding in that it shows that the ammonium chloride disappears during the fermentation and as a result it must be changed into albuminous substances (yeast protein) by the yeast. It further shows at exactly what stage of the fermentation it is consumed by the yeast.

The results of these experiments show positively that ammonium chloride added to the dough batch is a yeast food, and during the progress of the fermentation is utilized by the yeast for building new yeast cells. The fact that the ammonium salt disappears most readily during the 3rd, 4th and 5th hours of the fermentation, just at the time when the yeast shows its most active reproduction in the dough, and the fact that no ammonia from the added ammonium salt is recoverable as such from the bread (properly fermented) upon distillation with magnesium oxide, lead to the conclusion that the yeast consumes it and changes it into a yeast protein. Evidence, too, that it is a yeast food and not a mere enzyme stimulant or catalyst is shown by the experiment in which no increased gas production results when ammonium chloride is added to a cane sugar solution, using distilled water, whereas, when added to a dough where we have the necessary elements for yeast production a significant increase, 35.3 per cent in the quantity of gas produced, is noted. Nor can the disappearance of the ammonium salt be attributed to enzymes of the flour or to bacterial action, for in a dough made of flour, water, salt, sugar and ammonium chloride, the amounts of ammonia recoverable at the time of mixing and after standing 5 hours was identical.

The added ammonium salt then functions as a food for the yeast which is converted by it into albuminous matter and does not serve as a gluten conditioner, and if such action is noted it is a secondary one, being the result of the decomposition of the ammonium chloride. The idea of economically using ammonium salts to stimulate the growth of yeast in the dough, and thereby saving a large portion of the yeast otherwise necessary to leaven the bread satisfactorily, is novel. However, other writers have found and agree that ammonium salts used in the fermentation of wine, milk, beer worts, distillery mashes and synthetic media, serve as yeast foods. Pacter¹ used ammonium tartrate in what is known as Pacter's fluid for growing yeast. Jager² agrees that ammonium salts are consumed by the yeast for building up albuminous substances. Ehrlich³ finds that ammonium salt are

readily transformed into albuminous material by yeasts, and their presence in a fermenting media prevents the formation of fusel oils and succinic acid which he finds are formed from such amino products as valine, leucine, isoleucine and glutamic acid. That these higher alcohols (fusel oil) and succinic acid are formed in the dough is then self-evident since we have an abundance of these bases, especially glutamic acid, which forms nearly 30 per cent of the protein present in the flour. The writer has added fusel oil to a dough batch and obtained a flavor and odor not at all unlike many commercial breads that were made with excessive yeast or were not properly fermented. When using ammonium chloride, these higher alcohols and succinic acid that are formed, and remain in the bread when baked, are much diminished in quantity, and as a result, we get a sweeter loaf, and one of a flavor more like the natural flavor of wheat. The work of G. Heinzelmann and Joh. Dehnicke⁴ strongly supports the writer's views in this matter. They find the production of higher alcohols to be greatest in grain mashes, less in molasses and least in potato mashes. Their work shows that the nitrogenous yeast food in the mashes is of the utmost influence on the production of higher alcohols. They find that if asparagine and ammonium salts are added to the mash a diminution of higher alcohols results and that their production may even be almost completely inhibited by a sufficient quantity of asparagine or ammonium sulfate.

The more recent work of Delbrück and Classen,⁵ in which they utilize ammonium salts as the main source of nitrogen for growing yeast on a commercial scale, shows how readily available the ammonium salts are for yeast food. The work of Völtz,⁶ moreover, shows that yeast grown from ammonium salts is alike in composition to any other grown yeast, and that its physiological action and nutritive value is the same.

The most convincing proof, however, that the ammonium chloride is a source of nitrogenous food for the yeast is shown by the experiments performed in the laboratory in which yeast was grown in a solution containing cane sugar, ammonium chloride and calcium sulfate together with the necessary inorganic phosphates. The yeast thus grown was then utilized for baking a batch of bread. The yeast functioned like the regular compressed yeast and maintained a vigorous and healthy fermentation in the dough. The accompanying photograph shows the bread made from the yeast grown on mineral salts, having ammonium chloride as its sole source of nitrogen.

These three large loaves contained no yeast at all, the ammonium chloride being changed into protein by the yeast, we can substitute for small amounts we grow in the form of yeast protein from adding only a small amount of ammonium chloride to a dough batch, containing cane sugar, and how much protein we have by

¹ *Zeitschrift für Bakteriologie*, 26, 120 (1904).

² A. S. Pacter, in *Proceedings of the Association of Yeast and Ferment Industries*, 59, 1911, 1912.

³ *Journal für die Allgemeine Chemie der Gärung*, 30, 1911, 1912.

⁴ "The Technology of Bread Making," by William Jager, p. 139.

⁵ *Monatsh.*, 32, 203 (1901); *Biochem. Z.*, 10, 391 (1913).

deducting $\frac{1}{2}$ the quantity of yeast (5 lbs. would be an average amount) regularly used; 0.5 lb. ammonium chloride contains 0.131 lb. N; this $\times 6.25$ gives 0.82 lb. protein gained by converting the salt into albuminous matter. Compressed bakers' yeast contains 27 per cent dry material: 5 lbs. of yeast then contains 1.35 lbs. of dry material, 50 per cent, or 0.68 lb. of which is albuminous in character. We have not only as much protein produced by the yeast from the ammonium salt, but actually more than that lost by deducting half the yeast in the dough batch. The economic value of a process which can utilize such simple substances as sugar and ammonium salts and build therefrom complex but useful food proteins, cannot be overestimated. We have not only economy in building up a protein from a simple nitrogen compound, but we save a large portion, 2 to 2.5 per cent, of the flour and sugar from destruction by the yeast, and in addition we save all that grain which would be

chloride. Ninety-one grams of the dough in Experiment I contained 50 grams of dry material, or $\frac{1}{19}$ of the total dough.

TABLE I—AMMONIUM CHLORIDE EQUIVALENTS OF DOUGHS AND BREADS MADE WITH AND WITHOUT YEAST FOOD

Exp. No.	BREAD FORMULA (Grams)	Fermentation Hrs.	NH ₄ Cl Equivalent of Dough	Min. in Proof Box	NH ₄ Cl Equivalent of Bread
I	Flour 1000	0	0.135	115	0.121
	Water 645	2	0.102	63	0.141
	Sugar 45	4	0.135	60	0.124
	Salt 14	6	0.135	45	0.126
	Yeast 14	7	0.135	60	0.132
II	Flour 1000	0	0.725	120	0.592
	Water 645	1	0.691	75	0.535
	Sugar 86	2	0.641	60	0.471
	Salt 14	3	0.485	70	0.219
	Yeast 14	4	0.303		
	Yeast Food 14	5	0.169	50	0.131

The total ammonia as ammonium chloride was determined at various stages of fermentation from the dough extracts from the two formulas.

It is seen that in Expt. I the amount of ammonia obtained on distillation, though considerable, did not materially vary during the progress of the fermentation.

Bread was baked at various intervals of fermentation and the ammonium chloride equivalent for the total batch determined.

The ammonium chloride equivalent obtained from the dough in Expt. II at various stages in the fermentation process, decreased most markedly during the 3rd, 4th and 5th hours.

The ammonium chloride equivalent of a dough without added ammonium chloride is 0.135. If we deduct this from 0.725 we get 0.590 gram of ammonium chloride actually in the dough and this agrees almost perfectly with the quantity 0.592 that is added in the formula. At the end of 5 hours fermentation the quantity of added ammonium chloride left in the dough is the difference between 0.169 and 0.135 gram or 0.034 gram. Since most doughs are fermented 4.5 to 5 hours, some even 6 and 7 hours in practice before scaling the loaves, and an additional 2 hours during molding and proofing before the bread is baked, the consumption of the salt is complete when the yeast food is used in baking and the results of the analysis on the bread bear this out.

In Expt. II, 5 hours fermentation yielded the best bread, under the conditions of the experiment, and therefore represents the time best suited for properly maturing and conditioning the dough.

The bread without any added ammonium chloride yielded in some cases a trifle more, and in others a trifle less, ammonia than the bread with 5 hours fermentation and made with the ammonium salt. There is, therefore, no material difference in the ammonia content as measured by MgO distillation of bread made with and without ammonium chloride. The bread having 5 hours fermentation and having yeast food added to the dough when tested with Nessler's reagent, showed no greater coloration than bread which had no ammonium salt added to the dough. The writer has been unable to distinguish, by the Nessler test or by distilling with MgO, commercial breads made with the yeast food from those



BREAD BAKED WITH YEAST GROWN ON MINERAL SALTS HAVING AMMONIUM CHLORIDE AS ITS SOLE SOURCE OF NITROGEN

necessary for the production of the compressed yeast that is eliminated by the use of yeast foods.

For determining ammonia in this work, 50 grams of moisture-free bread were extracted with 500 cc. distilled water for 3 hours, with shaking at frequent intervals. The extract was then filtered and 300 cc. taken and distilled with 5 grams of MgO. In the experiments using dough, enough dough was used to give 50 grams of dry material and distilled water added to make the total water 500 cc. The dough was then carefully broken up by hand, working it in the water until all the starch was washed out and the gluten collected into a ball. After settling, the extract was filtered and 300 cc. used as above. The ammonia was collected in $N/10$ acid, using methyl orange for an indicator. Very good results are obtained and no trouble experienced in getting duplicate checks by this method if the rate of distillation and the quantity of distillate are the same in each case.

Table I shows the ammonia, figured as ammonium chloride obtained by the distillation of extracts of dough and bread made with and without ammonium

made without. In fact, all breads, whether made with ammonium salts or not, give a slight coloration if Nessler solution is applied to the crumb. It was found, however, that cheese, eggs, cakes, salt-rising bread, meat and meat extracts, and particularly saliva, gave very positive tests for ammonia with Nessler's reagent. Even compressed yeast gives an unmistakable test for ammonia.

Tests for ammonia in a commercial bread made with the yeast food containing ammonium chloride and other breads bought in the market were made according to the directions given by Prof. J. C. Summers¹ in a paper before the members of the National Association of Master Bakers at Salt Lake City and by distilling a water extract from these breads with MgO. The results are given in Table II.

TABLE II—TEST FOR AMMONIA ON VARIOUS BREADS

Bread No.	Per cent Ammonia (Nessler Solution)	Per cent Ammonia (Distilled with MgO)
1.....	0.00012	0.0040
2.....	0.0045
3 (made with yeast food).....	0.00008	0.0045
4.....	0.00016	0.0040
5.....	0.00012	0.0040
6.....	0.00008	0.0051
7 Salt-rising.....	0.00024	0.0153
8 Yeast.....	0.00024	0.0085

Although the method given by Prof. Summers is not to be recommended for determining the absolute quantity of ammonia in foods, it nevertheless gives valuable comparative results. The results from this laboratory show that the bread made with a yeast food containing ammonium chloride gave the lowest value for ammonia when comparing the color produced with Nessler solution against the color produced in a standard ammonium chloride solution. On the other hand, it will be seen that salt-rising bread and compressed yeast give high results for ammonia by both tests.

Even when a short process of fermentation is used the quantity of ammonium chloride left in the bread is insignificant. Experiments were made using increasing quantities of yeast and decreasing periods of fermentation. In only the most extreme case, where the dough was fermented only 1 hour, could traces of the ammonium chloride be found. Table III shows the quantity of yeast used, with the time of fermentation given the dough and the ammonia recovered from the baked bread. In each case 560 grams of flour were used and 4 grams of yeast food containing 0.321 gram NH_4Cl . The ammonia added in the form of ammonium chloride and figured on the dry materials of the bread was 0.0191 per cent.

TABLE III

Yeast Grams	Fermentation of Dough	Min. in Proof Box	Per cent Ammonia Dry Bread
8	5 hrs	31	0.0014
16	3	31	0.0031
32	1 1/4	31	0.0051
48	1	31	0.0062

To show that the ammonium chloride is not consumed by the enzymes of the flour or bacterial action, the following experiment was carried out: A dough was made of the same formula as previously used except no yeast was added. The dough contained 560 gram ammonium chloride. A piece of dough contain-

ing 50 grams of dry material was broken up under water immediately when mixed, and another after standing 5 hours, the amount of ammonia as ammonium chloride recovered in each case being 0.723 gram. Deducting from this 0.135 gram, the equivalent of ammonium chloride obtained from a dough containing no added ammonium salt, we have 0.588 gram, or almost the complete quantity, 0.592 gram added.

The following experiment shows that ammonium chloride does not stimulate the gas production of yeast in a cane sugar solution, using distilled water. If the ammonium chloride merely accelerated the gas production this experiment would demonstrate that fact. We were unable, however, to obtain any increase in total gas production repeating this experiment a number of times. This would indicate then that the ammonium chloride is utilized only and exercises a favorable increase in gas production only when there is a reproduction of new yeast cells. Under the conditions of this experiment there can be only a very limited reproduction since the necessary elements—phosphorus, potassium, calcium and magnesium—are lacking. However, in the dough we have these elements present and therefore get a tremendous increase in the quantity of gas produced as the experiment below indicates.

EXPERIMENT SHOWING THE EFFECT OF AMMONIUM CHLORIDE ON THE GAS PRODUCTION IN A CANE SUGAR SOLUTION

For the test, 200 cc. distilled water, 4 grams yeast and 20 grams of sugar were used. Temperature, 28° C.

Grams Ammonium Chloride	0	0.15	0.32	0.64
Cc. Gas Produced in 6 hrs.	880	885	890	895

EXPERIMENT SHOWING THE INCREASE IN GAS PRODUCTION IN DOUGH, USING NH_4Cl

Fermentation Hrs.	Control Dough Cc.	Dough containing 0.01% NH_4Cl Difference	Dough containing 0.02% NH_4Cl Difference	Dough containing 0.04% NH_4Cl Difference
0	110	0	0	0
1	180	80	80	80
2	285	105	105	105
3	390	105	105	110
4	410	20	105	110
5	510	100	105	110
6	605	95	85	115
7	700	125	105	110
8	880	90	110	150
9	980	100	105	150
10	1080	100	105	140
11	1160	80	105	140
12	1210	50	105	140
Total gas 6 hours	1120 cc			1815 cc
Per cent increase with ammonium chloride				16.2

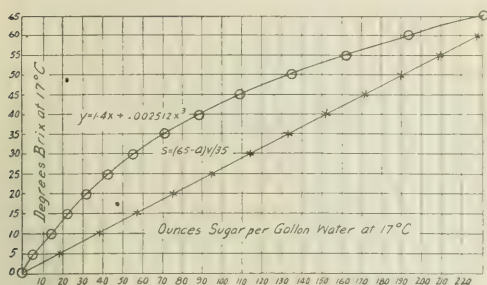
CHEMICAL LABORATORY
WALKER BAKING COMPANY
NEW YORK CITY

SYRUPS FOR CANNING AND PRESERVING

By JAMES B. McNAMEE
DISTRICT CHEMIST OF U. S.

In the canning of most fruits, syrups are used of 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290, 300, 310, 320, 330, 340, 350, 360, 370, 380, 390, 400, 410, 420, 430, 440, 450, 460, 470, 480, 490, 500, 510, 520, 530, 540, 550, 560, 570, 580, 590, 600, 610, 620, 630, 640, 650, 660, 670, 680, 690, 700, 710, 720, 730, 740, 750, 760, 770, 780, 790, 800, 810, 820, 830, 840, 850, 860, 870, 880, 890, 900, 910, 920, 930, 940, 950, 960, 970, 980, 990, 1000, 1010, 1020, 1030, 1040, 1050, 1060, 1070, 1080, 1090, 1100, 1110, 1120, 1130, 1140, 1150, 1160, 1170, 1180, 1190, 1200, 1210, 1220, 1230, 1240, 1250, 1260, 1270, 1280, 1290, 1300, 1310, 1320, 1330, 1340, 1350, 1360, 1370, 1380, 1390, 1400, 1410, 1420, 1430, 1440, 1450, 1460, 1470, 1480, 1490, 1500, 1510, 1520, 1530, 1540, 1550, 1560, 1570, 1580, 1590, 1600, 1610, 1620, 1630, 1640, 1650, 1660, 1670, 1680, 1690, 1700, 1710, 1720, 1730, 1740, 1750, 1760, 1770, 1780, 1790, 1800, 1810, 1820, 1830, 1840, 1850, 1860, 1870, 1880, 1890, 1900, 1910, 1920, 1930, 1940, 1950, 1960, 1970, 1980, 1990, 2000, 2010, 2020, 2030, 2040, 2050, 2060, 2070, 2080, 2090, 2100, 2110, 2120, 2130, 2140, 2150, 2160, 2170, 2180, 2190, 2200, 2210, 2220, 2230, 2240, 2250, 2260, 2270, 2280, 2290, 2300, 2310, 2320, 2330, 2340, 2350, 2360, 2370, 2380, 2390, 2400, 2410, 2420, 2430, 2440, 2450, 2460, 2470, 2480, 2490, 2500, 2510, 2520, 2530, 2540, 2550, 2560, 2570, 2580, 2590, 2600, 2610, 2620, 2630, 2640, 2650, 2660, 2670, 2680, 2690, 2700, 2710, 2720, 2730, 2740, 2750, 2760, 2770, 2780, 2790, 2800, 2810, 2820, 2830, 2840, 2850, 2860, 2870, 2880, 2890, 2900, 2910, 2920, 2930, 2940, 2950, 2960, 2970, 2980, 2990, 3000, 3010, 3020, 3030, 3040, 3050, 3060, 3070, 3080, 3090, 3100, 3110, 3120, 3130, 3140, 3150, 3160, 3170, 3180, 3190, 3200, 3210, 3220, 3230, 3240, 3250, 3260, 3270, 3280, 3290, 3300, 3310, 3320, 3330, 3340, 3350, 3360, 3370, 3380, 3390, 3400, 3410, 3420, 3430, 3440, 3450, 3460, 3470, 3480, 3490, 3500, 3510, 3520, 3530, 3540, 3550, 3560, 3570, 3580, 3590, 3600, 3610, 3620, 3630, 3640, 3650, 3660, 3670, 3680, 3690, 3700, 3710, 3720, 3730, 3740, 3750, 3760, 3770, 3780, 3790, 3800, 3810, 3820, 3830, 3840, 3850, 3860, 3870, 3880, 3890, 3900, 3910, 3920, 3930, 3940, 3950, 3960, 3970, 3980, 3990, 4000, 4010, 4020, 4030, 4040, 4050, 4060, 4070, 4080, 4090, 4100, 4110, 4120, 4130, 4140, 4150, 4160, 4170, 4180, 4190, 4200, 4210, 4220, 4230, 4240, 4250, 4260, 4270, 4280, 4290, 4300, 4310, 4320, 4330, 4340, 4350, 4360, 4370, 4380, 4390, 4400, 4410, 4420, 4430, 4440, 4450, 4460, 4470, 4480, 4490, 4500, 4510, 4520, 4530, 4540, 4550, 4560, 4570, 4580, 4590, 4600, 4610, 4620, 4630, 4640, 4650, 4660, 4670, 4680, 4690, 4700, 4710, 4720, 4730, 4740, 4750, 4760, 4770, 4780, 4790, 4800, 4810, 4820, 4830, 4840, 4850, 4860, 4870, 4880, 4890, 4900, 4910, 4920, 4930, 4940, 4950, 4960, 4970, 4980, 4990, 5000, 5010, 5020, 5030, 5040, 5050, 5060, 5070, 5080, 5090, 5100, 5110, 5120, 5130, 5140, 5150, 5160, 5170, 5180, 5190, 5200, 5210, 5220, 5230, 5240, 5250, 5260, 5270, 5280, 5290, 5300, 5310, 5320, 5330, 5340, 5350, 5360, 5370, 5380, 5390, 5400, 5410, 5420, 5430, 5440, 5450, 5460, 5470, 5480, 5490, 5500, 5510, 5520, 5530, 5540, 5550, 5560, 5570, 5580, 5590, 5600, 5610, 5620, 5630, 5640, 5650, 5660, 5670, 5680, 5690, 5700, 5710, 5720, 5730, 5740, 5750, 5760, 5770, 5780, 5790, 5800, 5810, 5820, 5830, 5840, 5850, 5860, 5870, 5880, 5890, 5900, 5910, 5920, 5930, 5940, 5950, 5960, 5970, 5980, 5990, 6000, 6010, 6020, 6030, 6040, 6050, 6060, 6070, 6080, 6090, 6100, 6110, 6120, 6130, 6140, 6150, 6160, 6170, 6180, 6190, 6200, 6210, 6220, 6230, 6240, 6250, 6260, 6270, 6280, 6290, 6300, 6310, 6320, 6330, 6340, 6350, 6360, 6370, 6380, 6390, 6400, 6410, 6420, 6430, 6440, 6450, 6460, 6470, 6480, 6490, 6500, 6510, 6520, 6530, 6540, 6550, 6560, 6570, 6580, 6590, 6600, 6610, 6620, 6630, 6640, 6650, 6660, 6670, 6680, 6690, 6700, 6710, 6720, 6730, 6740, 6750, 6760, 6770, 6780, 6790, 6800, 6810, 6820, 6830, 6840, 6850, 6860, 6870, 6880, 6890, 6900, 6910, 6920, 6930, 6940, 6950, 6960, 6970, 6980, 6990, 7000, 7010, 7020, 7030, 7040, 7050, 7060, 7070, 7080, 7090, 7100, 7110, 7120, 7130, 7140, 7150, 7160, 7170, 7180, 7190, 7200, 7210, 7220, 7230, 7240, 7250, 7260, 7270, 7280, 7290, 7300, 7310, 7320, 7330, 7340, 7350, 7360, 7370, 7380, 7390, 7400, 7410, 7420, 7430, 7440, 7450, 7460, 7470, 7480, 7490, 7500, 7510, 7520, 7530, 7540, 7550, 7560, 7570, 7580, 7590, 7600, 7610, 7620, 7630, 7640, 7650, 7660, 7670, 7680, 7690, 7700, 7710, 7720, 7730, 7740, 7750, 7760, 7770, 7780, 7790, 7800, 7810, 7820, 7830, 7840, 7850, 7860, 7870, 7880, 7890, 7900, 7910, 7920, 7930, 7940, 7950, 7960, 7970, 7980, 7990, 8000, 8010, 8020, 8030, 8040, 8050, 8060, 8070, 8080, 8090, 8100, 8110, 8120, 8130, 8140, 8150, 8160, 8170, 8180, 8190, 8200, 8210, 8220, 8230, 8240, 8250, 8260, 8270, 8280, 8290, 8300, 8310, 8320, 8330, 8340, 8350, 8360, 8370, 8380, 8390, 8400, 8410, 8420, 8430, 8440, 8450, 8460, 8470, 8480, 8490, 8500, 8510, 8520, 8530, 8540, 8550, 8560, 8570, 8580, 8590, 8600, 8610, 8620, 8630, 8640, 8650, 8660, 8670, 8680, 8690, 8700, 8710, 8720, 8730, 8740, 8750, 8760, 8770, 8780, 8790, 8800, 8810, 8820, 8830, 8840, 8850, 8860, 8870, 8880, 8890, 8900, 8910, 8920, 8930, 8940, 8950, 8960, 8970, 8980, 8990, 9000, 9010, 9020, 9030, 9040, 9050, 9060, 9070, 9080, 9090, 9100, 9110, 9120, 9130, 9140, 9150, 9160, 9170, 9180, 9190, 9200, 9210, 9220, 9230, 9240, 9250, 9260, 9270, 9280, 9290, 9300, 9310, 9320, 9330, 9340, 9350, 9360, 9370, 9380, 9390, 9400, 9410, 9420, 9430, 9440, 9450, 9460, 9470, 9480, 9490, 9500, 9510, 9520, 9530, 9540, 9550, 9560, 9570, 9580, 9590, 9600, 9610, 9620, 9630, 9640, 9650, 9660, 9670, 9680, 9690, 9700, 9710, 9720, 9730, 9740, 9750, 9760, 9770, 9780, 9790, 9800, 9810, 9820, 9830, 9840, 9850, 9860, 9870, 9880, 9890, 9900, 9910, 9920, 9930, 9940, 9950, 9960, 9970, 9980, 9990, 10000.

The strength of syrup used is governed by fruit and factors: (a) the acidity of the fruit, the quantity of the fruit, fruit shrinkage or absorption, and the sugar



of the formula in Table VI; namely, $y = 1.4x + 0.002512x^3$, where x = degrees Brix of syrup and y = the ounces of sugar added per gallon of water at 17° C. This last formula was obtained by interpolation of experimental results.

One of the practical applications of these experimental results is shown in connection with fruit jelly-making. In determining the amount of sugar necessary to add to a fruit juice or extract for jelly making no compensation need be calculated for extracts of less than 15° Brix. The right amount of sugar in ounces (more than 60° and less than 72° Brix) may be obtained by adding 1.8 times the number of ounces of fruit extract.¹

TABLE VI
OUNCES SUGAR PER GALLON OF WATER AT 17° C.
Calculated by McNair

Per cent Sugar 17° C.	Observed by Bitting	$y = 1.4x + 0.002512x^3$ (where x = degree Brix)	Calculated by Cruess and McNair $S = (65 - a)/35$
0	0	0	0
5	7	7.064	19.0
10	14.8	14.512	38.1
15	23.5	22.728	57.1
20	30.8	32.096	76.2
25	44.8	43.0	95.2
30	57.12	53.824	114.3
35	71.75	70.952	133.4
40	88.8	88.768	152.4
45	109.0	109.656	171.5
50	133.3	134.9	190.7
55	163.9	162.184	209.8
60	200.0	194.592	228.6
65		231.608	247.9
70		273.616	

The author would like to express his gratitude to Professor T. Brailsford Robertson and Assistant Professor William V. Cruess for assistance during this investigation.

P. O. BOX 125,
BERKELEY, CALIFORNIA

BANANA STALKS AS A SOURCE OF POTASH

By H. E. ELLIS and A. W. CRUESS
Received November 25, 1916

The great demand for potash salts during the past two years has led to the investigation of many materials, occurring either naturally or as waste products, with a view to the possible commercial utilization of their potash content. Ellis,² in an ash analysis of the banana stalk, called attention to the surprisingly high percentage of potash in this material. In every large American city thousands of these stalks are discarded as garbage weekly. The

possible treatment of such material for the recovery of its potassium suggested the following experimental work.

NATURE OF MATERIAL—The material used comprised individual banana stalks obtained from fruit markets after removal of the fruit. The stalk is of an endogenous nature, with its vascular bundles so arranged as to form a collection of tubes through which the sap flows. Such a structure permits of very rapid drying. The stalks varied in weight from 2 to 4 lbs., averaging about 3 lbs., and were found to be very constant in moisture, ranging from 91.2 to 92.6 per cent water.

COMPOSITION OF DRY MATTER—The stalks were chopped into pieces about one in. long and dried in the oven. The dried samples were exceedingly friable and easily broken or ground in a mortar. A sample was analyzed for fertilizing constituents with the following results:

	Per cent
Total nitrogen (N).....	0.44
Total phosphoric acid (P ₂ O ₅).....	0.42
Total potash (K ₂ O).....	10.46
Water soluble potash (K ₂ O).....	4.05
Moisture.....	92.6

The dry matter is as rich in potash as commercial kainit and may be considered nearly as valuable, since 74 per cent of the potash is soluble in water. Were this material used as a fertilizer, it is reasonable to assume that the organic matter would in time decompose in the soil with the formation of humus, resulting in the subsequent release of the remainder of the potash in an available condition. This material also approximates the composition and value of dried kelp,¹ which at the present time is being used to a considerable extent as a filler in commercial fertilizers. In certain respects, the material under consideration is probably superior to kelp for this purpose. Especially to be noted is the fact that banana stalks contain only very slight amounts of sodium and chlorine whereas kelp contains such quantities as to throw it into the class of kainit or other chlorinated salts.

EXTRACTION OF SALTS—Weighed amounts of the dry matter were charred sufficiently to destroy organic matter and the resulting char leached with successive small portions of distilled water. About 16 per cent of the dry matter was recovered in the form of water-soluble salts. A maximum yield was obtained with water representing 5 times the weight of original dry matter. The salts were dried to constant weight at 100° C. and analyzed with the following results:

	Per cent
Sodium.....	81
Potassium.....	10
Calcium.....	1
Magnesium.....	1
Iron.....	1
Phosphorus.....	1
Sulfur.....	1
Chlorine.....	1
Water.....	1
Moisture.....	1
Total.....	100

¹ B. McNair, "Failures in Jelly Making and Their Remedies," *The California Chemist*, No. 26, 46 (1916) 136.

² *J. Soc. Chem. Ind.*, 30 (1916) 456.

The above figures show that the leached salts consist of over 90 per cent potassium carbonate. The potassium is contained in a form which is not so easily lost as that of potassium chloride.

85 per cent potassium carbonate on the market, which in recent quotations was close to one dollar per pound. Every ton of fresh material will yield 27 pounds of this 90 per cent potassium carbonate.

METHODS OF HANDLING—By pressing the chopped stalks in a small cider press it was found possible to remove 73 per cent of the original moisture. This extracted juice was somewhat colored by dissolved organic matter, showed a specific gravity of 1.017 and contained 1 per cent potash. Since the original stalk contained approximately 1 per cent potash and 92 per cent water, the potash extracted by pressing represents nearly 70 per cent of the total. Probably the most efficient method of recovery, however, is to char the material. There are practically no difficulties encountered in this process. The nature of the material is a great aid in its own combustion. When heated, it begins to glow like charcoal and under a forced draft will burst into flame and support combustion, burning to an ash. In the presence of a free supply of air, there is enough heat furnished after the first glow begins to complete the charring without the further application of heat. This property can be made use of by placing the chopped raw material over a grating in a tall cylindrical heater, beneath which is a flame. The material in contact with the flame after drying begins to char and with the forced draft arising from the height of the cylinder, will furnish heat from its own combustion sufficient to dry the green material above it. Thus, by feeding the raw material in at the top and drawing off the ash at the bottom, a continuous yield of char can be obtained. This char can then be extracted with distilled water by any suitable means and the liquor evaporated to dryness. The dried and ground salts are clean and white and only slightly hygroscopic.

In large cities where considerable amounts of these stalks are available, it seems likely that some scheme of collection or of segregation at the garbage incinerators could be employed at small expense. The subsequent recovery of the potash has already been shown to be very simple and inexpensive, requiring no special or expensive apparatus. As stated above, one ton of fresh material should furnish in the neighborhood of \$25.00 worth of salts at the present market prices. This would seem to justify an expense for collection of about one cent per stalk (600 to 700 stalks make a ton), and still yield a fair margin of profit after deducting the nominal expense of treatment. The method of recovery lends itself readily to small scale manufacture and would in all probability be most practicable under such conditions.

SUMMARY

I—Dried banana stalks contain as much potash as kainit and compare favorably with dried kelp as filler for commercial fertilizer.

II—Charring and leaching of banana stalks yield 27 lbs. of 90 per cent potassium carbonate per ton.

III—The possibility of collection and treatment on a small scale is suggested.

THE RELATIVE AVAILABILITY OF ACID PHOSPHATE AND RAW ROCK PHOSPHATE IN INDIANA

FIELD TESTS¹

By S. D. CONNER

Approximately 80 per cent of the soils of Indiana are in need of phosphate fertilizers. The Purdue Experiment Station has been conducting field experiments testing the relative merits of acid phosphate and raw rock phosphate since 1904. Up to the end of the 1915 season 82 tests had been carried out, in which acid phosphate could be compared to raw rock phosphate. These tests were made on six different experiment fields in various parts of the state on a variety of soil types, and have been running from 2 to 10 years. In addition, tests were made in cooperation with farmers in five different counties on other soils. Table I presents a general summary of all these experiments. These tests are believed to give a fair comparison of the use of the two phosphates under average Indiana field conditions, with various crops and during different seasons on a large number of soil types. The treatments have been the same for the various plots under investigation, except that some have had acid phosphate, some have had raw rock phosphate and some have had no phosphate. As a result of the 82 tests it shows that without question it pays to use acid phosphate on these soils. Raw rock phosphate has also shown a profit, but much smaller than for acid phosphate.

The acid phosphate contained 16 per cent available phosphoric acid and has been valued at \$16.00 per ton. The raw rock phosphate was brown Tennessee rock containing 28 per cent total phosphoric acid and has been valued at \$7.00 per ton.

TABLE I. SUMMARY OF ALL EXPERIMENTS IN WHICH ACID PHOSPHATE AND RAW ROCK PHOSPHATE HAVE BEEN COMPARED (Average of Eighty-two Tests with Various Crops in Indiana)

Crop (No. of Tests)	Phosphate	Yield	Increase	Averages per Acre per Year			
				Phos- phate increase (lbs.)	Value of phos- phate (a)	Cost of loss	Profit or loss
Corn (36)...	Acid	43.04 bu.	5.49 bu.	190.5	\$ 2.95	\$1.52	\$ 1.43
	Raw rock	42.20 bu.	4.65 bu.	532.0	2.52	1.86	0.66
	None	37.55 bu.					
Wheat (33)...	Acid	15.28 bu.	4.31 bu.	190.5	4.63	1.52	3.11
	Raw rock	12.88 bu.	1.91 bu.	532.0	2.12	1.86	0.26
	None	10.97 bu.					
Legume hay (9)	Acid	2998 lbs.	320 lbs.	190.5	1.60	1.52	0.08
	Raw rock	2723 lbs.	95 lbs.	532.0	0.47	1.86	-1.39
	None	2678 lbs.					
Potatoes (14)...	Acid	112.0 bu.	29.4 bu.	500	14.70	4.00	10.70
	Raw rock	94.2 bu.	11.6 bu.	1000	5.80	3.50	2.30
	None	82.6 bu.					
Average (82).. (b)	Acid			205	\$ 4.06	\$1.64	\$ 2.42
	Raw rock			543	2.29	1.91	0.38

(a) Value of increase includes value of corn stover and wheat straw.

(b) Average length of time tests have been running, 3.47 yrs.

The following crop values were used in calculating values of increase:

	Value (Per bu.)		Value (Per ton)
Ear corn.....	\$0.50	Corn stover.....	\$ 3.00
Wheat grain.....	1.00	Wheat straw.....	2.50
Potatoes.....	0.50	Legume hay.....	10.00

¹ Presented at 53rd Meeting of American Chemical Society. This paper is based largely upon data published in Indiana Experiment Station Bull. 187, by A. T. Wiancko and S. D. Conner. Statistics of each crop and full particulars of the experiments may be found in that bulletin.

In analyzing the crop results obtained, the following facts are noted:

Acid phosphate has returned a crop increase over 6 times as profitable per acre as has raw rock phosphate. Acid phosphate has returned a crop increase over .7 times as profitable per dollar invested as has raw rock phosphate.

Each pound of phosphorus in acid phosphate has returned a crop increase valued at 28½ cents. Each pound of phosphorus in raw rock phosphate has returned a crop increase valued at 3½ cents. A pound of phosphorus in acid phosphate has returned a crop increase over 8 times as valuable as that returned by a pound of phosphorus in raw rock phosphate.

By taking the prices used in this paper for farm crops, the increases obtained by the application of phosphates would give a value of \$38.85 per ton for acid phosphate and \$8.40 per ton for raw rock phosphate. If the prices for farm products were reduced 20 per cent, the acid phosphate would have a value of \$31.08 per ton and the raw rock phosphate a value of \$6.72 per ton. The acid phosphate would still show a good profit and the raw rock phosphate would be used at a loss.

By calculating the phosphoric acid in all the crops grown, it is found that 224 lbs. of P_2O_5 have been recovered in the total increase caused by acid phosphate and 147 lbs. of P_2O_5 have been recovered in the total increase caused by raw rock phosphate. These amounts of P_2O_5 are approximately $\frac{1}{12}$ of the phosphoric acid applied in the acid phosphate and $\frac{1}{88}$ of the phosphoric acid applied in the raw rock phosphate.

Nineteen samples of raw rock phosphate were taken on the Indiana market in 1915 by the inspectors of the State Chemist. The analyses of these samples show an average of 28.8 per cent total P_2O_5 and an average of 1.8 per cent ammonium citrate-soluble P_2O_5 ; 1.8 per cent of all the raw rock phosphate used in the 82 tests would indicate an available phosphoric acid amount of 804 lbs. or over 5 times as much as was removed by the increased crops caused by the raw rock phosphate in 3½ years.

On the Scottsburg field,¹ which has been running for 10 yrs., raw rock phosphate came the nearest to paying as large a profit as acid phosphate, the net returns per acre for the 10-yr. period being \$31.52 for the acid phosphate and \$19.51 for the raw rock phosphate. On the Scottsburg field, 88 lbs. per acre of citrate-soluble P_2O_5 were added in acid phosphate in 10 yrs. and 26 lbs. of P_2O_5 were removed in the increased crops. If 1.8 per cent is considered the measure of the citrate-soluble phosphate in the rock phosphate used, then 72 lbs. of citrate-soluble phosphate were added per acre in raw rock phosphate in 10 yrs. while 26 lbs. of P_2O_5 were removed in the increased crops.

THE ACTION OF CALCIUM CARBONATE ON ACID PHOSPHATE¹

By EGBERT W. MAGRUDER

The reaction which takes place between calcium carbonate and acid phosphate is one of great interest both to the farmer and to the fertilizer manufacturer. It has been generally taught that calcium carbonate should not be mixed with acid phosphate because it would act on the mono- and di-calcium phosphates and convert them into the tri-calcium phosphate, which is insoluble in water and slowly available to plants. Consequently to find that Mr. J. S. Burgest, State Agronomist of North Carolina, in *Bulletin 220* of the North Carolina Department of Agriculture, recommended that ground limestone and acid phosphate be mixed in the proportions of 1200 lbs. of the former to from 400 to 1000 lbs. of the latter, was very much of a shock to me.

Mr. Burgest says: "No attempt has been made to leave the impression that acid phosphate mixed with ground limestone will not revert to what is called di-calcium and, to some extent, to tri-calcium forms. But these forms of phosphorus are still available to the crops, while the iron and aluminum phosphates are entirely out of reach of the plants."

To how great an extent acid phosphate is converted into iron or aluminum phosphates in the soil I do not know, but in the Eastern and Southern states experimental results have uniformly shown that acid phosphate gives much better results and is more profitable than ground phosphate rock. Di-calcium phosphate is, of course, a valuable fertilizer, and tri-calcium phosphate which has been formed by the reversion of acid phosphate would, without doubt, be more available to plants than ground phosphate rock on account of its fine subdivision.

If reverted phosphate is better for crops than acid phosphate, the fertilizer laws all need amending and the manufacturers of acid phosphate need to change their methods of manufacture. They should put out no mono-calcium phosphate, but only di- and tri-calcium phosphates.

The only recent experiments on the reaction between limestone and acid phosphate I have seen are those of Dr. R. N. Brackett,² of Clemson College, South Carolina. His limestone contained only a trace of phosphoric acid, and his acid phosphate was of the following composition:

Total phosphorus, percent	11.84
Water-soluble phosphorus, percent	1.11
Citric acid-soluble phosphorus, percent	1.11

The following table was used and distilled water obtained:

1. 100 g. acid phosphate	100	100	100	100
2. 100 g. citric acid	100	100	100	100
3. 100 g. water	100	100	100	100
4. 100 g. limestone	100	100	100	100
5. 100 g. water	100	100	100	100
6. 100 g. water	100	100	100	100
7. 100 g. water	100	100	100	100
8. 100 g. water	100	100	100	100
9. 100 g. water	100	100	100	100
10. 100 g. water	100	100	100	100

PERCENTAGE ANALYSES OF MIXTURES

Mixture	No. 1		No. 2		No. 3		No. 4	
	W-S	Ins.	W-S	Ins.	W-S	Ins.	W-S	Ins.
April 21st, Immediately after mixing	6.15	1.07	8.30	1.15	10.50	1.24	2.40	0.83
May 10th.....	3.05	1.30	5.84	1.26	8.66	1.37	0.99	0.98
June 12th.....	3.31	1.39	6.39	1.66	8.15	1.59	1.10	1.11
Sept. 13th.....	3.38	1.46	3.31(a)	1.33	8.05	1.46	0.87	1.08

(a) This is probably an error as an analysis in November, 1913, gave about five per cent water-soluble.

I was surprised that more insoluble phosphate was not formed in these mixtures, especially the half and half mixture.

In order to test the effect of larger mixtures than used by Dr. Brackett and also to try the effect of fresher acid phosphate, I made up some mixtures last summer and used acid phosphate a month old and some which had been made only a few days and was warm when mixed. I used ground oyster shells instead of ground limestone.

TABLE I—MATERIALS USED

Material	Percentages Phosphoric Acid	
	Total	Insoluble Water-Soluble
New acid phosphate.....	19.38	2.41 15.78
Month-old acid phosphate.....	18.13	1.04 14.90
Ground oyster shells.....	0.51

TABLE II—MIXTURES AND RESULTS OF ANALYSES

Acid Phosphate Used:	Date Analyzed	Old—		New—	
		Phosphoric Acid (%) Insol.	Water-Sol.	Phosphoric Acid (%) Insol.	Water-Sol.
190 lbs. Acid Phos.....	8/16	2.50	15.05	0.82	13.72
10 lbs. Oyster Shells.....	9/20	2.70	14.00	0.24	11.28
Theory		2.32	14.99	1.02	14.06
180 lbs. Acid Phos.....	8/16	2.45	14.50	0.79	13.38
20 lbs. Oyster Shells.....	9/20	3.44	7.08	1.50	3.05
Theory		2.22	14.20	0.99	13.32
160 lbs. Acid Phos.....	8/16	2.40	12.15	0.84	11.10
40 lbs. Oyster Shells.....	9/20	2.99	4.30	1.57	1.05
Theory		2.03	12.62	0.93	11.84
140 lbs. Acid Phos.....	8/16	1.65	10.08	1.14	10.58
60 lbs. Oyster Shells.....	9/20	3.26	1.50	1.95	0.65
Theory		1.84	11.05	0.89	10.36
100 lbs. Acid Phos.....	8/16	1.95	5.55	1.12	7.60
100 lbs. Oyster Shells.....	9/20	2.32	0.30	1.11	0.35
Theory		1.46	7.89	0.77	7.40

In studying this table there are some inconsistencies, but taking the results as a whole it is seen:

1—That the new acid phosphate is acted on more readily by the oyster shells than the older.

2—That action begins at once.

3—That the action continues on standing.

4—That the greater the amount of oyster shells the greater the action.

5—That with 30 and 50 per cent shells virtually all of the water-soluble phosphoric acid disappears.

These results, on the whole, agree with Dr. Brackett's. I intend to make further analyses of these samples.

It has generally been considered that water-soluble or mono-calcium phosphate is more valuable to crops than citrate-soluble, or di-calcium phosphate. If that is true then mixing larger quantities of calcium carbonate with acid phosphate would reduce the value of the phosphate very greatly, by reducing the water-soluble phosphoric acid to the vanishing point and also by increasing the insoluble phosphoric acid.

As the fertilizer laws are at present, fertilizer manufacturers certainly could not afford to mix much calcium carbonate with their acid phosphates on account of the high insoluble phosphoric acid which would be produced.

As this question is a very important one to both farmers and fertilizer manufacturers, I have thought it well to make public my results in order to have more light thrown on the subject.

F. S. ROYSTON GUANO COMPANY
NORFOLK, VIRGINIA

A CONTRIBUTION TO THE THEORY OF EMULSIFICATION BASED ON PHARMACEUTICAL PRACTICE¹

By LEO ROON AND RALPH E. ORSPER

Received November 22, 1916

INTRODUCTORY

The practical knowledge of emulsions, which has been handed down to the pharmacists from generation to generation, has been surveyed by physical chemists, but this pharmaceutical experience has been neglected almost entirely as an aid in developing a rational theory of emulsification. Several theories of emulsification have been proposed which differ according to the factor held responsible for the stability of the emulsion, but objection has been raised to all of them. It is probable that none of these theories is of universal application, and though each may cover special cases or classes of emulsions, their inadequacy is generally admitted.

The surface tension theory upheld by Plateau,² Quincke³ and notably Donnan⁴ was shown to be inadequate when Pickering⁵ emulsified "solar distillate" with the aid of such materials as the basic sulfates of iron and copper, hydrous ferric oxide, etc., materials which do not influence surface tension. The viscosity theory, whose origin is obscure, was attacked by Hillyer,⁶ who pointed out that although extreme viscosity was an important factor in the preparation of some pharmaceutical emulsions, nevertheless, viscous materials, such as 50 per cent glycerine or 6 per cent gum solution, are not able to emulsify kerosene or cottonseed oil, though dilute, comparatively mobile soap solutions do so easily.

While admitting the favorable influences of high viscosity and low surface tension, Pickering⁷ put forth the view that the deciding factor is the formation of films of insoluble particles around the droplets. Donnan⁸ attacked this hypothesis bitterly, but Bancroft⁹ pointed out that the criticism was beside the point and that the theory was not intended to be a complete one. Clowes¹⁰ has described experiments in which these films were distinctly visible and he attributes their action in part to a purely mechanical action in keeping the particles from coalescing, in part to lowering of surface tension and in part to repulsive action of the electrically charged particles.

Fischer¹¹ has recently proposed that emulsification is due to, or accompanied by, the formation of a hydration colloid compound. He says: "In reviewing the empirical instructions for the preparation of emulsions, and in our own attempts to formulate such as would always yield permanent results, we were struck with the fact that their production is always associated

¹ The work reported in this article constitutes the basis of a thesis submitted by Leo Roon to the Faculty of the Graduate School of New York University, in part fulfillment of the requirements for the degree of Master of Science.

² Pogg. Ann., **14** (1870), 44.

³ Wied. Ann., **35** (1888), 589.

⁴ Z. phys. Chem., **31** (1899), 42.

⁵ J. Chem. Soc., **91** (1907), 300.

⁶ J. Am. Chem. Soc., **28** (1903), 513.

⁷ Z. Koll. Chem., **7** (1910), 11.

⁸ Ibid., **7** (1910), 214.

⁹ J. Phys. Chem., **16** (1912), 504.

¹⁰ Ibid., **20** (1916), 415.

¹¹ Science, **43** (1916), 468.

with the discovery of a method whereby the water (or other medium) which is to act as the dispersing agent is all used in the formation of a colloid hydration (solvation) compound. In other words, when it is said that the addition of soap favors the formation and stabilization of a division of oil in water, it really means that soap is a hydrophilic colloid, which, with water, forms a colloid hydrate with certain physical characteristics and that the oil is divided in this. The resulting mixture cannot, therefore, be looked upon as a subdivision of oil in water, but rather as one of oil in a hydrated colloid." Fischer gave no experimental details of his work and though he promised their future publication, neither his method nor results were available to us. The work described in this paper had been under way for several months before the appearance of Fischer's article, but our results and conclusions coincide so closely with his views, that in the absence of his own data, our findings seem to constitute at least a partial confirmation of his theory.

PHARMACEUTICAL EMULSIONS

The preparation of emulsions is a regular practice in pharmacy, but the pharmacist, in contrast to the physical chemist, recognizes only the oil-in-water type of emulsions, even though he has, as official pharmacopoeial preparations, lanolin, carron oil, etc., which are of the water-in-oil type. These latter preparations, however, he classes with the ointments and liniments, respectively. Every pharmaceutical emulsion consists of three principal parts: (1) the liquid to be emulsified; (2) the emulsifying agent; (3) water. The liquids used are limited to fixed and volatile oils and other liquids immiscible with water, such as chloroform, ether, etc. The emulsifying agents most generally employed are gum arabic (acacia), gum tragacanth, Irish moss, dextrin, gelatin, extract of malt, yolk of egg. Of these, powdered or granulated acacia is by far the best. In addition to the standard emulsifiers mentioned above, condensed milk, casein, starch and various mixtures of any of those named have been used with more or less success.

There are two methods of preparing pharmaceutical emulsions, the English and the Continental.

1—The English method consists in triturating the gum with water to make a mucilage, and then adding oil and water alternately in small portions, triturating after each addition until the emulsion is completed. This method is not considered very satisfactory by most pharmacists. For example, Arny¹ states that "this method of manufacturing emulsion is slow and uncertain and cannot be compared with the Continental method in simplicity." It has been our experience that not more than two per cent of the average student of pharmacy are able to make good emulsions by this method. It is of interest to note that the hydration of the emulsifying agent occurs progressively and not all at one time and for the greater part is not accomplished in the presence of the internal phase.

2—The Continental method consists in first making what is called the emulsion nucleus with certain definite

quantities of oil, gum and water. This creamy, viscous nucleus may then be diluted with any quantity of water to form a good emulsion. In this case *all of the emulsifying agent is hydrated at one time and in the presence of the internal phase*. Remington¹ says concerning this method: "This has the great merit of never failing to produce a good emulsion if the proper proportions are used to form the nucleus, and if the directions are strictly followed." Text-books and practitioners are divided as to what may be considered the proper proportions of oil, gum and water for making the nucleus. The majority of pharmacists use the materials in the proportion of 4 parts oil, 2 parts acacia, 3 parts water. Remington and Arny both recommend 4 parts oil, 2 parts water and 1 part acacia; the National Formulary² recommends 8 parts oil, 2 parts acacia and 3 parts water. In any case, it is evident that the proportion of water to the emulsifying agent, acacia, is practically constant. The proportion of 4 parts oil, 2 parts acacia and 3 parts water is considered most reliable for making the nucleus and has been used as the standard for the purposes of this research. To make a good emulsion nucleus, *strict adherence to the mode of procedure* is just as important as taking the proper proportions of materials. The standard method consists in placing the oil (4 parts) in a dry mortar, adding the acacia (2 parts) and triturating until a smooth paste is formed. The water (3 parts) is added, not in portions, but all at once, when, upon trituration, a thick creamy nucleus is formed. This is now perfectly miscible with water in all proportions.

A survey of the literature shows that some physical chemists also have found that the use of certain definite proportions of materials leads to good emulsions. For example, Gad³ found that when oil containing the proper percentage of fatty acid was placed on the surface of a sodium carbonate solution, a beautiful spontaneous emulsion resulted, and from this he held that neither shaking nor any other mechanical process was necessary for the formation of an emulsion. His method consisted in taking a series of watch glasses containing 0.25 per cent sodium carbonate solution and then placing drops of oil, containing various amounts of free fatty acid on the surface of the solutions in the glasses. He observed that the oil which contained 5.5 per cent fatty acid solidified spontaneously at room temperature and that the oil containing very little more or less than 5.5 per cent yielded incomplete emulsions. He, therefore, concluded that the limits of good spontaneous emulsion were very narrow but quite narrow.

Robertson⁴ has published some interesting results which also serve to illustrate the importance of the use of definite proportions of materials. On the basis of his work, he states: "It is possible in the emulsion made parts of slightly varying amounts of oil in a given volume of water to obtain a series of emulsions of different degrees of stability."

¹ Remington's Chemistry, 14th Edition, 1906.
² National Formulary, 1906.
³ J. Chem. Soc., 1878, 187.
⁴ J. Chem. Soc., 1906, 7.

forms the internal phase and water the external phase; that is, the oil is suspended in spherical droplets in the water. If we increase the proportion of water, the resultant emulsion still continues to exist as drops of oil suspended in water until the proportion of water to oil reaches a definite critical value. When this critical ratio is reached, the character of the emulsion undergoes an abrupt change. From being a viscid, creamy white emulsion of oil in water, it becomes a fluid yellow emulsion of water in oil." Bancroft¹ does not agree with Robertson's conclusion that there is necessarily a critical ratio, with one type of emulsion existing below this value and the other type above it, although he admits the possibility of there being a given point at which an emulsion might become unstable.

A search of the literature revealed very little concerning quantitative measurements of the critical proportions of emulsions, nor could we find records of the results of varying the order in which the ingredients of emulsions were added to each other and our work was undertaken with a view of studying several typical emulsions from these standpoints. The results were rather striking and we believe throw some light on the process of emulsification. It is probably true that the critical values determined are valid only for the quantities used in our work and apply only to emulsions prepared by shaking in test tubes, but our basic conclusions are probably of universal application.

Only two emulsifying agents, acacia and soap, were employed. Acacia (gum arabic) is considered by pharmacists to be the best emulsifying agent, and soap has been mentioned by the physical chemists as the most efficient emulsifier. Only those emulsions were dealt with in which water constituted the external phase. As internal phases, substances were employed which represented different types of liquids immiscible with water: hexane, chloroform, carbon tetrachloride, benzene, white mineral oil and cottonseed oil. The work dealt with practical emulsions rather than with theoretical emulsions such as were prepared by Lewis² and Ellis.³

Those dispersions were considered as good emulsions which were uniform throughout in color and consistency, which were perfectly miscible with water, which uniformly wetted the walls of the containing vessel and which did not separate on standing into three parts—a layer of internal phase; a layer of external phase; with an interfacial ring of partially emulsified internal phase separating the two layers. On standing, most good emulsions cream, or separate into two layers, a layer of completely emulsified internal phase and a layer of external phase. In this connection, Scoville⁴ says: "Good emulsions often separate into layers on standing, but without showing any separated oil. An emulsion should not be condemned for this, because the separation is due, not to faulty manipulation in making the emulsion, or to improper ingredients

or proportions therein, but to excess of dilution, and a little shaking will quickly rediffuse it. The same thing occurs in milk—the best type of natural emulsion—in which the true emulsion portion separates as cream."

EXPERIMENTAL

The following materials were used in this research:

1. Hexane, specific gravity 0.691.
2. Chloroform, specific gravity 1.526.
3. Carbon tetrachloride, specific gravity 1.597.
4. Benzene, specific gravity 0.877.
5. Oil of turpentine rectified.
6. Mineral oil, specific gravity 0.853.
7. Cottonseed oil, winter yellow, specific gravity 0.921.
8. Squibb's soft soap. An alcoholic solution containing 50 grams of soap in 100 cc. of solution was used.
9. Powdered acacia (gum arabic) first selection.
10. Mucilage of acacia, 33 grams of acacia contained in 100 cc. of mucilage.

I—ACACIA EMULSIONS

All the acacia emulsions were made by shaking in 30 cc. test-tubes, except those containing cottonseed oil and mineral oil, which, because of their high viscosities, had to be made by trituration in a mortar. The method and order of adding the necessary constituents, was, however, the same in all cases. The acacia was added to and mixed with 10 cc. of the internal phase; 7.5 cc. of water was then added at once, and the mixture rapidly triturated (cottonseed or mineral oils), or briskly shaken in a test-tube. The quantities of internal phase, gum and water taken were in accord with the standard pharmaceutical proportions of 4 : 2 : 3, respectively, or in other words, 10 cc. of internal phase, 5 g. acacia and 7.5 cc. of water. The volumes of internal phase (10 cc.) and of water (7.5 cc.) were kept constant throughout, but the amount of acacia was varied and the effect on the condition of emulsification noted in order to determine the presence of a critical point, *i. e.*, the minimum quantity which would emulsify the given volumes of water and oil. Such points were observed and are indicated in the results given in Table I.

It was found on taking 10 cc. mineral oil, adding 5 g. acacia, triturating to a smooth paste and then adding water in 0.5 cc. portions, that the acacia immediately absorbed the water and formed large translucent lumps. On adding more water, vigorous trituration being maintained, the mixture grew whiter and whiter until suddenly a perfectly white, creamy emulsion resulted. At this point of emulsification, however, several of the rubbery lumps of acacia still remained, showing that 5 g. acacia were in excess of the amount necessary to emulsify the 10 cc. of oil. For this treatment, 11.5 cc. of water, in small portions, had been used, whereas when 7.5 cc. of water (pharmaceutical ratio 4 : 2 : 3) was added *all at once*, a beautiful white creamy viscid emulsion was produced. Evidently then, 5 g. of acacia are more than sufficient to emulsify 10 cc. of oil, and 7.5 cc. of water added at

¹ J. Phys. Chem., **16** (1912), 746.

² Z. Kolld. Chem., **4** (1909), 311.

³ Z. phys. Chem., **78** (1911), 352.

⁴ "Art of Compounding," 1895, p. 82.

TABLE I. ACACIA EMULSIONS.

INTERNAL PHASE	Mixture	Size of Globules		Trituration	Emulsion	Critical Point
		Grams	Microns			
Cottonseed Oil	A 1	5.0	3-8	20	Thick creamy	2.2
	2	3.0	5-10	35	Good	to
	3	2.5	10-30	150	Miscible	2.3
	4	2.4	15-40	180	but thin	grams acacia
	5	2.3	25-50	210	None	
	6	2.2	...	300	None	
Mineral Oil	B 1	5.0	4-8	30	Good	2.4
	2	3.0	8-15	60	Good	to
	3	2.7	15-30	150	Good	2.5
	4	2.6	20-30	150	Good	grams acacia
	5	2.5	15-30	220	None	
	6	2.4	...	300	None	
Oil of Turpentine	C 1	0.5	Good	Apparently None
	2	0.4	Good	
	3	0.3	Good	
	4	0.1	Good	
	5	0.05	Partial	
	6	0.02	Partial	
Benzene	D 1	5.0	3-10	0.09 to 0.10 grams acacia
	2	3.0	10-20	...	Excellent	
	3	1.0	15-20	...	and Stable	
	4	0.5	15-20	
	5	0.1	15-40	
	6	0.09	None	
Carbon Tetrachloride	E 1	0.50	10-25	...	Good	0.08
	2	0.10	15-30	...	Good	0.09 gram acacia
	3	0.09	20-50	...	Good	
	4	0.08	None	
Chloroform	F 1	2.0	8-15	...	Good	0.55
	2	1.0	10-20	...	Good	to
	3	0.56	10-30	...	Good	0.56 gram acacia
	4	0.55	None	
Hexane	G 1	0.5	25-50	...	Translucent	Between 0.005 and 0.01 gram acacia
	2	0.1	25-100	...	resembling starch paste	
	3	0.05	30-100	...	in color and consistency	
	4	0.03	50 & over	
	5	0.01	50 & over	
	6	0.005 (approx.)	None	

SPECIAL CASES.

- A (a) Emulsion 6, plus five drops of Emulsion 1 gave good emulsion.
 (b) Oil 10 cc. plus acacia 3.0 g. plus 15 cc. water gave no emulsion.
 (c) Oil 15 cc. plus acacia 3.0 g. plus 3.5 cc. water gave no emulsion.
 (d) Oil 10 cc. plus acacia 2 g. below critical point plus 7.5 cc. water gave no emulsion; plus 0.3 of 5 per cent NaOH solution gave a good emulsion.
- D (a) 10 cc. benzene plus 1 cc. mucilage of acacia gave no emulsion.
 (b) 10 cc. benzene plus 3 cc. mucilage of acacia plus 3 cc. water gave no emulsion.
- E (a) 10 cc. carbon tetrachloride plus 0.09 g. acacia plus 7.0 cc. water gave no emulsion.
 (b) 10 cc. carbon tetrachloride plus 0.09 g. acacia plus 15.0 cc. water gave emulsion, but not as good as that resulting from the addition of 7.5 cc. of water to Emulsion 3.
- F (a) 10 cc. chloroform plus 0.56 g. acacia plus 7.0 cc. water gave no emulsion.
 (b) 10 cc. chloroform plus 0.56 g. acacia plus 10 cc. water gave emulsion not as stable as that resulting from Nucleus 3 subsequently diluted with 3 cc. additional water.

one time will bring about better and more rapid emulsification than 11.5 cc. of water added in small portions.

Mixtures Ea and Fb show that adding an excess of water (more than 7.5 cc.) at once to the internal phase and acacia gives an emulsion, but these emulsions are not exactly of the same color, consistency, stability or general excellence as those made by first diluting to the required volume a previously prepared nucleus—the usual pharmaceutical method.

Mixtures Da and b where the critical point is 0.09-0.10 g. acacia illustrate well the fact that the hydration process of the acacia must be accomplished at the moment of agitation. In these cases, there were taken 3 cc. of mucilage of acacia (representing a g. acacia or ten times the quantity actually needed) and this was shaken thoroughly with the benzene. There was absolutely no indication of emulsification. Likewise there was no effect when benzene was shaken with mucilage diluted with an equal quantity of water. (Da)

Mixture A6 represents an incomplete emulsion of cottonseed oil. However, on adding 5 drops of a good

emulsion (1) and triturating, the emulsification of 6 was easily accomplished. This seems to show that a good emulsion is an emulsifier, a fact utilized by pharmacists in redeeming cracked emulsions by the addition of a small volume of a good emulsion.

Sodium hydroxide solution was added to the cottonseed oil which ordinarily contained some free fatty acid; in order to determine the effect of reduced surface tension caused by the soap formation: 0.3 cc. of 5 per cent sodium hydroxide solution was added to the incomplete emulsion A6. With the result that the emulsification was completed.

In order to illustrate the striking phenomenon of the existence of these critical points which appeared with the regularity and sharpness of titration end-points, a set of chloroform emulsions was prepared and photographed (see Fig. 1). Many important points are illustrated by this print. The upper layers are, of course, aqueous and the lower chloroformic. As the amount of emulsifying agent is steadily increased, the interfacial ring becomes broader and broader.

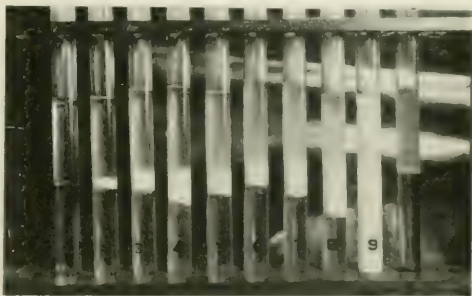


FIG. 1. ACACIA CHLOROFORM EMULSIONS.

Chloroform, 10 cc. Water, 1 cc.
 No. 1 2 3 4 5 6 7 8 9
 Grams Acacia 0.005 0.01 0.02 0.03 0.05 0.10 0.15 0.20 0.25
 No. 10, 8 cc. Mucilage of Acacia and 10 cc. Chloroform. No. 9, Water.

while the upper aqueous layer becomes more and more opalescent until at 9 we have a uniform white emulsion. The clarity of the lower chloroformic layers in Nos. 1 to 8 can be readily seen and illustrates what is meant by the term "incomplete emulsion," as used in the introduction. At the point of emulsification, No. 9, no emulsified chloroform can be seen and although on standing for some time, this emulsion creams downward because of the higher density of the chloroform, there will be at all times only two layers, one of emulsified chloroform, the other consisting of the excess dispersion medium. Tube 10 contains chloroform and some mucilage of acacia (equivalent to that in 9, diluted). These have been thoroughly shaken and it is very evident that the interfacial ring is narrower than in a static condition. It is at this point that the process of hydration, or the moment of emulsification, has been accomplished.

DISCUSSION AND CONCLUSIONS

All the test emulsions were prepared by shaking in a 25 cc. tambores flask, of internal phase with taken in a tube and 10 cc. of oil emulsion and 10 cc. of

burette. A definite quantity of water was then added from another burette, the contents of the test-tube suddenly and briskly shaken, and the degree of emulsification noted. The quantity of water was varied over a considerable range to determine the possible presence of critical points, *i. e.*, the minimum quantity of water required to bring about the emulsification of the given volumes of the other ingredients. Such points were found in all cases as is indicated in the results, shown in Table II.

TABLE II SOAP SOLUTIONS

INTERNAL PHASE	MIX	WATER	SIZE OF GLOBULES	EMULS.	CRITICAL POINT
Cottonseed Oil	H 1	2.0	1 and less	Good	1.4 to 1.5 cc. water
	2	1.5	1 and less	Good	1.5 cc. water
	3	1.4		None	
Oil of Turpentine	I 1	1.2		Good	0.9
	2	1.1		Good	1.0
	3	1.0	3-10	Good	10.0 cc. water
	4	0.9		None	
Mineral Oil	J 1	2.8	Av. 2	Good	2.6 to 2.7 cc. water
	2	2.7	Av. 2	Good	2.7 cc. water
	3	2.6		None	
Benzene	K 1	4.3	1-2	Good	4.3
	2	4.4	1-2	Good	4.3
	3	4.3	1-2	Good	4.3 cc. water
	4	4.2	None	water
Carbon Tetrachloride	L 1	7.1	1-2	Good	7.0 to 7.1 cc. water
	2	7.1	1-2	Good	7.1 cc. water
	3	7.0		None	
Chloroform	M 1	6.0	2 (approx.)	Good	5.8
	2	5.7	2 (approx.)	Good	5.8
	3	5.6	2 (approx.)	Good	5.6 cc. water
	4	5.5		None	water
Hexane	N 1	7.0	15 (approx.)	Good	6.8 to 6.9 cc. water
	2	6.9	15 (approx.)	Good	6.9 cc. water
	3	6.8		None	
*Hexane-Carbon Tetrachloride	O 1	10.1	Good	9.9 to 10.0 cc. water
	2	10.0	Good	10.0 cc. water
	3	9.9	None	water
*Hexane-Mineral Oil	P 1	3.0		Good	2.8
	2	2.7		Good	2.8
	3	2.6	Good	2.6 cc. water
	4	2.5		None	water

*Specific gravity 1.0 (see Special Cases below).

SPECIAL CASES

- H (a) Oil 10 cc. plus soap solution 1 cc. plus water in portions of 0.2 cc. emulsifies when a total of 5.6 cc. of water has been added. Compare above.
- (b) 1.0 cc. soap solution diluted with 1.5 cc. water (critical amount) plus 10 cc. oil gave partial emulsion.
- (c) Oil 10 cc. soap solution 1.0 cc. plus 5.0 cc. water gave emulsion but not so stable as one made by making Nucleus 2 and diluting it with 3.5 cc. additional water.
- J (a) Oil 10 cc. plus soap solution 1 cc. plus water in 0.2 cc. portions emulsifies when a total of 6.5 cc. have been added.
- (b) Oil 10 cc. plus soap solution 1 cc. plus water 5 cc. gave emulsion not so stable as one made by diluting Nucleus 2 with 2.3 cc. additional water.
- (c) 1 cc. soap solution plus 2.7 cc. water (critical amount) plus 10 cc. oil gave emulsion. This is an exception to the results obtained in all other cases.
- K (a) Benzene 10 cc. plus soap solution 1 cc. plus water in 0.5 cc. portions emulsifies when the total of 10.5 cc. water have been added.
- (b) 1 cc. soap solution diluted with 4.3 cc. water (critical amount) and 10 cc. benzene added gave no emulsion.
- L 1 cc. soap solutions plus 7.1 cc. water to which 10 cc. carbon tetrachloride were added, gave no emulsion.
- M Observations of this emulsion with high magnification showed that the very small globules contained nuclei closely resembling those in protoplasmic cells. These nuclei were seen to vibrate with a motion, which especially for the smaller globules, resembled very closely the so-called Brownian Movement. The larger globules contained many of these highly refractive particles of varying sizes. The larger particles vibrated rather slowly, but the smaller ones darted about very vigorously, often colliding with one another. The phenomenon was only observed in the chloroform emulsion.
- N 1.0 cc. soap solution diluted with 6.9 cc. water (critical amount) plus 10 cc. hexane gave no emulsion.

O & P A mixture possessing a specific gravity of 1.00 and a relatively low viscosity was prepared from 59.7 cc. hexane and 30.9 cc. carbon tetrachloride. Another mixture also of a specific gravity of 1.00, but of a relatively high viscosity, was prepared from 59.7 cc. mineral oil and 14.7 cc. carbon tetrachloride. These mixtures, of the same density as water, were then treated in the same way as the pure substances had been, to determine whether emulsification was dependent upon specific gravity. No relation was found.

In connection with some other work, it has been our experience that, in the preparation of large quantities of soap emulsions of certain volatile oils, in which definite volumes of soap solution and volatile oil were taken, that the addition of an excess of water to the soap and oil mixture produced much foaming and a comparatively thin emulsion resulted; that the addition of an insufficient amount of water produced an incomplete emulsion which streaked down the sides of the container; that between these limits of over-emulsification and incomplete emulsification there existed a point at which perfect emulsification occurred without foaming and streaking. This experience was found useful and was employed as a means of judging the excellence of the emulsions prepared from 10 cc. internal phase, 1 cc. soap solution and varying volumes of water. The foaming is plainly indicative of excess of water and the non-wetting of the sides of the container is a sign of incomplete emulsification due to insufficient water. The critical point between the incomplete and the perfect emulsion is strikingly sharp and may be determined within less than 0.1 cc. of water. At the critical point the emulsion seems to form almost spontaneously, and only one to two seconds shaking are necessary for complete emulsification. However, those systems which are within a few tenths of a cc. below the critical point in water content, will emulsify if allowed to "age" for about 10 minutes before being vigorously shaken. These critical points are applicable only to emulsions prepared with the quantities used in this research. For instance, if 20 cc. of benzene are to be emulsified with 2 cc. of soap solution, then 2 times 4.3 cc. water (critical volume for 10 cc. benzene and 1 cc. soap solution) will not be the correct value for emulsification. In general, as the total volume of the emulsion to be formed increases, we note a relative decrease in the critical volume of water.

If the water be added in small portions to the mixture of internal phase and soap solution, a larger volume is required to bring about emulsification. For instance, in Mixture Ha, 5.6 cc. of water must be added in 0.2 cc. portions before emulsification occurs, while if 1.5 cc. of water (critical volume) are added *all at once* to the mixture of internal phase and soap solution, and the whole then shaken, a rich, creamy emulsion is produced. The same fact is shown in Mixture Ja, where 6.5 cc. are used instead of 2.7 cc. (critical volume); in Mixture Ka, where 10.5 cc. are used instead of 4.3 cc. (critical volume); in Mixtures Hc and Jb, we see that adding more than the critical volume of water *at one time* and then shaking yields a thin, foamy emulsion incomparable in general excellence to those emulsions prepared by first diluting a completed nucleus (made with the critical volume of water) to the required volume.

Mixtures Hb, Kb and La show that no emulsification results if the requisite 1 cc. of soap solution be first diluted with the critical volume of water and this diluted (hydrated) solution of soap then shaken with the 10 cc. of internal phase. This is analogous to the use of mucilage of acacia in acacia emulsions. Hence

the hydration process of soap must be accomplished at the moment of agitation and in contact with the material to be emulsified. The mechanism of the formation of the emulsions may then be viewed as follows: the agitation disperses the internal phase and the resulting droplets are immediately coated with hydrated colloid formed at the same instant, this coating, according to Fischer's theory, being the *sine qua non* of emulsification. Mixture Jc apparently is an exception to this rule.

An examination of Table II will also show that the globules in soap emulsion are considerably smaller than those of the corresponding acacia emulsions. The special note under Mixture M is of interest since it describes certain vibrations of particles in the films surrounding the globules or perhaps in the globules

it is necessary for emulsification; (2) that this hydration compound is most efficiently used if formed at the moment of dispersion of the internal phase—in other words, the three constituents, internal phase, emulsifier and water, in critical proportions, must all be mixed at one time in order to form a properly hydrated nucleus; (3) slight variations from the proper procedure or from the critical proportions yield either less stable emulsions or none at all; (4) no emulsion results if the emulsifier is diluted (hydrated) before dispersion of the internal phase; (5) emulsions of better color, consistency and stability result from the dilution of a properly hydrated nucleus prepared from critical proportions, than are formed by agitation of the same quantities of internal phase, emulsifier and a volume of water equal to the total volume present in the above diluted emulsion.

We agree with Fischer in his statement that a hydrated colloid is an essential part of an emulsion, especially as applied to emulsion nuclei, but we do not agree with his contention: "An emulsion breaks whenever the hydrophilic (lyophilic) colloid which holds the aqueous dispersion means, is either diluted beyond the point at which it can take up all the offered water or is so influenced by external conditions that its original capacity for holding water is sufficiently reduced." If all the water be used to form the colloid hydration compound, we do not see how this nucleus may be so greatly diluted and still yield good emulsions.

SUMMARY

I—Definite critical points of emulsification have been shown to exist.

II—These critical points depend on (a) the quantities of internal phase and of emulsifier; (b) the nature of the internal phase and of emulsifier; (c) the procedure followed in the preparation of the emulsion.

III—Fischer's hydration theory of emulsification has been sustained, in part.

IV—Preparation of nuclei to be subsequently diluted lead to the best emulsification. This is in conformity with the usual pharmaceutical practice.

V—Nuclei of one composition are not suitable for incomplete emulsions of other compositions.

VI—Nuclei of one composition are not suitable for other internal phases.

RECEIVED JANUARY 11, 1917
NEW YORK UNIVERSITY, NEW YORK, U.S.A.

LABORATORY AND PLANT

RECENT DEVELOPMENTS IN CHEMICAL ENGINEERING EQUIPMENT¹

By H. D. MOORE

As it is impossible in the time at my disposal to describe adequately the development of chemical engineering equipment, I shall merely review briefly some of the more important phases in their history, under my observation in the course of my chemical equipment for the purpose of which I am president.

¹ Presented before the 1916-17 Annual Meeting of the American Institute of Chemical Engineers, Chemical Section, New York, December 1-11, 1916.

The company was organized twenty years ago when at the time was contained a small department, namely the operation of a sodium borate and soda ash refinery, incorporated under the name of the American Soda Ash Refining Company. At that period, the large majority of borates were produced by the use of simple methods, and no mechanical was used in the chemical composition of the sodium and soda. Mineral acids were used in the preparation of the soda ash, but it was not until 1911 that the soda ash was first produced by the use of the soda ash refinery. It is the purpose of this paper to describe the development of the soda ash refinery and the soda ash refinery.

was paid to the percentages of different elements contained in the iron. Frequently what appeared to be a high-grade No. 1 Pig Iron, would, when analyzed, prove to be an inferior grade.

Laboratory control established for us a reputation for quality and accuracy, and chemical castings, demanding the highest developed standards, immediately became one of our principal products.

It is now fourteen years since we entered this field, and for an active beginning joined issue with European manufacturers who were exporting to the United States the large pots used by caustic manufacturers and who largely dominated the American market as the domestic product was inferior. After careful research and development, assisted by the coöperation of our customers, we were finally able to produce caustic pots of a better quality, *i. e.*, giving longer life than those imported from Europe.

We next turned our attention to chemical retorts of one type or another for handling different acids, and to acid eggs and acid kettles, and ultimately obtained equal results in the manufacture of these.

After our success with these lines of chemical equipment, and several years before the outbreak of the present European war, we entered the field as manufacturers of vacuum dryers, pumps, and condensers, which apparatus has today so wide an application in the chemical field. We developed a full line of vacuum dryers, consisting of shelf dryers, rotary dryers, drum dryers, and vacuum drying and impregnating equipment, as well as the auxiliaries which go with such apparatus, namely: vacuum pumps, condensers, expansion tanks, reclaiming devices, dust collectors, etc. This equipment, which we have highly developed with new and patented devices, is especially useful where rapid drying free from atmospheric variations is required, or where in order to avoid injury to the materials under treatment, drying must take place at low temperatures. Our vacuum drum dryers are constructed to dry in large quantities and at low cost and without any practical loss of material, emulsions, pulps, extracts, white lead, glue, milk, acids, dyes, and other liquids containing solids. These liquids are reduced to dry forms economically and quickly and without danger of injury to the quality of the material. We have so far manufactured 5 sizes of vacuum drum dryers, the smallest having a drum 2 ft. in diameter by 20 in. face, the largest 5 ft. in diameter by 12 ft. face. All sizes are so constructed that they may be easily cleaned and kept in sanitary condition, which is a vital consideration when handling food products. The smallest dryer is so constructed that the casing over the drum can be readily moved back on a track so that free access can be had to all parts of the interior. The larger types are so arranged in size and convenience that a man can enter the casing and scour all parts of the interior.

Our patented method of applying the liquid to the surface of the drum is the result of many developments in our particular machine, and the present arrangement assures a very uniform coating on the drum as well as a large output. There is a large reservoir in

the bottom of the casing for holding a considerable quantity of material to be dried. This material is taken, as required, by a circulating pump located beneath the dryer and delivered to a supply pan immediately under the drum and slightly in advance of the knife or scraper, which removes the material. Only a small section of the drum surface comes into contact with the liquid material and, therefore, over three-quarters of the drum surface is active at all times in drying. The material is forced in the pan under sufficient pressure to insure a uniform coating on the drum. The extra supply of liquid, which escapes on the side of the pan, where the film comes out, overflows into the reservoir in the bottom of the dryer. By the time the material reaches the scraper it is dry enough for removal. It is automatically scraped from the drum, falls into a conveyor and from there is removed to a receiver. Two receivers are used, one on each end of the machine. While one is being loaded, the other is unloaded, an arrangement which permits the machine to be operated continuously.

Where the drum dips into the main body of the liquid, it is impossible, owing to the agitation and foaming of the liquid, to maintain always a constant level of the liquid material. This consequent change in level results in an irregular immersion of the revolving drum surface, with a constant variation in the moisture content of the dried product, loss of continuous service, low output and heavy cost of operation.

With our method, the drum does not come into contact with the main body of liquid, and, therefore, any material can be dried satisfactorily whether it foams in a vacuum or not. It is also to be noted that as some materials give over their moisture more readily than others, the speed of the drum, and the pressure of steam used in the drum, can be varied to suit the material being treated.

USES OF VACUUM DRUM DRYERS

One of the most extensive uses for our vacuum drum dryer has been in the production of powdered chestnut and hemlock extracts. Formerly, these extracts were put on the market in a liquid state, containing approximately 50 per cent moisture. They were shipped in tank cars. These materials, with this moisture content, can be treated in our machine and dried to a powdered form, having from 5 to 7 per cent moisture content. This dried material can be packed into bags and shipped in this manner to any part of the world. By handling it in this form the market for the material is not only very much widened, but the expense and trouble of tank cars is eliminated, and consequently transportation expenses greatly reduced.

Another important use for this machine has been developed in the recovery of dry sulfite waste from the waste liquors of paper mills. This product, owing to its recovery in a dry state, now brings a handsome profit to the paper mills, and secures another by-product that can be converted to many useful purposes. It further enables the paper mills to comply, actually at a profit, with the laws prohibiting the pollution of streams with sulfite waste.

The approximate capacity of our 5 ft. by 12 ft. vacuum drum dryer on the above mentioned extracts and sulfite waste, is 1000 lbs. of dry product per hour. The cost of operation is extremely low. We have dried products where the cost, including depreciation and interest on investment, steam, power, labor, and incidentals, has not exceeded 0.1 cent per lb. in reducing a product from a 50 per cent moisture content to a commercially dry product under a 7 per cent moisture content.

Vacuum shelf dryers and vacuum rotary dryers have also been extensively used in the recent chemical development in this country. They can be used to great advantage in drying some of the chemicals derived from coal-tar distillates. This use is in addition to their previously extensive application in the drying of both liquid and solid materials. These dryers are also especially valuable in handling solid materials; the shelf dryer for sheet rubber, fruit, albumen, etc., together with the rotary dryer, is available for use in drying reclaimed rubber, rubber compounds, paints, dyes, extracts, pastes, glue, soap, salts, starch, vegetables, etc. Where the quality of the material is not affected by being tumbled or mixed while drying, or is not of too sticky a nature, the rotary dryer is an ideal apparatus for drying in large quantities.

At the outbreak of the present European War, when the supply of many materials never made in America, was cut off, there was a sudden and large demand for chemical equipment, particularly in plants handling the many products produced from coal tar. In order to meet this demand, it was important first to make use of apparatus developed for these purposes in Europe. It was also essential to design new types of apparatus to suit conditions in this country and to make modifications in equipment which had been developed abroad.

Our company at once added to its already well established engineering and consulting staffs, a corps of experienced specialists, who, with the cooperation of chemical engineers associated with chemical plants, developed machinery to manufacture economically the new products so greatly in demand, and we are to-day supplying apparatus for the manufacture of a large number of these products, such as

Aniline	Meta Nitrindine
Acetanilide	Meta Phenylenediamine
Anisidine	Meta Tolylendiamine
Alpha Naphthylamine	Metanilic Acid
Alpha Sulfonamide	Naphthoic Acid
Amido Naphthol	Nitric Acid
Alpha Naphthol	Ortho Anisidine
Benzene Acid	Ortho Phenetidine
Benzothiole	Para Anisidine
Beta Naphthylamine	Para Phenetidine
Beta Naphthol	Para Nitroline
Beta Sulfonamide	Para Phenylenediamine
Carbolic Acid	Para Amidophenol
Caustic Soda, etc.	Phenetidine
Dinitrobenzol	Picric Acid
Dinitro Chlorobenzol	Sulfur Black
Dimethylaniline	Sulfonic Acid
Diphenylamine	Toluidine
Gamma Acid	Trimethylololol
H Acid	Xanthine

DEVELOPMENT OF ATMOSPHERIC DRUM DRYER

One of the first products we were called upon to produce machinery for was synthetic phenol. The method generally used in treating sodium benzene sulfonate, before fusion with the caustic soda, was to

take the liquor from the filter presses, evaporate it as far as possible in open pans containing heating coils and then dry the salt before fusion, either by means of heated air or by some other crude method. We, of course, easily determined that a vacuum evaporator should be installed for reducing the liquor to a certain density, thus doing away with the open pans. The problem that presented itself was how best to handle the evaporated liquor. Our engineers and chemists assumed that the vacuum drum dryer would be the ideal machine for treating the liquor as it came from the evaporator, but we found by actual experiment, that, owing to the peculiar nature of the liquor, it was very difficult to secure under a vacuum a good coating on the drying drum.

We next tried the vacuum rotary dryer, but found that this machine formed the product into large cakes or balls. It was impossible to extract the moisture from the interior of these masses without spending considerable time in drying, our object here being, as in all cases, to produce the most economical method for handling a given product. We found that the experience we were having with this product coincided with that which we had had on some other products, which we worked out by using an atmospheric drum dryer for reducing the moisture content to, say, approximately 12 per cent, and then finishing the process in a vacuum rotary dryer. This method produced the desired results and furnished a beautiful sodium benzol sulfonate salt ready for fusing with the caustic soda. A later experiment has shown that it was not necessary to reduce the moisture content in the sodium benzol sulfonate to below 12 per cent before fusing with the caustic soda, with the result that the vacuum rotary dryer has been eliminated, and the atmospheric drum dryer is used exclusively for handling the liquor as it comes from the evaporator.

We later found that our atmospheric drum dryer has many uses in chemical plants. The patented successful principles of operation in this dryer are the causes for its exceptional success in this field. It embodies the principles of our vacuum drum dryer. The same patented automatic device for applying the liquid to the drum, produces a uniform coating on the drum, and consequently a uniformly dry product. It is an ideal machine for drying materials that can be dried rapidly and without injury under atmospheric conditions, such as salts of nitric acid, sodium naphthalene sulfonate, and other similar products. The machine is continuous in its operation and is a great labor saver. The finished product is uniform, and when desired for fusion, is in excellent condition to go direct from the dryer to the fusion operation.

One of the early demands after the beginning of the European War was for a substitute for the manufacture of aniline oil. The improvements herein the improved design indicating to use what automatically runs the valve when open and closes it immediately when closed; the introduction of a pressure from steam, hollow shaft and valve, for the introduction of steam when desired, and the provision of a control for special cases.

BETA-NAPHTHOL DISTILLATION APPARATUS

Another development we have made is apparatus for the distilling of beta-naphthol. This consists of a still body, constructed of a special metal, and fitted with a cover in the usual way. The new feature of this still is the condensing and receiving system, the condensation being drawn into an air-cooled condenser consisting of a single pipe. This pipe leads into a steam-jacketed, 3-way valve, one of the valve openings attached to the condensing pipe, and each of the other two leads to a receiver. The steam in the jacket prevents the material from solidifying in the shelf, the material on entering the receiver passing between two glasses. By this means the operator can easily determine when it is shut off, and change from one receiver to another. These receivers are rectangular cast iron boxes with a door opening the full size at one side. Inside of the receiver is placed a steel box with tapered sides which fits as neatly as possible the full size of the receiver. The beta-naphthol solidifies in this box, which is easily removed and is dumped by taking out the tapered box. In addition to the foregoing, the still is supplied with a large tank in which are placed baffles to collect any material that may pass a receiver. Beyond this tank two smaller receivers are supplied, one for containing the liquid to neutralize the vapors if any should pass this distance from the still; the other receiver is for this liquor in the event that the air current is reversed in the pipe. This allows the liquor to flow from one tank to the other as the case may be. The entire apparatus is evacuated by means of a dry vacuum pump, and the still is heated by a direct fire.

RECLAIMING HIGH BOILING POINT SOLVENTS FROM WASTE

Another of our developments in the manufacture of sulfanilic and naphthionic acid and for reclaiming high boiling point solvents from waste, is a direct heated shelf retort, consisting of a chamber, provided with ducts passing from one side through an opening on the opposite side. Between the ducts, and inside of the apparatus, are formed shelves. The one side of this retort is provided with a door opening the full size of same. The retort can be operated either with or without a vacuum. The retort when operated under vacuum is connected with a dry vacuum pump and a condensing system between the pump and retort. The material is placed on the shelves in pans and the hot gases from the furnace, in which the chamber is placed, passed through the inside of the shelves. The regulation of the temperature on each shelf is made by dampers which permit more or less of the hot air to pass through the shelf. This type of retort is far more efficient and has a much larger capacity than the previously odd shaped affairs used for this purpose, and is much more rapid in its operation.

SPECIAL AUTOCLAVES

Another improvement that we have made is in the construction of autoclaves for the production of dimethylaniline. It has always been the practice to use an enamel or silica lining in the autoclave, which

has caused more or less trouble due to the checking and cracking and final deterioration of the enamel. This led us to develop an autoclave which uses as a liner a highly acid-resistant cast iron. The difficulty encountered in this construction was that the acid-resisting metal is more or less brittle and would not stand the high pressure necessary for the autoclave in the manufacture of dimethylaniline. This led to our adopting the method of backing up the acid-resisting castings with a lead lining.

ACID RECOVERY

The rapid expansion of the chemical industry has brought up seriously the question of economical acid-recovery plants. In this line one of our ingenious and unique developments has been the patented denitrating apparatus, which has for its purpose the distillation of nitric acid from a mixture of nitric, sulfuric and water. This particular form of construction of the machine enables this nitric acid to be distilled off at a high strength and reasonably free from lower oxides of nitrogen.

The reasons why results can be obtained from this apparatus and not from an ordinary plain still are as follows: The new type of denitrating apparatus presents a very large heating surface in contact with the acid mixture to be treated. The temperature of that part of the apparatus above the level of the acid mixture, cannot by any possibility rise above the temperature of the nitric acid vapors produced in the apparatus. By this means the strongest nitric acid vapors are not decomposed by coming in contact with superheated metal surfaces. Therefore, the very strongest acids, and fairly free from lower oxides of nitrogen, will result.

The distillation of the nitric acid is effected at a much lower temperature than is ordinarily possible. This is done by the injection of air at the bottom of the machine, which keeps the acid mixtures in violent agitation, and the nitric acid held in the mixture is removed most effectively by the sweeping effect of the air. The direct heat from the furnace is drawn through the double U pipes in the apparatus, which are always covered with acid. By this means the greater part of the heat is directly absorbed and the balance of the heat contained in the flue gases, after leaving the double U pipes, is drawn around, thus giving additional heating surface and giving the greatest degree of efficiency in operation. The distillation of the nitric acid is therefore effected under almost ideal conditions, and by the use of the air the factor of mass action (which has to be considered in an ordinary still when nearly all the acid is distilled off) does not occur in the new type of apparatus. By this I mean that when the ratio of sulfuric acid to nitric acid toward the end of a distillation becomes so great that a very high temperature has to be carried in the still, the nitric acid evolved must necessarily be weak.

For example, in handling a guncotton displacement system the first run-off of spent acid is, of course, reinforced with nitric and oleum, but the second displacement, which consists of approximately 18 per cent

the advance in the design of machines to meet new conditions. It is true that great secrecy surrounds many of the chemical manufacturing processes in this country, and where publicity would affect the earnings of chemical companies, it is wise to avoid undue publicity. But giving due regard to the protecting measures required, I believe it is nevertheless possible for manufacturing chemists to submit many problems to the manufacturers of chemical equipment, which the latter can solve to the benefit of both sides of the industry.

BUFFALO FOUNDRY & MACHINE COMPANY
BUFFALO, NEW YORK

EMULSIFICATION OF MINERAL LUBRICATING OILS: APPARATUS AND TEST METHOD

By P. H. CONRADSON
Received November 1, 1916

The simple apparatus and method of testing described, to determine the emulsibility and demulsification (demulsification value) of lubricating oils such as steam-turbine, steam engine, and crank-case oils, have been used in daily routine work for the last year or more in the writer's laboratory, and have been found to give satisfactory results considered from a practical service standpoint. They are simplifications of a much larger apparatus and more laborious method used previously for several years by the writer, in connection with investigations of principally turbine oils in actual service, with reference to trouble from emulsifications.

Others who have suggested apparatus and test

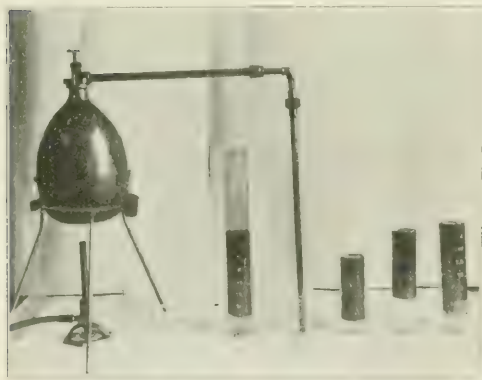


FIG. 1. OIL EMULSIFYING TESTING APPARATUS

methods in connection with emulsion tests of lubricating oils, as Phillips,² Herschel,³ and Bryan⁴ have written at considerable length and in elaborate detail on the subject; therefore, this paper will be confined to a brief description of the apparatus, method of testing, and interpretation of results.

Read before the 19th Annual Meeting, American Society for Testing Materials, June 27 to 30, 1916.

² *J. S. C. C. P. D. S.*, July 15, 1915.

³ Bureau of Standards, Washington, D. C.

⁴ Experimental Station, Navy Department, Annapolis, Md.

APPARATUS

Fig. 1 needs but little explanation. The apparatus consists of a 4-pint copper retort, provided with a delivery tube, which is joined to a metal or glass pipe having an inside diameter of about $\frac{7}{16}$ in. and about 15 in. long from the elbow. The lower end of this pipe is cut off diagonally to prevent thumping.

The glass cylinders are graduated to 250 cc. They have an inside diameter of about $1\frac{7}{16}$ in. and a length of about $9\frac{1}{2}$ in. from the bottom to the 250 cc. mark. They are $11\frac{1}{2}$ to 12 in. in overall length, and are made of thin glass, with a flat bottom.

In place of a copper retort for the generation of steam, a glass flask or any other suitable source of steam supply may be used; likewise, ordinary 250 cc. graduated glass cylinders, of dimensions given above, may be used where emulsion tests are required only occasionally.

METHOD OF TESTING

The cylinder is filled with distilled water up to the 20 cc. mark, then 100 cc. of the oil to be tested are added. To churn the mixture, steam at ordinary pressure is conducted through this oil-water mixture for ten minutes. The amount of steam passed through is regulated in such a way as to prevent the mixture from splashing over the top of the cylinder, but the rate may be as rapid as is practical. This is easily regulated by the height of the gas flame.

The churning is begun from the time the temperature of the mixture has reached 200°F. , or when the steam as such passes off the mixture. It usually takes from 1 to $1\frac{1}{2}$ minutes to reach this temperature, depending somewhat on the body or viscosity of the oil. However, even churning with steam for 15 minutes does not seem to make any difference in the results.

When the churning is completed, the cylinder is immersed for one hour in a water bath, kept at a temperature of 130°F. During this time the cylinder and its contents are momentarily inspected at intervals to note the behavior of the oil mixture. At the expiration of one hour the cylinder is removed from the water bath and the contents are examined for the following:

- (1) The number of cc. of separated clear or turbid water.
- (2) The number of cc. of separated emulsified layer.
- (3) The number of cc. of separated clear or turbid oil above the emulsified layer.
- (4) The percentage of water or moisture in the separated oil above the emulsified layer.

The number of cc. and condition of the emulsified layer is an indication of the emulsion-forming property or quality of the oil.

The number of cc. of clear or turbid oil above the emulsified layer, less the percentage of water or moisture contained in the oil, is the percentage of demulsibility of the oil.

The condition of the separated water or watery liquid under the emulsified layer, if any, gives an indication also of the behavior of the oil in actual service.

The amount of water held in the oil above the emulsified layer may be determined as follows:

The oil above the emulsified layer after the expiration of the test is carefully drawn off and shaken; then 20 cc. are mixed with 80 cc. of 88° Baumé gasoline (from Pennsylvania Crude) in a graduated, flat-glass precipitating tube having the lower end drawn out. The oil-gasoline mixture is kept at a temperature not over 80° F. for one hour, or the water or watery liquid may be separated from the oil-gasoline mixture by means of a centrifuge. The amount of water or watery liquid is read off and calculated to percentage by volume and subtracted from the oil above the emulsified layer. Of course, this determination is only necessary when the oil above the emulsified layer appears to contain an appreciable amount of water.

INTERPRETATION OF RESULTS

Fig. II illustrates the behavior of seven representative oils with this method, as they appear after expiration of the tests.

EMULSION TEST APPARATUS AND METHOD FOR LUBRICATING OILS



FIG. 11—REPRESENTATIVE LUBRICATING OILS AT EXPIRATION OF EMULSIFYING TESTS

Table I gives detailed results of tests of these oils. The first turbine oil shows the oil entirely free from emulsifying property or elements, only retaining a very small percentage of moisture or water after the ex-

TABLE I
EMULSIFICATION TESTS OF LUBRICATING OILS

Oil No.	Kind of Oil	Temp. of Water, °C.	Condition of Water	Emul. Layer	Kind of Emulsion	Temp. of Oil, °C.	Condition of Oil	Moisture in Oil, per cent	Density, per cent
1	Turbinol	40	Clear	None		100	Slightly turbid	0.2	99.8
2	Turbinol	36	Slightly turbid		Light foam	100	Turbid	1.0	99.0
3	Crank Case Oil	40	Clear	None		100	Very turbid	5.0	95.0
4	Crank Case Oil	1	Clear	1.0	Heavy thick	Trace	Practically all emulsion		0.0
5	Engine Oil	None		10	Thick milky	102	Very turbid	1.0	99.0
6	Engine Oil	37	Clear	8	Light foam	102	Turbid	1.0	99.0
7	Spindle Oil	30	Milky	148	Thick milky	None	All emulsion		0.0

piration of the soil. The second system of floors quite a little or completely free, but the condition of the simulated floor is high, and floors are composed of cement. The ground of water is moisture retained in the soil is much higher than in the first soil.

Consider now the 500 sample of sediment in the first of more finely stratified sections where clear and fine sandstratified layers less than 10 cm thick predominate, closely associated with thin, white, clayey, mudstone of little or very fine-grained, continuous, wavy, or laminated, or of the impression of the sand and a very large amount of sandstratified layer of 1/2 to 1 m thick nature to develop. In fact, the whole section is a fine-grained sandstone or clayey sandstone.

The first sample of engine oil shows at the end of the test a thick milky emulsion with practically no separation of water, and the separated oil above the emulsified layer contains about 4 per cent of water. The second sample of engine oil shows considerable amount of separation of water and much smaller amount of emulsified layer; this layer is of a light foamy nature.

It should be particularly noticed in these two cases that while 100 cc. of oil were used in the tests, 102 cc. of separated turbid oil were found; deducting the amount of moisture or water found in the separated oil, 4 and 3 per cent. respectively, gives 96 and 97 per cent of demulsibility. This is a clear illustration of the importance of giving a complete statement in the report of the behavior of the oil or oils in the emulsifying test, as simply stating the percentage of demulsibility is clearly insufficient, and in cases of this kind would be seriously misleading.

GALENA SIGNAL OIL COMPANY
FRANKLIN, PENNSYLVANIA

THE SAMPLING OF FERTILIZERS

By $E \geq \text{Id}_E$ we have

In considering the question of sampling fertilizers, the first basic idea to be realized is that we are not dealing with a homogeneous substance, but a mixture of a number of different ingredients, each of a different specific gravity, of a different texture, and of different sized particles. These factors all contribute to the tendency to unmix or to destroy the uniformity of the material and make the problem of obtaining *average* samples a most difficult one.

The manufacturer is first concerned in getting a proper sample of his raw materials, in order that he may know how to formulate his mixtures so as to be assured that his finished product will not only contain the amount of plant food specified, but that a proper sampling and analysis of the goods will confirm his guarantees. To accomplish this, when unloading bulk goods from a car, a small scoopful of the material is taken from each wheelbarrow or cart as it passes some specified point, these samples being placed in a large bag, so that every full quart will contain one of the entire sample. This bag is sealed. A man is found to take these samples, since it has been found that there are considerable discrepancies when handfulls are taken, the finer particles sifting between the fingers. When samples are taken from drums, the same plan is followed, the material being put in bags, and one bag taken from each such fraction. In sampling from bags, the manufacturer is usually given the four or five bags at the bottom of the lot, and one from each bag, and sometimes from all the bags. These are put in one large bag, from which a sample is taken. In some cases, the bags are numbered, and a sample taken from each, and the samples are then thoroughly mixed, and a sample taken. Some of these are the more important points in sampling grain. And this all in the first place, before the material has even begun its journey to the sampling laboratory, very seldom

and homogeneous in composition and mechanical condition.

In the modern fertilizer factory all sampling is supervised by the man in charge of chemical control. He is usually a graduate chemist, who has had special training in sampling methods. All mixed fertilizer shipments are controlled by samples taken regularly at the delivery point of the finished material, before it is bagged. These analyses are checked daily against the formulas, and discrepancies are corrected in the manufacturing processes. The chemical control man is constantly behind the sampling, devising new methods and bettering old ones, so as to insure the best possible samples.

Upon canvassing the fertilizer-consuming states we have found 8 different types of samplers in use in official state inspection, besides a few practices that

will then fill with the same material from the top of the bag that is in the bottom of the tube, the plug preventing any of the material from the bottom of the bag from being collected. Three states are using this kind.

By far the most common type is the so-called butter, lard or cheese tryer, which consists of a half round tube tapered slightly. This cannot remove an average sample, since the material nearest the point of withdrawal will tend to scrape out material further down the tube. Fourteen of the twenty-six states use this type, some of them with modifications. One state uses an iron spoon, one a cup, one a sugar tryer which is merely a slightly tapering tube about 2 in. in diameter and 8 in. long; one state uses a rice sampler, a tube about 9 in. long tapering from 1 in. in diameter to a solid point with a slot $\frac{3}{8}$ in. \times $2\frac{1}{2}$ in. about

half way, which is supposed to allow the sample to enter the tube. One state uses a tube open at the bottom and side but with a flange turned to act as a scraper to fill the tube. Wet goods tend to clog this type.

It would seem from the above that only the two types (Indiana and butter tryer) were in general use, and an investigation was undertaken to determine the accuracy of each. One large company after careful investigation found that a complete fertilizer having a large amount of its ammonia derived from nitrate of soda, upon being sampled from the bags, would almost invariably give one-half of one per cent more ammonia with the Indiana type of sampler than with the butter-tryer type, the supposition being that the larger crystals of nitrate

were dragged out when the butter tryer was withdrawn.

In order to test the accuracy of sampling by means of the butter-tryer type of sampler, a box was built with burlap ends. This box was filled with layers of materials crossways—first a layer of tankage, then one of acid phosphate, then one of bone meal, and finally one of nitrate of soda, the layers occupying approximately equal volumes, so arranged that a sampler passing through the burlap would pass through the layers of material in order as mentioned above. The sampling was done by the Indiana sampler and by the butter-tryer type. Four samples were taken, one from each end with each sampler.

The Indiana tube removed a sample with well defined layers corresponding to the layers in the box. The butter tryer when used from the tankage end



DIFFERENT TYPES OF FERTILIZER SAMPLERS

No. 1, Indiana sampler. No. 2, Open end double tube sampler. Nos. 3, 4 and 5, Butter tryer types. No. 6, Spoon. No. 7, Sugar tryer. No. 8, Rice sampler.

can scarcely be called samplers, such as cups and spoons. The sampler which seems best to meet all conditions is one designed at the Indiana station, which consists of two telescoping slotted brass tubes terminating in a solid pointed end. This enables the sampler to be inserted full length into the bag before any material can enter the sample chamber. This is then opened, the sample consisting of a complete core allowed to fill in, whereupon the sampler is closed and the tube withdrawn, unquestionably removing a core of the entire bag. Five of the twenty-six states canvassed used this type. Another type is quite similar to the Indiana sampler except that the end of the tube is open. The objection to this type is that in hard material a plug is likely to be formed when the tube is partially inserted, so that when opened the tube is already partly full, the top part of the sampler

of the box drew a sample which looked as if it were composed largely of tankage, this material having dragged out some of the acid phosphate, bone meal, and nitrate farther along the tube and displaced it; but when used from the nitrate end of the box, little tankage was in evidence, whereas nitrate crystals were distributed along the entire length of the tube.

The analysis of the samples taken by the Indiana sampler showed 16.17 per cent NaNO_3 when sampled from the tankage end and 19.71 per cent NaNO_3 when sampled from the nitrate end, this difference being due to the fact that the tube, owing to the closed end, was not quite long enough to reach through the entire box, so that slightly more nitrate was obtained when sampling from the nitrate end. However, with the butter tryer when sampling from the tankage end only 4.62 per cent of NaNO_3 was obtained, while when the sample was taken from the nitrate end 23.41 per cent NaNO_3 was obtained.

In another experiment a box was made up of similar layers of tankage, acid phosphate, bone meal, and manure salts. When sampled from the tankage end, the analysis of the sample taken by the Indiana sampler showed: Ammonia 3.62 per cent, total P_2O_5 15.65, and K_2O 3.59—which is close to the calculated analysis; but the sample taken by the butter tryer gave: Ammonia 4.35 per cent or 0.73 per cent more, total P_2O_5 15.13 per cent or 0.52 per cent less, while the K_2O was only 1.60 per cent or 1.99 per cent less than the other sample. The increase in ammonia and decrease in the other two ingredients would seem to show conclusively that the layer nearest the point of exit of the tube does drag out material collected toward the end of the tube and fill in the empty space itself. This was also definitely shown in the case of the nitrate of soda samples mentioned above.

We realize that the conditions used to test out this point are by no means ones that would be met with in actual practice, but it is only by going to such extremes that definite tendencies can be conclusively demonstrated.

Under these conditions, especially after the vibration of long railroad hauls may have caused segregation and stratification, it would seem that the conditions of the law were not being fulfilled when the butter-tryer type of sampler is used, when the law specifies that a core shall be taken through the sack or even when it specifies that an average sample shall be taken.

Further analysis of state methods reported above, that in most cases 10 per cent of the bags in a shipment are sampled, although some state sample as low as only 5 bags in a large shipment. Others will not sample shipments of 1 ton or less unless it is the only chance for a sample of that kind. There are few criticisms to offer on the percentage of the bags sampled.

In the rest of the numerous cases respecting the sampling is directly under the State Chemist, while in the other nine states under the Commissioner of Agriculture and the chemist only receives his actual analysis.

In previous one of the present laws authorizing the

inspectors are either appointed or recommended for appointment by the State Chemist, and are usually trained men and the positions usually permanent. In the other ten states the appointments are made by the Governor or Commissioner of Agriculture, often for political reasons, and the appointment is often for short periods, such as three months.

In conclusion I should like to recommend that the chairman of this division appoint a Committee of five members, two to be State Chemists in charge of fertilizer control work, two to be manufacturers' chemists, and one to be a commercial chemist largely engaged in fertilizer work: this Committee to formulate a standard method for the sampling of fertilizers. When a satisfactory method has been agreed upon, the Committee is to submit it to the A. O. A. C. for their official consideration and action, looking toward its acceptance and incorporation among their official methods.

LABORATORY OF ARMOUR & COMPANY
CHICAGO

AN IMPROVED TABULAR ARRANGEMENT FOR CHEMICAL FACTORS

By CLARENCE V. JACKSON

Received January 1, 1916

The writer for several years has been using a very convenient arrangement in his tables for gravimetric factors.

This tabulation has been found to be very satisfactory by many of his co-workers, and upon their suggestion, and in the hope that it will prove of help to others who may have frequent occasions to use factors, a brief description is given here.

The arrangement is illustrated in Table 2, and, for comparison, in Table 1, the usual method of tabulation is given.

A.		TABLE I			
Weighed or Found	Required	A.		B.	
		Factor	Equivalent	Factor	Equivalent
Calcium, Ca = 40.07					
Ca	CaCl ₂	1.0000	0.4401	0.4401	1.0000
Ca	CaO	1.0000	0.4401	0.4401	1.0000
Ca	CaCO ₃	1.0000	0.4401	0.4401	1.0000
Magnesium, Mg = 24.32					
Mg	MgO	1.0000	0.4401	0.4401	1.0000

TABLE 2					
Weighed or Found		Required		Found	
Element		Factor		Factor	
Calcium, Ca = 40.07					
1.0000	0.4401	1.0000	0.4401	0.4401	1.0000
1.0000	0.4401	1.0000	0.4401	0.4401	1.0000
1.0000	0.4401	1.0000	0.4401	0.4401	1.0000
Magnesium, Mg = 24.32					
1.0000	0.4401	1.0000	0.4401	0.4401	1.0000

By the proposed method, as shown in Table 2, the necessary factor required by the analyst is practically furnished as it is only necessary to remember that the factor for the substance "required" is obtained by dividing 10.0000 by the atomic weight of the element (rounding down from the "weighed or found" and leaving the "required"). This is shown in the column headed "required." Thus, 10.0000 by 40.07 "found" will give 0.2500 "required." The same will apply to the right-hand column shown at heading or, e.g., when

as, if CaO were "weighed" and Ca were "required" the arrow would point toward the left-hand column (shown in heading at bottom).

The arrangement is thus not only more logical but also is more efficient. Repetition of factors, in reversed order (shown in Lines 2 and 3 of Table 1), becomes unnecessary. Elimination of the chances of possible error resulting from confusion of columns, and saving of the time otherwise required to insure their avoidance.

are further advantages which should commend this method of tabulation, not only to those workers who make up tables of factors for special uses, but also to authors generally.

The arrangement, of course, may be employed for any system of factors which are arithmetically complementary.

CHEMICAL LABORATORY, BUREAU OF FOODS AND DRUGS
DEPARTMENT OF HEALTH, CITY OF NEW YORK

ADDRESSES

OUR ANALYTICAL CHEMISTRY AND ITS FUTURE^{1,2}

BY W. F. HILLBREND

In an address read at Philadelphia nearly twelve years ago I gave expression to some thoughts on the condition of analytical chemistry in our country as the condition appeared to me then to be. Those thoughts were based on an experience of many years, during which I was engaged wholly in analytical work of a more than ordinarily exacting nature, and especially upon observations that had been acquired in connection with several series of cooperative analyses of diverse materials. Since then my attention has been no less given to analysis, largely for the past eight years in a supervisory capacity, however, and I have had opportunity to note the conditions that now prevail with respect to chemical analysis and what an important bearing exact analytical work often has on problems of physical and electrochemistry, metallurgy, etc.

It seems to me then that I can choose no more fitting subject for my present discourse than a continuation of one so closely related to my life work, one in which I feel a deep interest and of which I may be presumed to have knowledge somewhat worth presenting on an occasion like this. Then, too, since my remarks will apply most directly to analysis as it concerns the producers of the raw materials and the users of the products of applied science, the subject is eminently a proper one for the present occasion, and particularly so in an institution where applied chemistry made one of its important starts in this country, in the old School of Mines, with which the name of Chandler is so inseparably connected.

Although I shall cover now some of the ground traversed in my address of twelve years ago, in briefly alluding to the conditions of analytical chemistry in the present year, 1916, there is much to be said in developing one or two of the ideas then simmering in my mind and other phases of the general subject not then mentioned. So my subject calls for a more unrestricted title than I gave it at that time, and I shall speak to you of our analytical chemistry and its future, purposely restricting myself to a consideration of conditions as they exist and may become in this country.

In the early days of chemistry there was needed a vast accumulation of observations to serve as foundations for the development of the science. At the very basis lay the need for knowledge of the composition of all kinds of matter. Hence, it came about that many, if not most, of the great chemists of the time were of necessity analysts, and the analytical branch of chemistry stood in high repute. That this condition did not maintain itself, that chemical analysis during the latter half of the past century fell from its high estate and came to be looked upon more or less as a handy tool for ulterior ends, a tool, moreover, which need not for most purposes be of the

sharpest or the best or entrusted only to the most careful and skilled operators—all this has been recognized and lamented by many. The reasons for the fall are also well-enough known and need not be discussed at length, but brief reference to some of them will be needed in view of later remarks.

Chief among the reasons for the neglect of analytical chemistry is the enormous development, first of organic chemistry and later of the so-called physical chemistry. The effect was brought about in two ways: (1) By mere displacement, as it were, owing to the far greater promise of new discoveries, however commonplace, or because of the strong interest attaching to new and unexplored fields of inquiry; (2) By the unfortunate fact that for a long period approximate analytical results were thought to suffice in most of the industries, and even in scientific researches. This meant that slipshod work and methods came more and more into use and less fundamental knowledge of analysis seemed to be demanded of chemists—all of which reacted unfavorably upon the standing of the analytical profession, tending to discredit it as a whole, even though it held members fit to rank with the illustrious pioneers.

In addition, some chemists came to feel that the field was an exhausted one, offering little to reward the research worker. How little this is true the events of recent years have abundantly shown. The growing sense of the important influence of small, even minute, amounts of this or that element or combination in a given material and the high value of many ores and commercial products has led to more critical examination of the methods used for determining the content of the substances in question in order to ascertain with greater precision the value of those materials, just as has been done long before for the precious metals, gold and silver. Such examination revealed not infrequently unsuspected defects in methods regarded hitherto as reliable and accurate, and that good results were due often to compensation of errors or were to be had only within a narrow range of conditions. One good effect of such investigations has been to make conservative analysts distrustful of all new methods and less reliant on some of the old ones until their worth and suitability have been put to far more crucial test than was formerly deemed necessary.

Yet, notwithstanding improvements made in important methods through painstaking research, it is evident that many methods will require a study differently directed or more profound than any yet made before light enough to meet even our immediate needs is thrown upon them. And who shall say what needs another century or even decade may bring forth? Are we not again and again even now confronted with the need to determine smaller and smaller amounts of a component and to make more and more perfect separations in order that the first may be possible? Are we to assume that a limit has been reached?

IMPORTANCE OF RARER ELEMENTS

Another fact shows how untrue it is that the field of chemical analysis has little new to offer. Few ever thought, not so long ago, to look for the rarer elements in an ore or industrial product

¹ Chandler Foundation Lecture delivered at a Chemistry University, November 7, 1904, copyrighted by Columbia University.

² To some of my colleagues in the Bureau of Standards, to whom the first draft of this address was submitted, I am under obligations for suggestions that have been most helpful in its further elaboration.

made from the ores. No use whatsoever was made of certain elements that are now serving most useful ends, either by themselves or in combinations. There are other elements, still chemical curiosities, for which no use has yet been found. Is there any more reason to believe for them than for the others that uses will never be found? Rare though they be, like gallium, indium, and germanium, and costly their extraction, the finding of a use for them will broaden the search for their ores and lessen the cost of production. With use will come a demand for methods of separation and determination, which must be accurate because of the small percentages in question or the enormous value of the material.

But there are other fields in which the chemist has to look to analysis of the highest order for help in solving his problems. For instance, the importance of exact analytical methods in connection with physico-chemical researches is very great and is, perhaps, best illustrated in the preparation of pure materials. There is no question that physical constants, even atomic weights, have been determined, not infrequently, upon materials of doubtful or at least unproved purity. The practice is all too common of assuming that a certain number of crystallizations or distillations is sure to yield a product of highest purity. Conclusive results can be obtained only when methods are devised and applied by which the amounts of any possible contaminant present can be proved to be without influence upon the results sought. A single instance, borrowed from the experience of the Bureau of Standards, may be of interest. In the preparation of pure alcohol to be used in the determination of a series of densities, tests were devised or confirmed for detecting the presence of minute amounts of ether, aldehyde, methyl alcohol, and water. The most delicate test for the latter was found to be the critical solution temperature of mixtures of kerosene and the alcohol to be tested. By this means the presence of 0.001 per cent of water in the alcohol could be readily detected.

In the field of electrochemistry there is a similar need for exact analytical data. In the determination of the electrochemical equivalent of silver, from which the value of the ampere is derived, researches extending over several years have shown that the purity of the electrolyte is of fundamental importance. Thus, it was found that the presence in the electrolyte of the amount of organic matter derived from filter paper by the passage through it of the distilled water used, was sufficient to cause an appreciable effect upon the structure and weight of the silver deposit. In this case delicate analytical procedures were devised for detecting minute amounts of such contamination. In the same research the study of the magnitude of possible occlusions in the silver deposits has involved the use of painstaking analytical methods at the Bureau and elsewhere.

Similarly, it is believed that the securing of accurate information regarding the operation of commercial baths for electro-deposition will depend largely upon the application of exact analytical method. Thus preliminary observation has shown that very slight differences in the neutrality of nickel baths may produce great effects upon their operation. Here the application of the hydrogen electrode as an analytical tool will probably be of service. The great number of empirical observations regarding the effect of addition agents in plating baths will become intelligible only when means are found and applied for determining quantitatively minute amounts of the addition agent, for instance, one part per million of fluorine of their decomposition product.

The application of some of the concepts of the modern theoretical chemistry has helped much to a better understanding of the limitations of some common methods of how to reduce the error of one or another of them within more or less ascertainable bound, and of why others are not open to improvement. The same principle applied to the development of new methods

will, it is to be hoped, lead more quickly to success than in the past by enabling the discoverer to take account from the start of earlier mistakes or omissions and thus avoid the wasted effort that has been all too common.

FAULTS OF 'NEW METHODS'

At this point it may not be amiss to point out certain criticisms that apply to many new methods as first published. Almost no new method that has been proposed has been so rigorously worked out as to show all or nearly all of its limitations. Generally the start is with the presumably pure single substance and the amounts operated upon are of considerable magnitude and do not cover a wide range of weights. This is not so serious a defect as to omit trying out a method that involves separations from other substances under a wide range of conditions as to relative and absolute amounts of the elements or compounds in question. A whole list is often given of results obtained in presence of other elements, but almost always the amount of the substance sought is considerable. No light is shed on the value of the method when that substance is in very small amount and the other greatly preponderates. Nor, in too many cases, is any proof afforded that results apparently good are really good and that more or less serious compensating errors are not involved. The consequence is often, as I have said, that one cannot take new methods at their face value or proceed to apply them under any and all conditions. They must first be more critically examined in order to complete and round out the work that was neglected. How this can be done will be discussed later.

What I have just said is not to be taken as necessarily reflecting upon the deviser of the incomplete method, nor need it deter others from trying to originate new methods or to improve old ones. There will be and must always be road breakers and pioneer surveyors. Some fertile minds are fitted to make brilliant reconnaissances and unfitted for the laborious working in of details. Both types of chemical workers are needed. The former will still find ample opportunity for flights of invention and there will be no lack of room for the able and painstaking delver into the depths.

In the address already alluded to and elsewhere I dwelt upon the unsatisfactory condition in which the art of analysis had been shown to be and expressed the conviction that our educational institutions must bear a large share of the blame in the matter. The faults which might be chargeable were perhaps more often those of omission than of commission, but I was able to point out no certain or even likely way which might lead to a better future. I think it may be worth while to reproduce certain of those paragraphs, with slight rearrangement, to serve not only as a record of work for which I am responsible but also as a guide to those who may hereafter come to realize themselves as teachers.

J. S. N. I. & Co., Ltd., 10, Broad Street, London, W. 1. Telephone: 2300.

Many suggestions addressed to the authorities in this area, as analysis, concern the information that has been reaching debate about the quality of the water that has caused "severe contamination" around it as it is fed in a few streams, one on the border line in nature. This has been known as to the quality of the streams, except that they have been "severely" from one substantial that a "lake" actually existed in the streams, bordering the river and the river itself. If the stream represented since then the water, as it goes and back down, what had become of the "contamination" of the polluted place below, then there is a contrast.

Now, my view that things would never become it had never been dramatically changed since the discovery of their impact that they probably never come in touch with anything which does not require any kind of environmental control from its immediate vicinity. I am confident that the fact that the fact that

that absolute accuracy is unattainable in analysis, but do you make it plain that approximation is possible and that it will be the closer the greater the care bestowed upon the tools and at every step of the analysis itself? Is a student ever required to find out by actual tests how good his water is and both the kind and amount of its contamination, if such there be? Is it customary to instruct him in the testing of his reagents and as to the character of the contaminations to be looked for in all of the more important ones, or is he allowed to go forth with the impression that the label C. P., while not a flawless title, is a sufficient guarantee for all the demands of technical analysis? Is he, in fact, ever cautioned to find out, by actual test, the errors with which his work may be affected, due to imperfections in his tools of the kind just mentioned? And that without such knowledge and the ability to make correction for the defects, or the courage to fight for better materials with which to work, he will occupy a false position with respect to himself, his employers and the community at large?

"Is the student's work ever checked against material of which the exact composition is known? I do not refer here to such things as simple salts, but to more complex bodies like limestone, cement, zinc ore or slag, in which many separations have to be made and all constituents should be determined. Is the student in such analyses religiously required to test the purity of his precipitates and the completeness of his precipitations by a careful examination of the filtrates? And is he taught that a satisfactory summation does not imply correct separations? Or that closely agreeing duplicates are not proof of good work?

"Only by such exercises can the young worker gain any knowledge as to his own power to do good work, and acquire that proper confidence in himself which is so essential.

"My experience of the past few years has convinced me that in these respects, at least, much is neglected that should not be neglected in the curricula of our colleges. It seems to me that if instruction in such fundamental essentials is not thoroughly drilled into the budding chemist, so that it becomes for him as much a matter of course afterwards to look to the quality of his tools as it is to weigh out his sample before analyzing it, he has received a scant equivalent for his years of study, and that he has good grounds of complaint against his alma mater if he comes to grief by reason of her neglect."

To the foregoing reasons for poor results may be added the youthfulness and inexperience of most of the instructors in quantitative as well as qualitative analysis. There must be young instructors, of course, but one of the rules which should hold for the young child in the Kindergarten or Montessori school ought to hold here too, namely, that the work should be led by or at least most closely controlled by one of experience and authority and of sympathetic insight.

If the conditions which I have sketched were true 12 years ago the question will be asked, and quite naturally: Have they improved? Candor compels me to say that evidences of improvement are few. In certain lines of work there has been some bettering of conditions, but we are still confronted with wide divergences in almost every direction between the results obtained by different analysts upon the same sample. I have many opportunities to note this fact in the cooperative work which is done upon the samples which the Bureau of Standards issues as standards for checking the skill of analysts or the value of methods used in industrial laboratories and educational institutions. The fact is further emphasized by the numerous requests received at the Bureau for umpire assays to settle the differences between commercial analysts, and still further by the comparative lack of sound or comprehensive knowledge of analysis among the young men who come to us from the colleges and universities.

While I believe now quite as strongly as I did twelve years

ago, that our educational institutions are not doing their full duty by their students in respect to the analytical branch of chemistry, I see no way by which the situation is to be relieved much under the prevailing educational system. Classes are too large and competent instructors too few for that individual oversight which is so essential to the attainment of the best results, and too little time can be devoted to analysis by students because of the multifarious demands made upon them in other directions. The conditions are far different from what they were, for instance, in Bunsen's laboratory, when students averaged two or three lectures a day and ambitious ones put in nearly all the rest of six days a week in the laboratory free from the harassing incubus of impending term examinations. This comparison is not made in a spirit of complaint, but merely to contrast ideal conditions, that have probably passed away even in Germany, with those which we have to face.

TEACHING STATES OF COLLEGES AND UNIVERSITIES MUST BE ENLARGED AND IMPROVED

If the defects noted are to be corrected in a measure, I see no way by which to accomplish this except by increasing the number of teachers and by extending the period of academic instruction, especially for those who contemplate following the most intricate art of analysis professionally and not merely as a prelude to something else which may bring greater financial returns. The adoption of this course, so often suggested, seems rather remote, yet it should certainly be adopted if we are ever to have a really competent body of instructors. As instructors, they would enter upon their teaching career with better preparation and wider experience, but this alone is not enough. Time should be accorded them, while teaching, to gain further experience in all manner of analytical procedures and to keep abreast of the advances made in the art of analysis. The benefits that would follow such changes would soon be manifest, but I doubt much if the exacting requirements of a great deal of our analytical practice would be fully met by them, so additional aids would still be welcome.

One of these aids we now have to a limited extent. I refer to the use of standard samples, such as are issued by the Bureau of Standards, following the practice for some time in vogue in the iron and steel industry particularly. The larger number of these samples, as most of you know, have been analyzed by eight to a dozen chemists who are expert in a given field of analysts and the averaged results are supposed to represent as closely as may be the actual composition of the material as a whole or as to certain of its constituents. If a chemist is able to analyze one of these samples correctly it may be presumed that his technique is good and that the results he obtains on the same type of material of unknown composition are to be trusted. If not, then either his technique or his methods are at fault.

In addition to these analyzed samples the Bureau of Standards has issued several single chemical substances (thus far only compounds of carbon) of the highest attainable purity, which serve as standards for volumetric or polarimetric analysis, or for calorimetry.

RELATIVE VALUES OF VARIOUS METHODS OF ANALYSIS NOW IN USE

The value of such aids as these to the analyst has been very great, and not only in the ways indicated. In connection with their analysis, prior to issuing them, many interesting observations have been made upon the relative values of various methods in common use. Our experience at the Bureau of Standards, extending now over a number of years, has shown that these methods are not all of equal trustworthiness and that one or another of them is affected by hitherto unsuspected errors, either inherent in the method as practiced or introduced by the presence of an unlooked-for element. The errors so detected may be very small and for some purposes negligible, but their existence is a disturbing feature and one which is sometimes

of moment. A few illustrations will suffice to make this point clear.

(1) There are several methods that are in daily use for the determination of phosphorus in steel. Most of them depend on the precipitation of the phosphorus as ammonium phosphomolybdate and many are the articles that have been written bearing on the proper conditions for forming and washing the precipitate. The wash liquid used in the alkalimetric method, which is probably the most widely employed of any of the methods, is a 1 per cent solution of potassium nitrate. Work done at the Bureau of Standards recently has shown that the solubility of the phosphorus-bearing precipitate in this wash solution, even in the absence of vanadium, is considerably more than has been suspected. In fact, on a high-phosphorus product, if an attempt is made to wash until the washings are neutral, the result may be several hundredths of one per cent low. This appears to be true whether the phosphomolybdate is precipitated in presence or absence of iron.

(2) The so-called evolution method for determining sulfur in iron and steel is one very much in vogue in industrial laboratories because of the short time required for the determination. In it the sulfur is driven out, mainly in the form of hydrogen sulfide, by boiling the alloy with hydrochloric acid, and collected in a solution of a cadmium salt with a view to determining the sulfur by titration with iodine. The method suffers, however, from defects, some of which are understood but others not, as is evidenced by the very discordant results that are reported by different analysts upon the same sample. So far as can be determined, the most discordant results are sometimes obtained by analysts who seem to follow precisely the same procedure. Evidently there is room here for some critical research.

(3) Manganese is determined in irons and steels by several methods, of which the bismuthate method affords perhaps the most concordant results in different hands when carried out according to certain closely prescribed details of manipulation and standardization of volumetric solution. There is still doubt, however, as to just what the conditions should be for obtaining a correct end-point in the titration.

(4) The methods in use for the determination of tungsten in ferro-tungsten failed completely in a particular instance that was brought to my attention by the chemist of a large steel plant. Works and commercial analysts differed by several per cent in their reported results. A partial explanation for the disagreement was afforded by finding columbium to be present in the alloy, an element hitherto unnoticed and unsuspected in such material. Attempts to devise a convenient and accurate method to meet the conditions have not been very successful, so far as I am aware. Here again is room for an interesting study.

In the analysis of a brass, one of the Bureau of Standards series of analyzed samples, somewhat discordant results for lead were reported by different analysts. It was found that those results which had been obtained by depositing the lead electrolytically on the anode in a process involving a slight error by reason of co-precipitation of small amounts of silver and cadmium, those having been present presumably in the colloidal form in the solution, were removed from the operation that had proceeded.

These examples show what a wide field there is for studies of a very refined character upon many of the methods that are in wide use before it can be said that we really know them.

Under a standard sample are those which are employed as actual checks upon analysis, do not fully meet our needs. They do not tell the analyst whereon the defect of his method may lie, if defects there be. How then may we hope further to benefit the practicing body of industrial and commercial analysts and instructors as well, who have no time for exhaustive methods

of direct determination or of separation, the latter involving often more difficulties than the former?

STANDARD METHODS OF ANALYSIS

Before attempting to answer this question I must take up the subject of standard methods of analysis. By a standard method is meant in a restricted sense one which has been put forth by a body of recognized standing, usually a committee acting under the auspices of some technical organization, for use in determining the value of a particular kind or type of material. This country has taken a decided lead in the direction indicated. The following quoted paragraphs are repeated from a paper yet to be published in full that I presented to the Second Pan-American Congress nearly a year ago.

"Most by far of the so-called standard methods are so by virtue solely of their having been put forth as such in a recommendatory way by some organization without imposing any obligation on any one to follow them. This condition takes away much of their standing in comparison with those methods of which the use is binding upon any body of chemists. There are, again, those methods which have been proposed as standard by individuals and are generally without organized backing. It is thus evident that discrimination must be exercised in deciding which of the very many methods put forth as standard have any claim to be considered such.

"The main arguments against standardizing methods have been: (1) That the individuality of the analyst should not be suppressed; (2) That to make methods standard would tend to prevent their improvement and to discourage search for better methods; and (3) That a given method may be applicable to a given material only within a narrow range of its possible compositions, as illustrated by pig iron and steel.

"The answer to the first of these objections is that experience has shown abundantly that for commercial purposes good agreement among analysts is seldom to be hoped for unless each worker uses the same method in which every step and condition of the procedure has been minutely prescribed. It is for commercial purposes that standard methods are most needed, and they need not always be the most exact methods if the latter require the expenditure of time so great or the employment of apparatus so expensive as to defeat the end in view. For many umpire analyses and for those upon whose results no commercial transactions are dependent, the analyst has ordinarily full liberty of choice.

"The first part of the second objection rests upon a misapprehension. In the minds of those who were pioneers in the movement for standardization it was probably never contemplated that methods once adopted should endure beyond the life of their usefulness. Either the committees responsible for them would revise them as occasion demanded or new committees would undertake their revision. This is the trend of intention here in the United States and undoubtedly wherever standard methods have obtained a foothold. It is, further, noticeable that the establishment of standard methods should tend to discourage attempts to improve them in the laboratory before they come to their place. If it is necessary to improve a method and become standard, the movement is considered to merit serious consideration, and it is in the whole development of the standardizing movement that the use of practice and experience would come into play to prevent duplication of the same old-fashioned progress.

The third objection must be attended to as well. There is nothing to be said of its nature. It seems the common sense of standard methods is sound. The difficulty referred to may be (1) that the method is not sound in its laboratory conditions, as in the case of the 'iron in steel' test, and (2) that the method is not sound in its commercial conditions, as in the case of the 'iron in steel' test, and (3) that the method is not sound in its commercial conditions, as in the case of the 'iron in steel' test.

partial one only—calls for employment of a variety of standard samples for a given material, covering adequately its usual range in composition, of each of which samples the composition has been determined accurately. Iron and steel are examples of this kind. If then, by applying this method to the particular standard sample which lies nearest in character and composition (mineral as well as chemical) to the material he is to test, the analyst obtains correct results, he is usually justified in concluding that the results he gets in the ordinary course of work upon similar material are also correct.

"The use of standard samples does away in a measure with the need for standard methods, for any method that will yield the true composition of the standard is a suitable one for a given analyst. Even so, it is usually only when this acceptable method is employed with strict adherence to a certain procedure that it yields a correct result. Thus prescribed and limited by a competent authority it may become a standard method for use in all hands. Nevertheless, a standard method is not always applicable to a complex material throughout the whole range of its possible compositions. In such case modifications of the method must be suited to the special conditions, or different methods altogether are called for. The determination of the need for such variations or changes is one of the duties of the committees entrusted with the choice or formulation of standard methods. These committees have also to consider, in special cases, the need of a refined method for umpire work and of another less detailed for work of a more routine character."

The principles which should lie at the basis of a standard method have been stated by me in a paper on Standard Methods of Sampling and Analysis and Standard Samples,¹ as follows:

- (1) That its limits of accuracy and its applicability are clearly defined and understood.
- (2) That it should yield sufficiently accurate and concordant results in the hands of different analysts.
- (3) That it should not demand such close adherence to detail or such manipulative skill and judgment, or such time consumption as to affect seriously its usefulness.
- (4) That it should have been tested upon material of high purity or upon material carefully analyzed by independent and reliable methods.
- (5) That the results obtainable upon a given class of materials should not be too dependent upon the composition (steel, iron).

These principles, however, have been seldom rigidly observed as to the methods hitherto offered. Having been prepared as a rule by different bodies of men of varying caliber and judgment, and sometimes by compilation of existing data rather than by direct rigid experimentation and trial, the methods are of very unequal merit. No argument seems to be needed to support the assertion that the preparation of such methods should be entrusted only to men of much experience and sound judgment, who have ample time to devote to most critical study of them. Unfortunately this last condition is one that is seldom possible to meet. The consequence is that too often the results do not measure up to the high standard that should attach to such methods. Nevertheless, an admittedly imperfect method is better than none if its limitations are well understood, for it affords a better basis for fixing the value of many articles of commerce than a variety of methods of uncertain relative and even absolute merit.

VALUE OF STANDARD METHODS DEPENDENT UPON REAGENTS OF HIGH QUALITY

There is another requirement, however, without which the best of standard methods will avail little, namely, reagents of uniformly high quality. The need for enforceable specifications for reagents has long been apparent and the American Chemical Society at one time endeavored to bring about improvement in

the quality of reagents. It is unnecessary to go into an exposition of the reasons why comparatively little came of this attempt. Some promise of relief seemed to be afforded, however, by the appearance on the market of "analyzed" or "tested" reagents, the bottles bearing statements of the nature and amounts of impurities present or that certain possible contaminants were absent. But it soon appeared that these statements could not be taken at their face value without risk, and the situation is particularly deplorable just now. The following recent observations are worth recording.

In sodium carbonate purporting to be free from phosphorus and silica both were present in amounts which condemned the reagent utterly for a variety of uses. Sodium hydroxide was found to be very impure, in marked contrast with the statement on the bottle. Sodium sulfide contained not only much thiosulfate or polysulfide but was black with iron sulfide, although said to be free from iron. Lead chromate, alleged to carry 0.0003 per cent of nitric acid, held 7 per cent of lead nitrate.

No condemnation is too severe, even in the present times of stress, for the manufacturer who so mislabels his wares. We certainly need a new law or an extension of the Pure Food and Drugs Act to protect the chemist.

FAULTS OF COMMITTEE WORK

Committee work, then, as hitherto practiced does not conduce to the production of results of consistently high standard. My experience makes me feel strongly that the advances to be expected through committees of professional societies are too often slight and are secured at a cost of time and effort quite incommensurate with the gains. This is especially true because: (a) It is difficult to hold the necessary frequent conferences of members widely separated, from which it results too often that the approval of a society is given to what is practically one man's work; (b) the members of committees sometimes lack a real conception of what a standard method should be in the light of the criteria by which they should be judged; (c) if competent in this respect the members are not often able to devote the needed time to actual and painstaking experimental work; (d) different methods are in the hands of different committees, without direct control by some head which has authority and is competent to see and direct that the fundamental principles are observed and followed in each and every case, to the end that the results shall be uniformly of high grade and consistently reported.

NEW INSTITUTION FOR STANDARDIZATION OF METHODS SUGGESTED

These and other considerations lead to the conclusion that such work should be in the hands of a permanently constituted body of well-salaried men under a director of the very highest ability as an analyst and of excellent tact and judgment. These men should be appointed only with the expectation that they are entering upon their life-work. It should be the intention to retain at all reasonable cost the services of those who prove thoroughly acceptable. Acceptability includes, of course, not only analytical skill, but also diligence, absolute honesty, and the highest conception of the dignity of this work. The beginnings of such an enterprise would be beset with uncertainties and the output not always of the desired quality, but as the men gained experience and insight into the fundamentals of their general work, improvement would come and in the end there would be gathered in this institution a band of men of unrivaled experience and knowledge, whose recommendations would carry such weight that little hesitation would be manifested by technical societies and legislative and industrial bodies in giving them their formal and practical sanction.

But the field of work for an institution of this kind should not be restricted to the comparative study of different methods that are applicable to the determination of one or more elements in a given class of materials, such as irons and steels, brasses

¹ THIS JOURNAL, 8 (1916), 466.

and bearing metals, but should include the preparation, analysis, and issuing of standard samples of many kinds, both commercial articles for direct checking of analysis and pure substances and solutions intended for calorimetric, volumetric, and other uses.

Furthermore, and this is very important, the institution should not act independently of the many industries which it is established to aid, but should tactfully maintain the closest and most sympathetic relations with them all, inviting indeed coöperation of the most intimate nature. Such coöperation would be very valuable oftentimes in exposing difficulties and thus indicating the directions which research in the central laboratory should take. It should include occasional visits to and from the laboratories of one side and the other for consultation and the actual carrying out of analytical operations, whereby misunderstandings may be sometimes cleared up and the causes of differences ascertained more readily than by any amount of correspondence.

The institution should also be a court of last resort in disputes as to the value of articles of commerce that are subject to chemical test, not only as to the correct chemical composition but also with regard to the causes for the differing results reported by others, and in general should be a clearing house of information and a source of inspiration in all that relates to chemical analysis.

Before taking up the next phase of my general proposition, it is desirable that the functions which the proposed institution should eventually exercise be clearly understood. At the risk of some repetition I will therefore summarize and for convenience group them under the three heads, Research Work, Referee Work, and Educational Work.

I—Under *Research Work* fall: (a) Critical comparison of methods of analysis in use or proposed for different classes of materials in the light of the criteria already presented; (b) improvement of existing methods when possible and devising of new ones if the old are inadequate; (c) recommendation of the methods found to be best suited for commercial needs, accompanied by complete and unambiguous details of procedure together with a statement of the accuracy ordinarily attainable; (d) determination of the causes of disagreement in the results of analysis of the same material by different analysts; and (e) preparation of specifications for reagents.

II—*Referee Work* covers: (a) The making of impure analyses in cases of irreconcilable disagreement between different analysts; and (b) the preparation and issuing of standard samples for checking methods and the skill of analysts, for volumetric analysis, and for the calibration of instruments such as polarimeters and calorimetric bombs.

III—*Educational Work* involves: (a) Coordination of researches in progress, so that the results when available will be better suited for intercomparison and therefore be more useful; (b) assisting in the wider adoption of standard and method already accepted and found to be satisfactory; (c) study of and recommendations regarding the best method of teaching analytical chemistry; (d) preparation and publication of bibliographies upon analytical chemistry; and (e) answering questions of all kind relating to chemical analysis.

I have purposely refrained from including methods of physical testing, for fear of overlapping the legitimate field of an institution intended for chemical research. However, it might be proper to consider eventually if many methods of physical testing that are ordinarily employed by chemists should not be regarded as falling within the scope of an institution of the kind proposed. In any event it should cooperate in the coordination of the results of chemical and physical testing.

At the present time much of the literature published as the result of research and investigation is of such nature as to make the results of limited value, largely because the investiga-

tion was not suitably planned or the results adequately recorded and reported to permit of comparison of one worker's findings with those of others who have preceded him. A permanent body which could obviate such a large amount of wasted effort as is now evidenced would in this field alone accomplish a great good for our science. Many investigators would be glad to avail themselves of its advice and criticism, and in many cases the scientific results put forth from our educational institutions and private laboratories might, through the coordinating influence of such a body, be made of greatly increased value.

Let us now consider how such an institution might be brought into being. There occur to me but three ways: (1) Through one of the existing scientific bureaus of the Federal Government, preferably and naturally the Bureau of Standards; (2) through endowment and control independent of the Government; and (3) through private endowment under some form of Federal trusteeship.

The first and second of these plans have their advantages and disadvantages, which will be now set forth.

In favor of the first is the prestige which governmental support and control would lend. Although on first thought it may not always be easy to see why prestige should attach to the decisions of a bureau of the Government in so much greater degree than to an independent establishment, that it usually does is a fact that has been many times borne in upon me.

The prestige attached to the Government is based on several factors, of which it is not easy to estimate the relative potencies. One is that the National Government represents the interests of all the people, that it is disinterested, having no small group to serve exclusively, that it seeks the welfare of the lowly as well as the exalted, that owing to this sense of responsibility and accountability serious scientific work undertaken by the Government is usually conducted in a manner to command the respect of the scientific world. These two factors have supplemented, perhaps, a third, which is that the people regard the Government as a coordinating center having to do with matters of general concern, so that when the Government speaks it is usually not the opinion of an individual but with the authority of the entire Government and for the entire people. That the public looks up to its Uncle Sam as counselor and adviser is attested by the innumerable inquiries that come daily in his mail from all parts of the country. The conscientious attention paid to these inquiries has had no small share in molding public opinion.

The readiness with which all interests cooperate freely with Government agencies is especially marked in cooperative scientific research. As the essence of the proposed institution would be cooperation in fundamental chemical research, the Government plan would present a strong case.¹

Evidence that prestige attached to the name of chemistry is distinguished from the general public's estimation arising from Government institutions is afforded by a recent tendency toward the use of methods of testing that are discredited by the Government. This tendency is particularly marked with regard to methods that are used for making oil delivery grade determinations. It is true that the Government may not be heard enough in technological matters by the Government chemists, but rather on par with the nation's technology in matters as affecting the use of the oil. If the Government takes notice of the same matter, that is to determine the amount of unsaturated material, through this test, the result would be heard about as a good known way to make general and desirable determinations of gravimetry. If this is the case, it is a good method of determining the amount

¹ It is interesting to note that the Government has already taken steps to coordinate the work of its various scientific bureaus. The Bureau of Standards, the Bureau of Mines, the Bureau of Chemistry, and the Bureau of Naval Ordnance are now working together on a number of projects of common interest.

ment laboratories should be awake always to the importance of maintaining and improving the accuracy of their methods and further that they should be afforded encouragement and every facility to enable them to live up to these requirements.

An additional argument for having the work done at the Bureau of Standards is the help that would come through its facilities in physics. The chemical institution proposed would need to utilize the standardizing facilities of the Bureau named for all measuring apparatus and to a considerable extent the optical work would have a material bearing upon chemical work, especially in the newer fields of spectro-chemistry, refractometry, and physico-chemical methods generally. It would seem undesirable to duplicate this expensive equipment if it can be made available for the chemical work under consideration.

It has long been my hope that at the Bureau of Standards we might gradually build up a section which should be the clearing house in all matters of the kind under discussion. We are frequently asked to settle disputes regarding the content of a given element or compound in a great variety of materials and to give information on all manner of analytical procedures. Our ability to grant such requests has been, however, far too limited from lack of a sufficient number of specially trained analysts and the inability of those we have to spare the requisite time for such problems. These problems often involve a considerable amount of research, for our aim is not only to determine the true value of the material in question but also to ascertain if possible the causes of the differences reported by others. I regard this latter point as of even greater importance than the former because of its educational value. Under the present conditions of Federal support I see little prospect of a full realization of my hope. The cost of upkeep of such a Division would be out of proportion to that of other phases of the Bureau's activities, for its complete realization would be financially equivalent to establishing a new institution.

Other serious objections to support and control by the Government are: (1) The instability of a work that is dependent on annual Congressional appropriations; (2) the likelihood that at any moment in emergencies the men engaged may be called upon to assist in entirely foreign kinds of work; (3) the restrictions of the Civil Service regulations and the inflexibility of the salaries attaching to all statutory positions. The objections enumerated are very important, for without assurance of permanency and continuity of work the success of such a scheme as I have suggested would be highly problematical and its lasting or even temporary interruption when once established little short of calamitous.

The restrictions under the third objection make it difficult or impossible in the first place to select men for particular kinds of work, or to give timely promotions to deserving men, or even to appoint anyone unless a vacancy happens to exist in the grade for which a desired man is qualified. This lack of flexibility in the appointment of new men and the promotion of old and tried ones is one of the most serious handicaps to efficiency in Government service. These statements are in no way to be taken as condemnatory of the principles for which civil service stands, for the situation in Government service, even with the limitations stated, is vastly better than it was before the Civil Service Commission was established, when political influence controlled appointments, promotions, and dismissals in no small degree. The particular objection that statutory salaries are inflexible might be met by the provision of a special fund, as has been many times done for other purposes. Such funds are less subject to salary restriction than those called statutory, but Congress has been wont to look upon them with disfavor. The objection that was based on the uncertainty of Congressional appropriations would not hold so much for a separate bureau or establishment as for the supposed case of merger with an ex-

isting bureau. This follows from the fact that the effect of Congressional action is far less likely to result in abolishing or even hampering seriously the work as a whole of an established Bureau than of one of its divisions.

ADVANTAGES OF INDEPENDENT ENDOWMENT

In favor of independent endowment is the greater stability in a certain sense of an institution so supported and a greater freedom of action and choice of men, offset in a measure by its lower prestige. This latter weakness might hold more during the earlier years of its existence, for under proper guidance there would seem to be no reason why it should not in time merit and obtain much, if not all, that now attaches to institutions fostered by the Government. The greater stability alluded to lies, however, rather in a surer continuity of existence than in certainty that the institution will be able always to fulfil its functions in full measure. In times of stress or through unfortunate investments the income might be much curtailed or even cut off entirely, contingencies which Government establishments may be less concerned about.

There is this to be said further in favor of independent endowment and control, that if the control were in the hands of the technical organizations most concerned chemists would come to regard the institution as more peculiarly their own child, in the growth and performance of which each might take pride but for whose conduct they themselves alone would be responsible. Certainly the time is ripe for chemists to be represented by a national institution which should serve for fundamental work of interest to all chemists the same function that private and industrial laboratories serve for their clients.

A compromise between these radically different suggestions for support and control remains to be considered, namely, through private endowment under some measure of Federal control, either of the funds or the work. The Smithsonian Institution is a well known example of Federal administration of a private bequest with control of appointments by the Civil Service Commission. The relation of the Bureau of Mines to its work on radium and some other experimental researches is suggestive of how Government supervision of work might be made compatible with outside control of all expenditures except, perhaps, for the salary of the Government official in charge. If Congress could be persuaded to contribute a building and to locate it on the grounds of the Bureau of Standards, where its staff would be in close touch with men engaged in many fields of testing and research, physical as well as chemical, the conditions might be ideal for attaining the maximum of success. Such juxtaposition might fail in its aim, however, if salaries in the two neighboring laboratories had no common basis. Stated a little differently, this means that salaries for statutory positions under the Government ought to be materially increased, for as already intimated, I regard the payment of adequate compensation as vital to the success of my general proposition.

The kind, degree, and manner of control to be exercised by the Government would need careful consideration, particularly with respect to the choice of the staff, for if with any sort of Government control appointments could be made only through the Civil Service a serious hindrance to successful operation would arise.

Finally, the question must be asked: What is the likelihood of such an establishment ever becoming a realization? To this no answer is immediately at hand. Certainly nothing will come of the proposal if it does not meet with the approval of the best judgment among chemists, and then still nothing unless a popular sentiment in its favor is awakened, nourished and made to grow by persistent discussion. The needed impulse and the demand created, the rest should not be so difficult now that we are awakening to the importance of chemistry to the life of the nation. The interests of the great chemical

industries, or of industries at whose foundations chemistry lies, could surely be depended upon to create, through endowment or influence upon Congress, an institute for analytical research which would be the first of its kind and which would help to place this country in the very forefront of progress among nations. The industries have received so much from pure science in the past without adequate return that the time seems ripe for them to contribute generously towards its further development, especially along lines which promise so much to themselves as those which I have indicated. It might even be that some private benefactor would arise to do for chemistry what has been so magnificently done for astronomy, terrestrial physics, biology, and the study of the causes and prevention of disease. Given a properly prepared field, I do not feel that I am over-optimistic, considering the wave of interest in matters pertaining to chemistry that is sweeping over the country. The preparation of the field should be entrusted to a carefully selected and energetic committee.

IMPORTANCE OF COÖPERATION WITH INDUSTRIES

I have already intimated that, whatever plan might be adopted, the closest coöperation should be sought and maintained with the industries. Indeed, an advisory board of outsiders should be selected to assist the director in the planning and administration of the scientific work, and the connection of this board with the affairs of the institution should be very real and not nominal. The laboratory itself should be, however, in no way debarred from taking the initiative without reference to the board proposed. Indeed, the laboratory force would often be in far better position to know or learn the weak points in current procedure than any advisory body.

Here let me interject parenthetically a word on a subject that has been far too much neglected by chemists in the past. It seems that now is the time when they should bring pressure to bear to secure that share of official as well as private recognition which is their right by reason of the immense importance of their work to the general welfare. The relative ease with which hundreds of millions of dollars are obtained for military purposes offers a startling contrast to the almost complete indifference of the great scientific interests of the country to Government aid to science. Without raising controversy over the relative value of military and scientific preparedness it is certainly true that if the scientific societies presented their case for Government aid to science with a fraction of the efficiency with which the case for national defense has been prepared, there is scarcely any ideal for such an institution that could not be promptly realized. It is time that chemists entered the field far more than they have done to show how they can contribute to the general welfare and what they need in the way of countenance and support.

It would be going too far afield at this early stage to propose even tentative details for the organization and conduct of the proposed establishment, which some of you will perhaps recognize as patterned in its objects and scope somewhat after the international institute for chemistry that Professor Wilhelm Ostwald advocated in great detail a few years ago.¹ Ostwald had in mind an institute of international scope to cover the whole vast domain of chemistry. I propose one of more restricted and only of national scope. What might grow out of a well-established and successful organization in the United States with respect to international coöperation may be left for the future to determine. World-wide coöperation from the start would be ideal, but even under normal conditions the task would be

¹Only after the address was prepared did that of Professor C. O. Henderson, President of the Chemical Section of the British Association for the Advancement of Science, become known. This came to my attention. Professor Henderson's address contains observations and suggestions which parallel in a measure portions of the lecture, although without specific reference to analytical chemistry.

herculean, as it is at present impossible of accomplishment. Let us therefore proceed with only our own immediate needs in view, in the certainty that if our initiative succeeds others will copy and that when the time is ripe we may expect to lead in bringing about the broad world coöperation that must eventually come.

BUREAU OF STANDARDS, WASHINGTON, D. C.

THE FIRST REPORT UPON THE CHEMICAL INDUSTRIES OF THE UNITED STATES AND THEIR RELATION TO NATIONAL PREPAREDNESS

By C. A. HENDERSON

Received December 20, 1916.

To those who have studied the historical development of Chemical Industries in the United States the recent discussions and papers upon *Industrial Preparedness*, *Chemical Statistics*, *Tariff Legislation*, etc., that have appeared in *THIS JOURNAL* have a strangely familiar sound. The situation which confronts the manufacturer of chemicals in the United States to-day is not a new one and the present endeavors to make a statistical estimate of the needs of our chemical industries are not the first efforts which have been made in this direction. History has, at times, a strange method of repeating itself. If we of to-day could only transport ourselves to the United States of a century ago we might hear, then, as now, the same fears expressed concerning mushroom prosperity and unpreparedness, we might listen to the same arguments in favor of anti-dumping laws and we might read the same resolutions proposed by Committees who had met in convention to investigate the industrial situation.

The efforts of our great grandsires to solve a condition of affairs so similar to that of the present is not only interesting but instructive. The first business of the ancient Romans, when they met in conclave, was to determine the *consulta patrum*; we can do no better than follow their example.

GENERAL INDUSTRIAL CONVENTION HELD IN 1831

On October 26, 1831, there met in New York City a General Convention of the Friends of Domestic Industry, consisting of about 500 delegates from 13 different States. These delegates, who represented all the leading industries of that time, divided themselves into a number of committees, whose work was to prepare a series of reports upon Iron and Steel, Salt, Sugar and Molasses, Glass, Chemicals and other industries. These reports, which were widely distributed as separate pamphlets, were collected the following year into a single volume which was printed as a 200 page book at Baltimore in September, 1832.

This collection of reports is preceded by an Appeal to the People of the United States and is followed by a Memorial to Congress in which the recommendations of the various Committees are summarized. The volume is carefully edited and contains a vast amount of information, accessible to historian and statesman. A few extracts from the introductory Appeal will serve to illustrate the bearings of the early report upon present conditions.

"The event that followed the French revolution gave a new and unexpected direction to the enterprise of commerce. The disturbed state of the continent of Europe, and the prevalence of universal war, throughout the nations of that quarter of the globe, placed the United States in the position of the only country among many sovereigns, and of stationary ground, likely to command a supply to the nations, that all other nations seek into each other, concerned with those which are concerned in giving a mutual commerce, commerce represented the title of the marketing nation, included the commerce of the United States, the commerce, and left to the United States the preliminary commerce of peace. To the United States, commerce of commerce, to the United States, commerce of commerce, that has been commerce, the United States, commerce of commerce."

This picture of snug prosperity is followed, however, by another picture which should make the present-day apostles of Unpreparedness pause and reflect.

"It was one result of this state of things that, while our countrymen were intent upon gathering the harvest which the distracted condition of the world had strewn before them, they were unmindful of the future and neglected to treasure up the elements of strength and prosperity which lay hidden in the bosom of the nation; and which, as they were independent of foreign legislation or external accidents, were most likely to furnish the means of a stable and enduring happiness.

"Troubles soon afterwards broke out at home. A war threatened and our citizens were suddenly called to meet a tremendous emergency. Our commerce was put in fetters by non-importation acts and embargoes; and the crisis that succeeded found us without the most ordinary resources of an independent people. Our armies went to the frontier clothed in the fabrics of the enemy; our munitions of war were gathered as chance supplied them from the four quarters of the earth; and the whole struggle was marked by the prodigality, waste and privation of a thriftless nation, taken at unawares and challenged to a contest without the necessary armour of a combatant.

"When it pleased Heaven to rescue us from the imminent hazards of this doubtful and disproportioned conflict, we saw around us a nation of eight millions of people possessed of a territory nearly equal to the continent of Europe, rich in the ungathered resources of every kind of wealth—just emerging from a war of two years and a half, with an enemy who had never assembled an army of more than 30,000 men—and yet deranged in all its channels of industry, exhausted, and on the verge of bankruptcy. Nothing but the most perverse neglect of the fundamental precepts connected with the proper administration of the concerns of a commonwealth could have produced such a result!

"These disasters opened our eyes to some important facts. They demonstrated to us the necessity of extending more efficient protection, at least, to those manufactures which were essential to the defence of the nation."

The New York Convention recognized the importance of chemistry to the manufacturers "essential to the defence of the nation" for we note upon their minutes for the third day of the meeting the following resolution:

"In convention, October 28th, it was

Resolved, That a committee of five be appointed to report on the subject of Chemistry, as connected with the Manufacturers and the Mechanic Arts."

The chairman of the Committee thus appointed was Isaac Tyson, Jr., of Baltimore. The name Isaac Tyson¹ is memorable in the early history of American Chemistry and Baltimore 100 years ago gave promise of becoming a great center in this branch of industrial activity. It is worth a passing note that there were 24 delegates from Baltimore at the New York Convention and only 6 from Pittsburgh. The associates of Isaac Tyson upon the Chemistry Committee were Christain Keener, another Baltimorean; William Parmenter of East Cambridge, Mass.; Edward Roberts of Philadelphia; and Thomas Bakewell of Pittsburgh.

The report of the above Committee is the first definite statement of any importance regarding the condition of the Chemical Industries in the United States. As it is inaccessible to

¹ The firm of Howard Sims and Isaac Tyson began the manufacture of chemical and paint-manufacturers on Pratt Street in Baltimore in 1810, and a century ago they (Howard removed) to Washington Avenue where they engaged extensively in the manufacture of copperas, chromate of potash, chrome yellow and other chromic pigments. The raw material for the latter consisted of chromate of iron obtained from Bare Hills, Maryland and from Chester County, Pa. The importance of the chrome yellow industry is mentioned in the Committee's Report.

most members of the American Chemical Society, the original report is here given in full

**REPORT OF THE COMMITTEE ON CHEMISTRY
GENERAL CONVENTION FRIENDS OF DOMESTIC INDUSTRY
NEW YORK, OCTOBER 26, 1831**

"The Committee, in discharge of the duties assigned them, report that chemistry, as connected with the business of life, may be considered a modern science. Its early history gives it rather the character of an occult art, associated with the visionary theories of the alchemist. And for a long period, it was signalized neither by usefulness nor by dignity. Finally, however, the improved state of society, and the progress of civilization, excited the genius of a few, who, by a series of brilliant discoveries, astonished the world; and, by the application of these to manufacturers and the arts, administered to the comfort and the necessities of mankind. Though long taught in the schools as a science, it is only a short period since the United States were dependent on foreign countries for every article in this interesting and important department of manufactures.

"Intimately connected with science and the healing art, and essential to other manufactures, chemistry received very little or no attention from the enterprise and skill of our country, until the late war. That event suddenly cut off the usual supplies from foreign countries. The consequent advance in price was excessive, and the inconvenience sustained by that class of manufacturers who consumed chemicals, incalculable. This state of things gave the first impulse to chemistry in our country.

"The return of peace, however, brought foreign competition, which soon threatened to extinguish the infant and yet inexperienced establishments which had crept into existence during the war. The large importations which, at that period, inundated the country, caused a reduction in prices, alike ruinous to the importer and his competitor, the American manufacturer.

"This depression, however, would have been but temporary, had there been no interference on the part of the government. The foreigner would have prevailed in the contest—and the market becoming his, the prices would have been in accordance with his own remorseless interests.

"Happily for the nation, and more particularly for that numerous laboring class who are dependent on chemical manipulations—and the agriculturists, who find in this class a customer instead of a rival—happily also for the other classes of manufacturers which owe their existence to chemistry, the tariff act of 1824 placed the seal upon the policy of the nation. By this act, and not until after its passage, was the manufacture of chemicals established in the United States.

"Until it became the policy of the nation to encourage a domestic supply of chemicals, prices were constantly fluctuating—were generally high, and oftentimes seized upon for purposes of speculation, to the great injury of consumers. Domestic competition has caused prices to settle at a minimum rate. The manufacturer is now so near the consumer, that his wants are anticipated and scarcity is unknown—because the raw material, being unlimited in quantity, and individual enterprise commensurate with it, the demand is seldom allowed to overtake the supply. When alum was an article for import, the price was generally \$7.50 per cwt. During the late war it rose to 18 c. per lb. The price at present is about 3¹/₄ c. per lb.

"Copperas was subject to greater fluctuations, varying with the vacillating policy of the importer, or the foreign manufacturer, or the contrivance of the speculator. The price was often \$7.00 per cwt. and sometimes below the cost of importation. During the war it advanced to 17 c. per lb. It now sells for 2¹/₄ c. per lb.

"Epsom salts, which is one of the leading items in the chemical department, is an offspring of the tariff of 1824. And what

is the result of this parental relation? A mineral which had remained for ages unnoticed and even unknown, was dug from hills previously considered barren and valueless, and, by an admirable process of chemistry, converted into magnesia and Epsom salts, of a quality superior to the foreign. But the effect of a protective system is more clearly shown by the following list of prices of Epsom salts, at the different periods before and after the duty of 4 c. per lb. was imposed by the tariff of 1824:

Year	1820	1823	1824	1826	1831
Price, cents per lb.	11 to 12	7 1/2	10	7 1/2	3 1/2

"Those who seriously contend that the duty on foreign merchandise is a tax on the consumer to the full amount of that duty, will here find a case difficult to reconcile with their theory, the present price of Epsom salts being 3 1/2, while the duty is 4 cents per lb. Nor is this all—the improved manufacture and reduced price of Epsom salts! has very nearly excluded the use of the coarse and nauseous article, Glauber salts, of which latter only a small quantity is at present made and consumed.

"The usual price of refined saltpetre was about 13 cents per lb. before the tariff of 1824, when a duty of 3 cents per lb. was laid upon the foreign manufacture, which is its present price. The treasury tables for 1830 show that only \$80.00 worth of it was imported.

"Sulfuric acid was worth 7 cents per lb. previous to 1824—since only 3 and 4 cents.

"The sulfate of quinine, when first manufactured, sold at an enormously high price; and its value in France was said to be \$2,000,000 per year. In 1828 it was worth from \$7 to \$8 per oz. and its manufacture was soon after commenced in the United States. At the close of 1831, it was selling in Baltimore for \$1.50 per oz., but has latterly advanced to \$2.75, because of the increased cost of the material out of which it is made.

"Many other articles show a similar result, but the cases cited will sufficiently illustrate the principle contended for. It may be safely stated that the general price of chemical articles is one-half less than it was before the establishment of their manufacture by the protecting tariff of 1824. Hence it would appear that \$1,000,000 per annum have been saved to present consumers in the United States, by this new application of domestic industry, talent and capital; besides the employment and subsistence of a large number of persons, variously engaged in the laboratories, or furnishing materials; and the chief part of the latter would have remained, as they had been for ages, valueless—nor on the account of the encouragement and protection afforded.

"The large consumption caused by the growing wants of our country, if dependent on the laboratories of Europe, would have either enhanced prices or have justified the maintenance of former rates—for, until the business was undertaken in this country, the foreign manufacturers seem not to have discovered how cheaply they could work.

"The intimate connection between chemistry, and the art of dyeing, bleaching and calico printing; and their mutual dependence on each other, need not here be insisted on. The importance of the former cannot be duly estimated, without taking into view the various interests into which it diffuses itself.

"The protection offered to several chemicals has not only reduced prices, but almost entirely excluded the foreign article. Indeed, as to alum and copperas, the exclusion seems complete—for the treasury tables of 1830 do not show that one lb. of either was imported. The price of many chemical articles are as low in this country as in Europe, but nevertheless your committee are of the opinion that it would be unwise to repeal the existing duties, because experience indicates that the

foreign competitor, from a disposition to get rid of his surplus stock, and with the less creditable design of strangling the growing establishments which have deprived him of a market, will crowd his productions upon us, regardless of the calculations which usually govern trade—enduring the present loss with the hope of distant gain, which is to be the fruits of victory obtained in prostrating his rival.

"The chemist asks to be protected from such an enemy. Your committee might further illustrate the principles they contend for, by a more detailed examination of the department referred to them; but in so doing they would extend this report to an unreasonable length, and multiply arguments on a question which, fortunately for the country, is already settled.

"Besides the articles previously noticed, the chemical establishments of this country manufacture calomel and various other mercurial preparations, Glauber salts, Rochelle salts, tartar emetic, ammonia, sulfate of quinine, oil of vitriol, tartaric acid, aqua fortis, Prussian blue, chrome yellow, chrome green, nitric acid, muriatic acid, barilla, oxalic acid, chloride of lime, chloride of soda, refined saltpetre, refined borax, refined camphor, acetic acid, acetate of lead, nitrate of lead, prussiate of potash, bi-chromate of potash—and the endless developments of the science of chemistry are almost daily adding to the list.

"It is a highly interesting fact that nearly all the materials used in chemical establishments are the produce of our country. Brimstone, saltpetre, quicksilver, cream tartar, and Peruvian bark are the only material exceptions; and it happens that our competitors in manufacturing chemistry are without domestic resources for these same excepted materials. Both draw their supplies from the same sources. Nor is the fact less interesting, that the articles used in chemical factories, other than the exceptions just alluded to, are generally of a character useless, and sometimes loathsome.

"Clay is used in the manufacture of alum; iron ore and pyrites for copperas; a magnesian mineral for magnesia and Epsom salts; copper ore, old copper, and the scales which occur in the manufacture of copper, for blue vitriol. The blood which flows from the slaughter-house, the horn shavings which are swept from the comb-maker's shop, and the trimmings and scraps of leather, which would otherwise encumber the currier, are all converted into Prussian blue, the prussiate of potash and ammonia.

"Even the atmosphere we breathe is made subservient to the cause, and is converted into merchandise by its combination with brimstone, in the formation of oil of vitriol and other chemicals.

"Your committee, believing that a more particular allusion to a few facts may be useful in giving the interest of chemistry to be appreciated, take the occasion to state that chrome yellow, also named orromine, first made in 1826, is the result of American chemistry. It was originally discovered in the United Mountains, and sold for its weight in gold. It was first made artificially in France, by Vauquelin, from the carbonate of iron discovered in 1826, and named by the Government of Van in 1829. The discovery of this yellow was followed in considerable quantities in Baltimore, in the State of Maryland, where the works were opened for manufacturing it into chrome yellow. The price was first 50 cents per lb., but before the competition of the French came to the market, it was reduced to a gradual decline to 10 cents per lb.

Some years ago the chemists of the Dutch Government, chrome yellow in England, and later, that from France that is valuable market was opened to them, for the Dutch could not produce it for the same article. But the British manufacturers, finding the price of this substance so reduced, were induced to breed it from the coal and iron scales in a small way, and gradually increased the amount of their production, so that they are now in a position to give credit to a British manufacturer, and set the same

* One of the members of the *London Magazine*, *Almanac* for 1828 said: "The United States, which used to be furnished with Epsom salt from this country, now takes the whole supply from a manufacturing establishment in Baltimore—making a price salt cheaper in Europe, and at a less price."

petition of an American manufacturer. "Free Trade" was no more the policy of England then, than it is her practice now.

"A further evidence of the great resources of this country, as developed by chemistry, is found in the existence of vast masses of alum and copperas ore on the Chesapeake Bay, near Baltimore. In searching for bituminous coal, of which there are strong indications, this mineral was brought to light. It consists of partially decomposed vegetable matter, with clay and sand and iron pyrites distributed through the mass, and the whole covered with a bed of iron pyrites. This mineral, dug and exposed to the atmosphere, undergoes a spontaneous combustion, and gives rise to the formation of sulfate of alumina and iron, which, lixiviated, requires only evaporation and crystallization. Preparations are now being made in Baltimore for manufacturing, from this mineral, alum and copperas to an extent fully adequate to the wants of the community.

"Beds of iron pyrites also exist of great extent in the towns of Strafford and Shrewsbury, Vermont—from which the country east of the Allegheny Mountains has been principally supplied with copperas for many years. They are worked by two incorporated companies, manufacture 2,500,000 lbs. per annum, employ 75 men, consume 3000 cords of wood, pay for transportation by wagons, canal, river-craft and coasting vessels, \$20,000—using considerable quantities of lead, iron and gunpowder.

"In the neighborhood of Liberty, in Frederick County, Maryland, there exists a copper ore, which, besides being adapted to yielding metallic copper, is, by a slight chemical treatment, converted into blue vitriol.

"But it would swell this report beyond its proper limits were your committee to give in detail the history and resources of the manufactures of this country. They are able to enumerate thirty chemical establishments in the United States. The capital invested in these concerns, according to the best estimate that can be made, is \$1,158,000. The value of the articles produced may safely be put down at \$1,000,000, the number of hands employed at 900, and the number dependent on them for support 4000. Nearly the whole value of chemicals is paid in labor and fuel—the cost of most of the materials used being inconsiderable.

"Pot and pearl ashes enter into the composition of many chemicals—giving a home market for a large quantity of the product of the forest.

"Almost every chemical process requires the aid of heat. Immense quantities of fuel are consequently consumed in the laboratories. One establishment in Baltimore requires 4000 cords of wood per annum, besides considerable quantities of anthracite and bituminous coal. The total value of fuel consumed in chemical operations in this country is estimated at \$120,000. The benefit accruing to the landed interest, by reason of this great demand on the forests and the mines, and the employment given to the laboring class, in cutting the wood and mining the coal, and in transporting both to these new markets, cannot but be appreciated by all reflecting persons.

"The smelters of the lead of our own mines in the Far West, here find an important ally. Large quantities of this metal are used in the construction of chemical works, and some is consumed in the manipulations. But your committee forbear to trespass upon the duties of the committee appointed on lead and its manufactures.

"Your committee have no accurate data by which they can learn the quantity of tonnage employed in transporting the materials used, and the chemicals manufactured from them.

"The sulfur, from the volcanic mountains of ancient Sicily, the quicksilver from Spain, the saltpetre from the East Indies, and the Peruvian bark from South America, form considerable items in our foreign trade, and give no small employment to the shipping interest. But it is the coasting trade that receives the chief benefit.

"The chemical establishments are few, compared with the number of their customers—and their goods are consequently distributed along the whole line of our coast.

"Should any change be made in the existing tariff, your committee suggest some amendments which the new developments of the science have made necessary.

"Sulfate of quinine is manufactured from the Peruvian bark, and promotes the important trade with the Pacific. The consumption in the United States is, in part, supplied by the chemists of France, the duty being only 15 per cent. If the duty on sulfate of quinine were increased, and the bark from which it is extracted admitted free of any duty, the entire consumption would be derived from our own laboratories, and the increased trade with Peru would greatly benefit the commercial interest. Instead of importing the quinine in its small bulk, not appreciable as a freight, and by a short voyage, and from a country that excludes almost everything American, cotton excepted—we would, on the other hand, receive from distant Peru the more bulky bark—paying for it in household furniture and various other American manufactures, and even in the quinine itself, extracted from the material.

"Saltpetre is one of the most costly articles used by the manufacturing chemist. Small quantities of very inferior quality are found in the limestone caves of the western states; but the crude material is limited, and the refining process costly—therefore few are disposed to engage in that business, and these few on a very small scale. There is no interest in this country to be benefited by a duty on saltpetre.

"Your committee are of the opinion that the following articles might safely be admitted free of duty. Some of them, if not strictly within the sphere of the present inquiry, indirectly belong to it: Peruvian bark; crude saltpetre; nitrate of soda; quicksilver; crude borax; crude camphor; cream tartar; galls; gum arabic; gum senegal; gum copal; gum tragacanth; gum shellac; platina; caoutchouc.

"The time and the occasion are suitable to suggest that many foreign chemicals are only charged with the small duty levied on articles not enumerated in the tariff. Such of them as interfere with the establishments of this country, or such as would be produced with a suitable patronage from the government, ought to bear a heavier duty—and such as are not adapted to our climate or resources, might be declared free of duty.

"And, as there is always a strong temptation, by distinguishing them under a name not found in the law, in order to bring them under the *ad valorem* duty of 15 per cent (that being the duty of non-enumerated articles) it would be expedient to make all non-enumerated chemicals subject to a much heavier duty. Every article would then come in review before the country, and each would be either made free of duty, or be assigned to its proper place in the scale. And specific duties, the committee think, should be always preferred to the *ad valorem*, if practicable.

"Having already named the articles which may, without interfering with any domestic manufacturing interest, be exempted from all duty on their importation, it now becomes proper to furnish a list of such as require further legislation, to relieve the country from an unnecessary dependence on foreigners, as follows: sulfate of quinine, carbonate of magnesia, sugar of lead, nitrate of lead, acetate of iron, roll brimstone, all the preparations of mercury, sal ammoniac, Rochelle salts, soda, solutions of tin, verdegriis, tartar emetic, chromate of potash, bi-chromate of potash, chloride of lime, chloride of soda, tartaric acid, chrome yellow, Prussian blue, prussiate of potash, barilla, soda, carbonate of soda, magnesia.

"If Congress should determine to abolish the duties on imported articles, not coming into competition with similar articles made or produced within the United States, the labor of the officers of the customs would be much diminished—and it

is respectfully suggested, whether the contemplated law ought not to require these officers to keep a particular and separate account, accessible to the public, at each custom house, of the quantity and value of all merchandise imported, whether free of duty or subject to specific or *ad valorem* duties? The statistical information thus obtained would be of great importance to the manufacturing chemist, as well as to every other class of persons. The law might, with great propriety, also provide for a more prompt diffusion of the information thus obtained. Statistical facts are valuable in proportion to the promptness with which they are known. When delayed, they are more a matter of curiosity than of practical usefulness.

"A well-organized system of statistics would not only be a guide to the statesman, enabling him to legislate on the intricate subject of trade understandingly, but it would inform the merchant on the important matter of consumption and supply, and save him from the many errors into which he is liable to be led, by reason of his unavoidable ignorance in this particular. Such intelligence often, and promptly, communicated, would, in a great measure, prevent the occurrence of that scarcity and consequent enhancement of price, which so frequently takes the consumer by surprise; and on the other hand, would guard against that excessive glut and consequent ruinous reduction of prices, which have done more to involve the enterprising merchant and injure the manufacturer, than all the foreign competition that can be combined against them."

On behalf of the Committee,

ISAAC TYSON, JR., *Chairman*

The remarks which this Report of the Committee on Chemistry makes upon the effects of foreign competition, the necessity of an adequate protective tariff and the importance of a well-organized system of statistics are as applicable to-day as they were 85 years ago.

But the principal lessons to be drawn from this early report upon industrial preparedness are contained in the Memorial which the Friends of Domestic Industry transmitted to Congress.

The thought that the only successful method of combating militarism is by means of an efficient industrialism is not lightly to be dismissed. In reflecting upon the downfall of Napoleon the Memorial asks the following momentous question:

"Has it not been a matter of common remark, since the close of the late wars, that it was not the artillery of Wellington and Blucher, nor even the noble enthusiasm of the youth of Germany, but the mightier machinery of the power-loom and spinning jenny, the splendid miracles of Arkwright and Cartwright, that sustained the cause of the alliance in all the fields of Europe for twenty-five years in succession, and finally overthrew the greatest military empire that ever existed?"

The dangers which threaten domestic industries at the conclusion of a foreign war can be illustrated no better than by the following account of what happened in the United States after the Napoleonic wars.

"Everything goes on prosperously until the war comes to a close. Within a few months after, our markets are inundated with British goods cheaper than we can make them of equal quality, and the manufacturers are in their turn involved in one common ruin. It is in this way that the fluctuations incident to those distant and uncertain exchanges reach successfully all the great branches of industry. The results, which your memorialists have thus described are not accidental, but the regular consequences of the state of things to which they are attributed, and must continue to recur from time to time, whenever such a state of things exists."

In commenting to Congress upon the possibility of future occurrences of the kind in which even the United States might

be involved, the Memorial sounds an admonition which is almost prophetic.

"At this moment, the danger of such an occurrence appears to be again very imminent; but whatever may be the issue of the present crisis, it is, at all events, clearly the duty of an American statesman to suppose, and to act upon the supposition, that the country is continually liable to be drawn into war with any of the foreign powers with which we have relations. If then we look to these foreign powers for our regular supply of the ordinary comforts of life, what is to become of us during these periods of occasional hostilities, which may last three years or thirty as the quarrel happens to turn? By what miracle are we to find, at a moment's warning, resources, before unemployed, which will furnish us with substitutes for this supply? Are we to extemporize at the commencement of every war, as we did at that of the last, a set of manufacturers sufficient to meet the demand of twelve, fifteen, or, looking forward only to the end of the next five and twenty years, twenty million consumers, only to see them all shaken to their foundations by the return of peace, and sinking in one general ruin as they did before? Your memorialists can hardly imagine how an intelligent person can be so totally blind to the most obvious considerations of expediency as to counsel such a policy. They leave it with confidence to your honorable body to decide, whether it be not the duty of a prudent government to provide, by every imaginable means, against the recurrence of such widely spreading disasters; whether, were it even true, as it is not, that domestic manufactures would be, in the end, dearer than foreign ones, an annual pecuniary sacrifice of considerable extent made in this form, would not be decidedly preferable both on the score of interest and feeling, to supporting the incalculable losses and miseries of every kind produced by these convulsions."

With this final warning we must bring our citations from the Report of the Friends of Domestic Industry to a close. It would be interesting to quote more fully, but enough has been given to indicate the resemblance of conditions a century ago to those of to-day. In addition to the light which the Report throws upon the early state of our chemical and other industries, it contains premonitions that are full of meaning and conveys lessons that are set forth

"With such a lustre he that runs may read."

80 SOUTH STREET, NEW YORK CITY

THE HUMAN SIDE OF THE DEVELOPMENT OF CHEMICAL INDUSTRY

By G. W. FLEMING

Numerous writers and speakers have called frequent attention to the great service which chemistry has rendered to humanity. In every field of industry she has been active, every product of man's labor has felt her magic touch. Modern civilization can be measured most accurately by considering the influence which chemistry has had upon industry and industrial operations. It is unnecessary here to tell what she has done. We are more concerned with the future than with the past, and judging the future by the past, the benefits which chemistry during the coming years will confer upon humanity will be infinitely valuable. On no other volume is imposed the task of having, at the close of her process, preparing, and making the way easy for her, and providing her greatest wealth. It is the purpose of this paper to indicate how the past has been done.

It should be perfectly obvious that the amount of so primary a technology as the science of human beings. The science of chemical industry is a part of the science of human beings. The human factor is the most important. He who knows how to use the science of human beings, makes the most of the science of human beings.

Published by the American Chemical Society, 1917. Copyright, 1917, by the American Chemical Society, New York City.

commonwealth in which every member is a factor in the development of the whole. The chemist is only a fraction in this commonwealth but the more he is organically a part of it the greater is his power of service. Like everyone else he does not exist by himself alone but is dependent for his existence upon every other human being that is a part of the social organism.

In the last analysis all of the relations between human beings are mental relations. The instruments of connection between human beings may be material but the relation itself is spiritual. In so far as the chemist renders service he does so by impressing himself on other people and affecting them either directly through personal contact or indirectly through the products of labor in the fabrication of which he has had a part. Human relationship, therefore, is the end toward which we are perforce all compelled to work. Each man must impress other people and he must in turn be impressed by them. There is no such thing as independence. We are all dependent, and in seeking for what we may nominally call independence we are simply shifting our dependence from one point to another. It is foolish to talk about being independent and it is unwise to seek independence, because it cannot be obtained. Still more important than this: it is best for us that we should not seek independence but that each one of us should seek to be dependent upon every one else, thereby conforming to the best conception of human relationships and to the economic law according to which the best service only can be rendered.

What we propose, therefore, is that the chemist should strive against anything that would tend to isolate him and separate him from his fellowmen. What we will try to show is the means by which he can avoid these tendencies; how he may more effectively integrate himself into the social organization.

INTERFERENCES IN GROWTH OF CHEMISTRY

Perhaps what we have in mind can best be visualized by considering here what has been believed by some to have interfered with the growth of chemistry in this and other countries. For instance, the cry has come from England that technically educated men have not been sought for as the occupants of high official and business positions. It has been claimed that a scientific education did not help towards social or public advancement, that in England a man with a classical education was sought after, not the scientific man. Assuming this to be so, it is perfectly clear that the advancement of the chemist in England has been retarded by a lack of public appreciation of the service which he renders or can render to the nation. What, then, is the chemist in England going to do about it? Apparently he is dissatisfied, which in itself is all right, but being dissatisfied does not alone change inexorable facts. In every chemical problem that confronts the chemist when facts stand in his way he does not get excited about them but seeks to surmount them by careful study and the devising of ways and means. This should be the attitude of the chemist in England, and by organized publicity—advertising if you will—he should seek to change public opinion so that it will accord to him a higher recognition.

That the English chemist is taking this view is indicated by a recent address by G. G. Henderson before the Chemical Section of the British Association for the Advancement of Science, Newcastle-on-Tyne, 1916. In discussing the synthetic production of nitric acid from the air and the great advantage it would be to England, he laments that England has done nothing in the matter except to appoint a Committee to consider possibilities. Then he goes on to say: "This case is only too typical of many others. A number of different causes have contributed to bring about this state of affairs, and the responsibility for it is assigned by some to the government, by others to the chemical manufacturers, and by still others to the professors of chemistry. I think, however, it will be generally admitted that the root of the matter is to be found in the general

ignorance of, and indifference to, the methods and results of scientific work which characterize the people of this country." He adds, however, that he thinks that the English leaders in science have done all that lay in their power to awaken the country to the inevitable and deplorable results of this form of "sleeping sickness" and that he believes that a brighter day is dawning and that if they rise to the occasion now, chemistry in that country will attain the position of importance which is its due.

Let us take another case. Germany has made great advances in chemistry. Some think that this is due to her system of education and probably this is partly true. Some think that it is due to the farsighted wisdom of public men. This, too, is probably partly true, but the real success of chemistry in Germany in my own opinion has been due to its greater popular appreciation. Historians have long since dropped the idea that kings and rulers in general amount to very much in the progress of a nation, and have adopted the broader conception that progress ultimately is in the people of a nation, their developing thoughts, their appreciation of the world that is about them.

The lesson to us in the United States is this—that if we wish chemistry to become a more potent factor in the industrial growth of our country we must take such steps as are necessary to bring about a popular appreciation of its value. Universities will help, government aid will help, but these too depend upon popular appreciation both in their beginning and in their execution; after all they are mere incidents to fundamental active causes. Create a demand for universities and universities will rise, as it were, over night; create a demand for governmental interest and governmental interest will come quickly and effectively, but demand is borne of popular appreciation.

POPULARIZING CHEMISTRY

Mr. Elwood Hendrick in an article that appeared not very long ago in one of our popular journals emphasized this point in urging the popularization of chemistry, and he expressed the thought that chemists would not come into what they believed to be their own until this was done. Mr. Hendrick's suggestion would indicate the advantage of chemists generally advertising their profession, not necessarily, however, in the form of paid advertisements, but in properly written articles for the popular press. The desirability of such a procedure properly carried out is fairly obvious, but subject to some limitations, which we will consider further on.

As an illustration of what we can accomplish in this direction I would refer to Robert Kennedy Duncan's writings (particularly his *Chemistry of Commerce*) as having been exceedingly efficient in popularizing chemical knowledge, and to the fact that Duncan's efforts in this direction probably resulted in the establishment of the Mellon Institute. As another example of a very commendable effort to popularize chemistry, I would refer to the Chemical Expositions, the second of which was held last September in the City of New York. When the first Exposition was proposed, many chemists expressed a great deal of doubt as to its wisdom and practicability, but as the time approached for the opening of the Exposition, its value to chemists became more clearly recognized and it received from them a very generous and hearty support. So successful was the first Exposition that immediately a second one was projected. This received even more generous support and two of our largest chemical societies decided to hold meetings at the same time. The public press has been full of matter descriptive of the Exposition itself and the accomplishments of chemistry thereby illustrated, and gave much space to the papers and discussions presented at the meetings of the two chemical societies. These Expositions were distinctly advertising in their character and great expenditures with the expectation of profitable return were made by the exhibitors themselves.

Our National Departments of Agriculture and Commerce have done much in popularizing chemistry. The work Dr. Wiley started in the Department of Agriculture has extended the knowledge of chemistry in popular fields through the publication of numerous bulletins and leaflets. More recently the Department of Commerce has, through special investigators, been instrumental in increasing the knowledge of the relation of chemistry to industry. Similar work has been done to some extent by the Department of the Interior. All of these efforts have been of great advantage to chemists.

It seems hardly necessary that I should go further in emphasizing positive aspects of this phase of my subject. Let us consider now some of the criticisms that have been offered on work of this kind. The most general criticism is that when an attempt is made to popularize a science such as chemistry many unscientific statements will be made and true representations will often be incorrectly interpreted by the public. This is undoubtedly so. Erroneous ideas have been promulgated in this way, but the chance to err is not confined to popular presentations. We know that many errors have crept into scientific literature necessitating laborious effort later on for their correction. To err is human, and the danger that error may occur should not act as a preventive of public statements, whether these statements are made in the scientific or popular press.

Another objection comes from those who hold that the profession of chemistry is of a very exalted character and that the serious chemist will not descend to ordinary popularizing effort. Our own Code of Ethics would prevent the chemist from advertising in a sensational manner, and requires the professional chemist to publish scientific papers in the technical journals before they are given to the popular press. It seems to me that our Code of Ethics is correct in this respect. We do not want to advocate sensationalism and we do want to build up our technical journals, but after the requirements of our Code have been complied with there still seems to be a field open to the chemist in which he can with perfect propriety popularize his science.

The advocates of the study of pure chemistry are also apt to look down upon this popularizing scheme. To them popular science is offensive and it may be that some of them can hardly be expected to sympathize with the views I am here presenting. The student of pure science is, however, almost in a class by himself. The utmost that he does in affecting the world's processes is by furnishing information, studies and generalizations to be applied by the practical chemist in furthering the interests of the entire world. Far be it from me to depreciate the value of the pure scientist. We all draw upon him for help in our practical efforts. It must be admitted, however, that he lies essentially outside of the plan that we are proposing. He indulges more or less in an esoteric culture and his light, though it is not hidden, is reflected to the world at large only by those who can practically direct that light to the illumination of ordinary things. In spite, therefore, of all that may be said against the popularization of chemistry, I am still convinced of the wisdom of such a purpose, because it is only by so doing that even the student of pure chemistry will be given an opportunity to carry on his studies. So firm is my belief in this that I would extend this effort so that it would reach and include the most humble members of society.

In order to present in picture form, as it were, the dependence of the chemist for his success upon the popular appreciation of chemistry, let me present the following sketch. A chemist makes what he believes is a discovery of great financial value. If he has money enough of his own he may be able to make that discovery a source of financial profit, but in so doing he will have to be something in addition to a chemist, for the larger part of his effort will be along lines which are essentially non-chemical involving the organization of business, the advertising of the product or process, and its sale for use. In proportion as the

public is capable of appreciating what he has accomplished, to just that extent will he make a financial success. Suppose, on the other hand, this chemist is not a man of means and wants to interest financial people in his discovery. As things are today he will first encounter skepticism, even ridicule, and if finally he is successful in having his discovery appreciated by financial interests, it will be because he has been able to convince them of its human aspects, and it may be that before he is through a great part of the value which he has seen in his discovery will have been absorbed by what the financial interests think is their proper return. The ordinary business man of today very naturally thinks that his business ability is more valuable than the technical ability of the chemist. He wants the lion's share. There is no use in closing our eyes to this fact. Many a poor inventor or discoverer has been so discouraged in his early efforts for recognition that he has been almost ready to drop his entire proposition. He says the blame lies on an unappreciating public, and this is true, but if it is true, how incumbent it is upon the chemist to make the public appreciative! He can do this only by studying the public, finding wherein the public should be educated, and recognizing all its limitations, working with wisdom toward the accomplishment of his purpose.

I think that I have said enough along this particular line to indicate to you my views as to what the chemist should do in the direction of trying to develop a popular appreciation of his work. If there is truth in what I say I am quite sure the open mind of the average chemist will discover it. If I am wrong he will soon find the vulnerable point in my argument. I would like now to pass to another aspect of this question, which relates more particularly to the chemist himself. What I have said so far deals for the most part with the attitude of mind of the chemist toward the public. What I propose to say now deals with the attitude of mind of the chemist towards himself. I have referred to a relation existing between the chemist and the public. In this relation there are two parties, the public on the one hand, and the chemist on the other. The problem before us is: What should the chemist do to develop and improve his attitude of mind towards himself? This is an exceedingly difficult subject, and if it were not that I am fortified by a belief in its importance, I would not dare to speak upon it. I cannot think of anyone holding a higher opinion of chemistry as a profession than I do, and all that I am saying is actuated by a profound belief that the chemist is only beginning now to climb the ladder that reaches to a power of service unequalled by any other profession.

The delicacy of this subject is such that I feel impelled to approach it in the form of questions. In putting these questions, let us consider first some facts, and then we can come to the questions themselves. Let us first consider the young chemist just leaving his college or university. Like all students graduating in various courses, he has yet to learn what business life really is. They think they know what it is, but we know that there is no college or university that teaches it. The difference between the chemist and most other graduates is noticeable in this. The chemist enters a more or less isolated laboratory, most of the others go directly into the commercial world. The chemist in this laboratory—be it analytical or research—is not dealing with people but with inanimate material things. He may stay in the laboratory a few months, a few years, or he may last time, as the case may be. He may be doing excellent work, but here is the question: If he takes his proper place as a man in the world's process? Is he not too much isolated? Is he in the second class position directly in the power over others? Is his social interest being developed or is it being retarded by his growth?

PROF. J. H. HARRISON

If we think that laboratory chemist is a general case, then taking their proper place in the world to which they must resort, upon

mind, there is nothing more to be said; but if we think with his intelligence and education, the chemist has a mission outside of the indirect service he professionally renders to society, then our question leads us to urge that the barriers which ordinarily isolate the laboratory chemist should be broken down so that he can get out more into the pulsating business world. He may not be able to do this alone, and perhaps the duty devolves upon us; perhaps there are some of us who have it in our power to help bring about this liberation. If we want chemists to have a greater personal influence in the world, and by this we mean to include those chemists who are subordinate to us individually, is it not proper for us to ask ourselves whether at times we do not rather selfishly stand in their way? Cannot those of us who are employers of chemists give our employees more opportunity to become familiar with the commercial aspects of the work they do? If we do this, will they not become better and more profitable employees? In our dealings with non-technical men representing large business interests, could we not more regularly and persistently ask to be brought into contact with their chemists if they have them, thereby helping to pull them out of their seclusion? If we are asked to organize a laboratory in a commercial concern, could we not say that the work of the chemist would be greatly helped if it were so arranged that he would know the actual use to which his reports were to be put? Could we not do something in urging that the laboratories in which such chemists are expected to work should not be hidden away in inaccessible places? Could we not do many things suggested by the occasion to break the bonds which the young chemist, led by false hopes, may have often slowly forged? Is it not possible that with our colleges to-day filled with students of chemistry, these students should be advised against accepting positions of an isolated character?

You will see that I am basing my argument on two hypotheses, which are intimately related. One is that social relationship is one of the great purposes of life, and the second is that without such social relationship no individual can really be successful in the development of any important enterprise. I have argued, therefore, that the chemist's success depends upon a social recognition of his worth, and second, that the chemist should enter into as broad a social relationship as possible. In popular terms one of these means that it pays to advertise, and the other means that the chemist should get out upon the broad highway.

I propose now to say a few words on the disadvantage which is sure to result from antagonism. I propose to advocate in all our dealings a conciliatory spirit. It would seem almost unnecessary to say that if the chemist is to advertise, he should avoid offending the persons who read his advertisements, just as it is perfectly obvious that the salesman who is trying to sell goods should not make himself *persona non grata* to the purchaser. A good salesman—and that is what we should all try to be in one form or another—subordinates his own views and makes them as inconspicuous as possible, but no less effective. What he tries to do is to find out the views of his customer so that he can furnish the customer with what he desires. I wonder if sometimes chemists are not a little more pugnacious than they should be. I sympathize with the feeling of an analytical chemist who will set his results up against the world and insist that he is right, but many years of experience have taught me that the chemist who does this without regard for the effect upon other chemists is doing a very foolish thing. I believe it is a good rule never to put anybody "in wrong." I believe it is far better, even in the case of commercial opponents, to help the commercial opponent out of his difficulties rather than to push him in deeper. Again, are we not at times a little too virulent in asserting our ideas respecting public officials—administrative, legislative and judicial. They are human beings, just as we are, they are representatives of the whole people, and if their views differ somewhat from ours, is it not

very much better to work patiently and steadily to change their views, directing them into constructive paths, rather than to confirm them in their views and drive them to unwise extremes by opposing them vigorously?

Let us take as an illustration a subject on which perhaps chemists are divided at the present time, although the division may be by no means equal. Many chemists are seeking to have our National Government help the chemical industry to become more firmly established in this country. Some think it can be done by subsidies, others by protective tariffs, others by embargoes, and so on. Now I would not argue in this meeting for or against any of these propositions. I simply say that if you are in favor of any one of them it is unwise because he opposes you to incur the antagonism of any public official, even if he be of an opposite political faith. Practically all public officials have their ears to the ground; they are trying to find out what their constituents want, and no one should blame them for this. In so far as they are representatives they are doing only their duty. It is perfectly proper for us to try to convert a public official to our way of thinking. It is still more proper for us to try to convert the people he represents to our way of thinking, but I consider it the height of foolishness to attribute to public officials dishonest purposes, ignorance, stubbornness and all the other sins of commission and omission. My point is very clear—such accusations do not lead you anywhere but into trouble.

I believe firmly that the obstacles which we meet in our social acts in endeavoring to get our plans consummated do not differ essentially from the obstacles which the chemist meets in the ordinary routine of his work. If he finds a chemical reaction is not progressing satisfactorily, he does not close his eyes to this fact and denounce some devil or anthropomorphic god because it has interfered with his work. He tries to find the cause of the trouble and remove it. So I say that if you have social obstacles to overcome, find their cause and remove it, bearing in mind that there is no easy way by which this can be accomplished—in fact that there is only one way—education backed by good-fellowship.

HUMAN EFFICIENCY

We have heard in recent years a great deal said about efficiency, it may be that some foolishness has been uttered. The word "efficiency" is used in various ways. We have the efficiency of a process considered by itself; we have this efficiency as compared with other processes; we have mechanical, chemical and human efficiency. I am interested primarily in this paper in human efficiency. What does it mean? Broadly speaking it means coöperation without friction. Perhaps we should say that coöperation cannot be had with friction. Of course it would be absurd for me to attempt to solve the eternal problem of human friction in a paper of this kind. All I can do is to indicate some ways by which it can be reduced. While the realization of frictionless humanity is far away, symptoms of it have certainly appeared at times. Efforts in the direction of reducing human friction conspicuously numerous at this time are to be found illustrated in factory welfare work, Workman's Compensation Acts, pension systems, etc. All of these have been justified by the increase in human efficiency they have produced. A man whose welfare is of no account is not a good workman.

Human efficiency, however, demands right men in the right places. The difficulty that the employer experiences is in knowing whether he is picking the right man for the place or not. If the man has been educated rightly the employer is better able to form an opinion. Particularly is this true regarding foremen and the higher grades of labor. Graduates of such institutions as give technical education are made more nearly right for places in chemical and other industries. More general industrial education such as that being advanced in some states will undoubtedly add to human efficiency. Even then the making of a

man suitable for a given position comes after he commences employment and is largely the work of the employer himself.

Industries do not merely require men, however, they are complicated machines of which the men form a part. The proper fitting and adjusting of these machines to the men employed is the big problem only partly worked out as yet. Each industry has its own requirements, these requirements continually changing with the growth of society. Who has not been face to face with the requirements of an industry? These requirements are almost vitalized by competition. Industries come and industries go, they are planted and they are reaped, but their volume increases from year to year. We must not, however, allow ourselves to think of industries and industrial processes as though they were other than inanimate things. We should not waste our tears over their rejection when they are worn out, provided others take their place. This is growth—the sloughing off of the old and the putting on of the new.

NEW PROCESSES

The chemical engineer has a great deal to do with the development and administration of new processes. Many an old fogey has damned the chemical engineer, who has rendered his processes and his equipment antiquated and idle. The mechanical engineer also has received his malediction. We are sorry for the old fogey and would, if it were possible, provide insurance for him, but we would do nothing to retard the fate of his equipment.

The development of a new process is the result of many separate factors. New processes are like the waves of the sea; they cannot rise much higher than the level of the sea itself. They rest on general industrial growth and are not much above the level of that growth. This is true of all processes, chemical processes included. Their growth depends upon the growth of the mechanical art, its method of fabrication, and all the materials that enter into construction. It depends upon highly developed foundry practice, mining, building construction, farming and transportation, and last, but not least, all those branches of human development which are manifested in the home, social organization, governments and international relations. I emphasize this human factor because so many processes have had to wait years for the time to ripen for their introduction, indicating, in other words, that not alone should our endeavors be directed to the development of processes, but they should also be directed in a general effort to accelerate the coming of the fullness of time. The fullness of time means that the social level has been sufficiently raised.

New processes are of two kinds: *first*, those which provide improved methods for making old and well known products, and *second*, those which involve the making of new products to take the place of old, or new products which serve entirely new purposes. A new process which is intended to provide methods for making an old product, if it is to be successful, must involve economy of some sort, economy of material, investment, time or labor. Necessity creates the demand for such new processes. Competition—domestic and foreign, is the impelling force. The wise manufacturer recognizes that the development of a new process may be his salvation. It is impossible in this paper to discuss all the demands which compel the invention of a new process. We will discuss only the human or labor element.

LETTING DOWN LABOR COST

If labor here in the United States is higher in price per unit of product than it is abroad, it is manifest that with free competition the manufacturer must to modify his process so that the item in cost will not militate against him. He may not be willing to modify his process, and his first instinct may be to limit the competition by a protective tariff or some similar restrictive measure. One objection to this, except as a last

resort, is that it removes some of the pressure which makes for improvement of process. We may dislike the pressure but we know after all that it is a good thing. We cannot allow anything to interfere with such pressure as makes improvement necessary. Such improvement may be possible. It is much wiser to insist that it is possible than to insist that it is not. Success is often accomplished by doing what is apparently impossible, but assuming that the manufacturer cannot get the protection he wants, how will he go about improving his process? We will offer only a few suggestions.

ADVANTAGES OF MANUFACTURING IN LARGE UNITS

The first consists in manufacturing in large units. By this means overhead charges are reduced and materials can be handled more cheaply by mechanical means, thereby either directly or indirectly reducing the cost of the labor factor. In this direction it would appear that the United States has been pre-eminently successful; there is probably no country in the world which equals us in this line of development. The second consists in subdivision and specialization of labor. It is obvious to all that it is through this method that most of our industries in this country have been successful. The third is radical development of process. If we take a given process and consider all of the operations, step by step, we are able tentatively to classify these steps into two kinds—the essential and the apparently necessary. The apparently necessary step is not by any means an essential step. An apparently necessary step is one that the state of the art has not eliminated. An essential step is one that we feel justified in saying cannot be eliminated, no matter what the state of the art is. By a radical development of process it may be possible to eliminate apparently necessary steps. The burning down of a house in order to roast a pig was in the mind of the Chinaman of fiction an apparently necessary step. It was, however, eliminated by the Efficiency Engineer of his day. Fourth, by doing by machinery what was theretofore done by labor. An essential step in a process may still appear essential, although instead of performing the step by manual labor it is done by machinery. This much does not involve the elimination of a step. Doing by machinery what was theretofore done by labor is the obvious method of reducing labor costs. It usually entails, however, additional cost for investment, power, and repairs, and also the employment of a higher class of labor. It is perfectly obvious that where labor is cheap machinery is unnecessary, but that where labor is high, competition compels the use of machinery, and that this is the proper and natural order of things.

MECHANICAL EFFICIENCY MUST LEAD TO HUMAN EFFICIENCY

This is perhaps to you a somewhat new claim, but certainly the methods to be followed in achieving how a process can be improved. If I should go into the methods by which new processes for making old or new products might be worked out, it is probable that this study would be still more academic, and I will not attempt here to touch upon that branch of the subject. What you may consider *academic* is what I have said, however, has a very practical bearing upon the general subject I am endeavoring to present. As I have already indicated, I am interested in human efficiency. Mechanical efficiency that does not lead to human efficiency is of no importance. Considered in the most general manner, human efficiency is the ease with which a man can perform his work. Human efficiency is a means rather than an end, but I would stress the relative and ask you to consider human efficiency in terms of *useful* things. It is a truism that the most efficient man has spent some money. The cost of labor usually means greater expenditures and higher efficiency.

A man has a natural and normal amount of energy, the highest energy for which we are made, and all efforts must be the

velopment of its parts is well worth while. If you believe with me that an appreciative public is necessary for the proper growth of the chemical industry, you will also agree that we need a public which shall have the power of appreciation which can come only as a result of the general raising of the level of social conditions.

The chemist by working for improvement in processes involving a saving of labor, and at the same time involving the employment of a better grade of labor is contributing his part to the better development of a high social organism. If the chemist, however, simply endeavors to improve a process without regard to the possibility of that improved process involving the employment of a higher type of labor, then his work is incomplete. It is true that his process may with cheap labor be able to manufacture products which are used by the entire community, and which consequently can be sold at a reduced figure and thereby benefit society, but many difficulties will lie in his path if he does not at the time that he reduces the quantity of labor necessary in the process, also create a demand for a higher quality. I therefore ask those of you who are engaged in the development of processes, such development being forced by competition and the requirements of the industry, to consider whether it would not be better for you to put your mind in the attitude that in your development of process you may possibly be able to get better results by the use of more intelligent and higher priced labor than you could by sticking to low-priced labor and possibly handicapping yourself and your process and preventing its fullest development.

CONCLUSIONS

I have endeavored in this paper to present several aspects of a very large and important subject. Some parts of it may appeal to you and other parts may excite your opposition. In the main, however, I believe all of these parts are related to each other consistently and logically. If you believe, as I do, that a better social organism is the highest purpose for which anyone can work, you will accept what I have said and include in the proposition many extensions on which I have not touched. If, however, your minds are more practical, I think you will accept many of the things I have presented to you purely on account of their practical value. Therefore from whatever standpoint you approach the subject, am I not correct in stating that practical business success in all lines of business, including those involving the use of chemistry, is dependent upon popular appreciation, is dependent upon social growth, on which the power of appreciation rests, and that everything which tends to increase the power of appreciation helps appreciation itself, and that anything that increases appreciation increases the chance of success of a business enterprise? Or to put it negatively, anything that interferes with an increasing power of appreciation, anything that tends to prevent appreciation or creates those antagonisms which operate against appreciation is pretty sure to hinder the growth of a business enterprise.

If this fundamental proposition is accepted, we can readily see how important it is for the chemist in attempting to build up chemical industry in the broad sense to do everything in his power to raise the general level of human knowledge and education and of social conditions, for it is that level that determines the power of appreciation. Assuming this power of appreciation to exist and to be growing in strength, you will also, I think, agree with me that the chemist should do everything in his power to create a greater appreciation of the value of chemistry in solving the problems of industrial life, for it is only through such appreciation that the chemist himself will be able to exert fully that ability for service which we all believe he possesses. But if the chemist is to impress himself on the public through legitimate advertising, should he not also endeavor to develop that attitude of mind which makes him con-

tinually a factor in social growth? Should he not break away from all influences that tend to isolate him, and that, if they do not make him a peculiar being, at least have the effect of preventing him from having the fullest influences over others? Should we not do everything in our power to broaden the horizon of the chemist, to increase, as it were, his circulating power in the social organism? Should we not, as chemists, by very simple methods do all we can to pull chemists individually out of all such surroundings which tend to narrow and handicap them?

Now having done all of these things, should we not go a step further and recognize the peculiar position which the chemical engineer occupies in the development of chemical processes? Our minds naturally operate discontinuously. We think of a chemical process and its development as an independent thing, as though it were not a part of all of the other processes continually operating in society. We think that with the development of a process our work is ended; we think that with cheaper manufacture of given products we can sit down with satisfaction and consider our efforts successful. But philosophers tell us that there is no such thing as discontinuity, that everything runs into everything else continuously and is a part of a complete whole. Some fancifully have said that if a man could destroy a single atom, the universe would fall to pieces. This is fanciful but it expresses a true conception. There is such a thing as solidarity—not the solidarity of labor, not the solidarity of industry, but more surely the solidarity of society. All things operate in circles. We have continuous production and continuous consumption, in which material things circulate around and around, never completely stopping. This is so of all human affairs. Effects are unending. All the ends we work for are but the means to other ends. The development of a process was the end yesterday, but to-day it becomes a means—a means by which the social level is raised, which in turn becomes a means by which other processes are developed.

This is why I have expressed my opinion that in the development of a process it can hardly ever be said to be complete unless it results in the substitution of quality of labor for quantity, whenever such a development has for its purpose the saving of labor. Development of a better quality of labor is essential if we are seeking broadly to increase the power of appreciation on the part of the public. It would be manifestly foolish for me to advocate that chemists should seek to impress Hottentots and Fiji Islanders with the power of service in chemistry. It would take centuries of education to bring them up to the point where we of America are to-day. It is equally foolish to think that we can expect as much appreciation from common labor as we can from intelligent labor. In saying this I make the assumption with which I hope you will agree—that every member of society, the ignorant and the wise, the poor and the rich, the bad and the good, the sick and the well, are all integrally a part of society and each one has his individual influence in determining the average social level which measures the power of appreciation.

I have endeavored in this paper to avoid taking any position which is negative in its character. I do not believe that there is such a thing as a negative force; the nearest we come to it is inertia. I have endeavored to make positive suggestions which I submit for your consideration with the daring hope that these suggestions may find lodging places, temporarily it may be, in your minds, and if, after these ideas have stayed in your minds for a short time, they then take their flight, I have the still more daring hope that after you have forgotten them, they may, though unconsciously to you, have left some faint imprint.

THE CHEMIST IN THE CANNED FOOD INDUSTRY¹

By W. D. BIGELOW
Received December 1, 1916

The canned food industry was based fundamentally on scientific research. It would appear that this fact should have suggested to the pioneers of the industry the advantage of the cooperation of scientific men. Apparently, it did not. The laboratory was not appealed to as frequently as might have been done advantageously. The progress in the industry has been largely haphazard and there have been many blunders and enormous losses that might have been avoided by scientific control. At the same time, the laboratory has demonstrated its usefulness to the industry in many ways.

DISPOSAL OF BY-PRODUCTS

The disposal of by-products is a question to which the canning industry has not given adequate attention. Some of the by-products may be used for the preparation of food. For instance, pulp may be prepared from the peelings and cores of tomatoes. In all such cases, every possible precaution should be taken to see that the material is proper for the manufacture of food. Decaying matter must be excluded. This work has a very close relation to the general question of factory sanitation. Some plants have found the laboratory of great assistance in connection with such matters.

ECONOMICAL DRYING OF PRODUCTS AND WASTES

Questions often arise regarding the use of some cannery by-products in the manufacture of stock foods and fertilizers. Very little has been done in this direction except in the case of certain by-products which are fed in their natural state or preserved in stacks or silos. In order to transport offal from the cannery for a considerable distance or make it available for general market purposes, it must first be dried to prevent decomposition.

Some experimental work has been done on this subject, but it has not been accompanied by proper engineering skill. Experimental work is still needed to determine what substances can be dried economically. Products of this nature contain a large amount of water and their drying would be expensive. Most canneries run for a very short season, and whether the value of the by-products is ever such as to make it practicable to install expensive drying equipment and maintain it for a season lasting but a few weeks is yet to be demonstrated. Certainly, in many small plants it cannot be done.

SUPPLIES

Questions are constantly arising in which the canner will profit by being able to consult some one of scientific training. Articles of all kinds are being offered with extravagant claims regarding their value. Often these articles are of such a nature that the manufacturer is not in a position to form an opinion regarding them. Products are offered which are claimed to have superior merit for almost every operation of the canner, from saving fuel under the boiler or keeping the boiler tubes free from incrustation to the cleansing of the floors and factory utensils or sweetening or flavoring the food.

Some of these articles are satisfactory, but are offered under coined names at prices far in excess of their value. Others are utterly fraudulent and worse than useless. Such products sometimes contain artificial sweetening material or preservatives which packers do not desire to use.

SPOILAGE PROBLEMS

It sometimes happens that an unusual amount of spoilage is noticed during the canning season. In extreme cases this may cause a loss of several hundred or even several thousand dollars a day and it is of the utmost importance to learn immediately the cause of this spoilage in order that it may be corrected.

¹ Presented 52nd Meeting, American Chemical Society, Urbana, Champaign, April 19, 1916.

Spoilage is occasionally found in the store-room after the packing season is over and the canner desires information regarding its cause, in order that he may make provision to eliminate it from future packs. It is often desired to fix the responsibility for spoilage in order that, if it is due to defective cans or other supplies, claims may be made against the party properly responsible. It is probably in fixing the cause of spoilage that the chemist is able to render the most immediate assistance to the canner and it is in such questions that experience in the industry is most essential.

Certain acid fruits, such as strawberries and red cherries, formerly corroded the can and dissolved an appreciable amount of tin and iron. For that reason, the color of the product was often unsatisfactory, especially with red fruit, as the coloring matter was bleached out. The flavor of the product was also sometimes impaired. Eventually a sufficient amount of hydrogen gas was liberated by the solution of tin and iron to bulge the ends of the can, and, though still bacteriologically sound, the food became unmerchantable. This was overcome by the use of enameled cans, but immediately a new difficulty arose. The enameled can was found to pinhole badly, thus exposing the contents of the can to air and leading to contamination. This was probably due, as suggested by Walker, to the influence of the unsaturated groups of linseed oil present in the lacquer in depolarizing hydrogen set free by the action of the fruit acids on the metal wherever an imperfection in the lacquer occurred. For several years the losses sustained by some packers owing to this cause were greater than the entire profits of the pack. Recently, as a result of further laboratory study, this difficulty has been largely overcome.

SPOTTING OF CANS AND PRODUCTS

Instances are constantly arising in which packers find some imperfections in their product which make its appearance less attractive or, at least, unusual, and thus possibly not acceptable to consumers. The difficulty may be one of flavor or color or general appearance. It may be confined to the external appearance of the cans. Small dark spots occurring at the surface of a light colored product may cause unfavorable comment. A trivial imperfection may make the difference between profit and loss on a season's operations. These difficulties are often unattended by any change in material or factory procedure, as far as the packer is aware. It is the business of the chemist to find their cause and to suggest a remedy.

As an illustration, we may refer to the occasional formation of black patches on the inside of corn cans. These patches consist of finely divided iron sulfide, apparently in colloidal form, intimately mixed with a mass of the starchy material of the corn. Because of its colloidal nature, the amount of iron sulfide present in these patches is very much less than it appears to be. There is no objection to it, except that its appearance is unsightly. As a result, much corn has been discarded and a great deal more sold at a loss to the packer. Of the whole, a good many thousand dollars were lost by the industry from this cause alone during the season of 1914.

The cause of this formation was difficult to explain. As a result of the concerted study of several laboratories interested in the industry it has been partly explained, and many of the conditions leading to the formation have been outlined. Consequently, the loss during the past season was very much less, and it is hoped that direction, which have recently been published will lead to the elimination of this difficulty in the future.

RESPONSIBILITIES OF CHEMIST TO THE INDUSTRY

In final proceedings it is understood that, in its final opinion, the Court is not governed by testimony suggestions offered or caused to be made made by it during the course of a trial. Fortunately, or unfortunately, the chemist is not permitted an opinion

dictum. He is held responsible for every opinion he expresses, even though he may base it on an imperfect or incorrect statement of facts. When such an opinion is found to be erroneous, not its author alone but the whole chemical profession suffers in reputation.

The average food manufacturer seems to ascribe a sixth sense to the chemist. Consciously or unconsciously he attributes to him some almost miraculous knowledge. He does not fully understand that the chemist uses only ordinary faculties and that his only advantages are a knowledge of some special means of study and a training in observation.

To many food manufacturers, a chemist is a chemist, and all are measured by the same rule. They do not realize that a chemist may be an authority on the analysis of steel or paint and still be utterly ignorant of the chemistry of foods. They do not know that a chemist may be well informed in the manufacture of jelly or ketchups and yet know nothing of the questions involved in the packing of canned foods.

Even those packers who have had larger experience with chemists and understand better our method of arriving at conclusions are likely to attach undue importance to a casual opinion expressed in conversation. Any opinion that we express is likely to be understood by them to be based on experimental work and a full knowledge of the premises. We should be very careful, therefore, in expressing an opinion regarding a subject which we have not thoroughly studied.

IMPORTANCE OF SPECIALIZATION

In many lines of technical work, we do not make this mistake. Those of us who have not studied explosives realize our lack of information and do not hesitate to say we do not know. We who know little of the technology of iron and steel and nothing of armament would not presume to examine a sample of steel to determine its suitability for armor plate. In food chemistry, however, and especially in the manufacture of foods, we are all experts. Almost everybody thinks he knows a great deal about food. Just why, it is difficult to understand, unless it is because we all eat food.

The fact remains that there is probably no branch of chemistry regarding which there is less information among well informed chemists who have not made it a specialty than the chemistry of foods, and particularly canned foods. The readiness of chemists who have had no experience in the manufacture of foods to give an opinion in that field has afforded many illustrations of the truth of the old adage, "A little knowledge is a dangerous thing."

It explains some of the misinformation that has been given canners even by reputable laboratories. This has usually been done in personal conference or by letter in reporting a sample sent to the laboratory, but not infrequently the information thus given has been made public in newspapers, trade journals, or even in scientific publications. I will cite a few instances to illustrate what I have in mind.

MISINFORMATION AMONG CANNERS

There is a general belief among canners that the use of hard water in the preparation of brine or syrup added to canned foods results in a tougher product than would be obtained with soft water. It seems reasonable to suppose that this would be true. The thought at once suggests itself that when peas are heated for the purpose of sterilization the calcium bicarbonate dissolved within the peas may be changed to insoluble calcium carbonate, making the peas tougher or harder than they would otherwise be. It has also been suggested that calcium sulfate, being less soluble in hot water than in cold, would be thrown out of solution to a considerable extent when the peas were sterilized. As a result of this general, but erroneous, belief, canners frequently have submitted samples of water to chemical laboratories and asked whether the water was too hard for canning peas or beans.

Laboratories have examined such water and have condemned hard water for the reason given above. In this they appear to have been governed by a prevalent superstition rather than by the results of experimental work. It did not occur to them that the carbon dioxide formed in processing would redissolve any calcium carbonate that might be formed by the higher temperature, or that the calcium sulfate precipitated by lowered solubility during the heat of sterilization would dissolve again after the product cooled.

Again, salt manufacturers have advertised their brands as relatively free from calcium and magnesium and, for that reason, have claimed that these brands of salt could be used by canners without toughening their vegetables. This claim has often been accepted by chemists, and salt has been approved or condemned on that basis.

Again, some of the objectionable colors found occasionally in canned foods have been explained by chemical laboratories as due to iron in the water employed and canners have been warned, as the result of chemical analysis, not to use water from certain wells because of its high iron content. In making this last suggestion, chemists have not taken into consideration the fact that there is more iron absorbed by canned food from the tin plate than is carried by any water which they could possibly consider using.

An article has recently appeared in the trade papers alleged to have been written by a chemist employed by a lithographer. The name of the chemist was not given. His report proved to his own satisfaction that there is no object in removing food from the cans as soon as opened. To prove this, he determined the acidity of a number of foods as soon as the cans were opened and again after a lapse of a number of hours. From the fact that the acidity did not increase materially, he argued that no tin could possibly have gone into solution and, hence, that there was no objection to storing food in the open can. The obvious method of determining tin in the food at intervals in order to ascertain whether the amount had increased does not appear to have occurred to him. He did not consider the influence of oxygen in promoting the solubility of metals when the food is exposed to the air, although his report quoted a letter from the Bureau of Chemistry in which this influence of oxygen was mentioned.

Every food chemist knows that leaving food in an open can does not make it injurious to health, though the amount of tin and iron dissolved is somewhat increased. The article just referred to throws no light on this subject, but is evidence that experience in the field of chemistry pertaining to the printing of labels does not qualify a man to conduct an investigation with any question relating to the contents of the can.

The publication of opinions of this character is not confined to popular journals and trade papers. We find them also in scientific literature.

A few months ago an article on the iron content of tomatoes appeared in *THIS JOURNAL*. The writers, after determining the amount of iron in the samples examined, procured samples of soil in the localities in which the samples were grown and commented on the relative iron content of the tomatoes and of the corresponding soils. Toward the end of the article, the writers casually referred to the fact that the samples were canned. They made no mention of the method of canning, the conditions under which the product was stored or the age of the sample. All of these factors would govern the amount of iron in canned tomatoes. Under all conditions, the amount dissolved from the can is immensely greater than the amount of iron originally contained by the tomatoes. Even that fact, however, can scarcely explain the high iron content of these particular samples.

DIFFERENT CLASSES OF CANNED FOODS

Wrong conclusions have often been reached by confusing different kinds of canned foods and assuming that a certain condition in one class of foods was due to the same cause as an apparently similar condition in another class. For instance, acid fruits dissolve an appreciable amount of tin and iron, owing to the solvent action of the fruit acids. Errors have sometimes been made by assuming that tin dissolved in some other types of foods, such as canned pumpkin or shrimp, was also due to acidity, when, as a matter of fact, it is apparently due to the presence of certain amino bodies. The solution of tin in foods of this class is not accompanied by the generation of hydrogen and does not form springers.

Attention has already been called to the fact that springers (cans under very slight pressure) are often caused in acid fruits by the hydrogen liberated by the action of the fruit acids on the metal of the container. It sometimes happens that cans of other products (such as corn) which do not dissolve tin and iron, are found under slight pressure and are apparently springers. Erroneous conclusions have sometimes been reached by assuming that the pressure in these cans is due to the same cause as that in cans of acid fruits that appear to be in the same condition. This is not merely an academic question. Responsibility for spoilage involving many thousands of dollars is sometimes at stake. It is often of the utmost importance to determine whether the responsibility rests with the can manufacturer, the canner, or the conditions under which the finished product is stored.

VARIATIONS IN CAUSES OF SPOILAGE

In the enforcement of municipal food laws and regulations and, to a certain extent, in the enforcement of state laws, there is sometimes a failure to discriminate between canned foods which have spoiled by reason of improper sterilization or leaky cans, and those which have become more or less swelled by reason of the hydrogen generated by the action of the fruit acids on the metal of the container. Foods of the latter class, though neither decomposed nor injurious to health, are undoubtedly not merchantable and their sale or use should not be permitted. The condition of springers, and even of what appear to be hard swells in acid fruits, is usually due to the character of storage after the product was canned and, when the goods are criticized, responsibility should be placed where it belongs. The designation of such a product as decomposed is unscientific, because it is not true. It is unjust to the manufacturer, for the product was merchantable when it left his hands and would have remained so with proper subsequent treatment. A chemist who makes a decision of this kind works injury to the chemical profession in the minds of business men who are conversant with the situation.

It should not be understood that chemists are more prone than others to inaccurate statements regarding the manufacture of foods. Magazine writers give vivid descriptions of processes they have not seen and even prominent authorities on dietary diseases and in the practice of medicine not infrequently make statements which show a complete lack of information of the technology of foods of a generation ago, much less the practice of the present day.

It not infrequently falls to the lot of a chemist in the dining industry to explain to business men, as well as he can, how it is possible that a man who makes definite and positive statements regarding a subject of which he has no knowledge is not necessarily equally erroneous in his views on other matters.

SOME OBSERVATIONS ON THE PRESENT STATUS OF THE SUBJECT OF THE AVAILABILITY OF NITROGEN IN FERTILIZERS¹

By CHAS. B. LIPMAN

In order to gain a clear comprehension of our present-day views on soil fertility it is necessary to divest one's self largely of traditional theories, formulas and fancies of the vintage of 1850. If this is so of soil fertility in general, and no progressive scholar in soil science will deny that it is, it must of necessity be true of that one phase thereof which concerns itself with the availability of some of the plant food elements. These statements are not intended as destructive criticism as the following discussion will indicate. They are meant only for the purpose of arousing from their lethargy those who are either too conservative or too indolent to keep abreast of the scouting parties in soil fertility studies. No one rises with greater alacrity than the writer to render homage to the last two generations of investigators for their splendid contributions to our knowledge of plants and soils. No one appreciates more deeply the value of the gigantic work in chemical analyses of plants, soils, and fertilizers which the investigators mentioned have achieved. We could not very well have done without these numerous analyses. They constitute the growing pains of our adolescent period and as such are presumably ineluctable and necessary accompaniments of normal development. But once we have successfully weathered them, once they have contributed their quota to the creation of our modern views, they have served their purpose and the bona fide scientist must move on to a sounder and fact-fortified science and a saner philosophy with respect to crop production. Everything which I have to say to you to-day takes its origin on such a basis of thought and action as I have just described and is an attempt to make as nearly lucid as my humble powers will permit the answer to the question, "Where do we stand on the problem of the availability of fertilizer nitrogen today?"

Let us first understand clearly the meaning of the term "available nitrogen." In the case of phosphorus and potassium, availability means but one thing, and namely, that some mineral compound containing the element in question is soluble in the soil moisture. So far as we can at present determine it makes but little difference to the welfare of the plant if the latter assimilates potassium from the sulfate, nitrate, phosphate, or any other mineral salt. Likewise, it seems to be a matter of indifference to the plant, as it were, if phosphorus is presented to it in the form of calcium, potassium, magnesium, or other phosphate. The only condition upon which availability depends, therefore, in the case of all the other essential chemical elements than nitrogen to plant growth, is that they must be in some compound which is soluble in soil moisture. This is not necessarily the case, however, with nitrogen. In fact, the situation with respect to the latter element is very complicated. Some plants appear to assimilate nitrogen with benefit in a large number of water-soluble forms whereas others may assimilate these same forms but be incapable of all except the nitrate form. Still others may use nitrogen in the form of ammonia without apparent injury, but are much less wasteful of nitrogen under those circumstances and need much more of it in the form of ammonia than in the form of nitrate to produce one pound of dry matter. Availability of nitrogen, therefore, if I may repeat again, is by no means as simple a consideration as the availability of the other essential elements presented. Fortunately, however, we know that the nitrate form of nitrogen is the only one which can be used advantageously and economically by terrestrial plants (free and mobile green aquatic plants are of course an exception). True, and not merely fully considered,

tion of the points brought before you in this paragraph, but you can find a detailed discussion of the theoretical considerations involved therewith in Russell's "Soil Conditions and Plant Growth," and in the papers by Schreiner and his associates, and in that of Miller and Hutchinson on the general subject of the forms of nitrogen assimilated by plants.

METHODS EMPLOYED FOR THE DETERMINATION OF "AVAILABLE" NITROGEN IN FERTILIZERS

The methods thus far employed for the determination of availability of nitrogen in fertilizers have been of two classes, *viz.*, vegetation and laboratory tests. The former class of methods is the most reliable since it permits our obtaining an answer to our question directly from the plant, which is of course the organism affected. On the other hand, it is obvious that the method of vegetation tests is expensive, onerous, and extremely tedious. Besides, no determination of availability of nitrogen fertilizers for a series of crops on one soil may be regarded as pertinent to another group of soils even if the same crops be under consideration. All of this means that a logical consequence of the vegetation test method for the availability of nitrogen in fertilizers would be empiricism run riot. Even if it were possible to consummate the huge task involved in such procedure, and it is very doubtful if it would be, the results would always be open to the suspicion of incompleteness.

The second class of methods must in the nature of the case be arbitrary for some time to come. The latter circumstance does not preclude, however, the possibility of their thorough correlation with vegetation tests so that they may become firmly established as specific criteria. The laboratory methods are based on the general principle, or more correctly speaking, on the general assumption that the rate of oxidation of organic nitrogen is an index of the rate at which it may be rendered available to the plant. This is strictly so only in the case of the neutral and alkaline permanganate methods which are described in *Bulletin 107* (Rev.) of the Bureau of Chemistry, United States Department of Agriculture. In the case of the other partially accepted laboratory method, namely, the determination of ammonifiability of the organic nitrogen of the fertilizer, this is only partly true since the process of ammonification in soils partakes of the nature both of oxidation and reduction reactions. In other words ammonia formation in soils represents the algebraic sum of the reduction and oxidation reactions with respect to nitrogen of soil microorganisms.

In the first class of laboratory methods purely chemical reactions are involved while in the second class bacterio-chemical reactions obtain. It will be seen, therefore, that to be valid the first class of laboratory methods must be correlated with the actual supply in vegetation experiments of available nitrogen from any given nitrogenous fertilizer. In the case of the second class of methods it must be demonstrated that a more or less definite relation obtains between the capability of fertilizer nitrogen to ammonify and the usability of such ammonia or substances produced therefrom in a similar ratio for plants. In the case of the purely chemical methods the correlation has sometimes been made satisfactorily and sometimes very unsatisfactorily. In the case of the bacterio-chemical method under analysis, similar though on the whole better, results have been obtained. For these reasons it occurred to the writer that in many soils the oxidation or ammonification of organic fertilizer nitrogen might not indicate the actual rate of transformation of organic nitrogen through all stages into the final nitrate form which in all probability is the form at the disposal of all terrestrial plants in the soil.

THE NITRIFICATION METHOD AND THE COMPARISON THEREWITH OF OTHER METHODS

With the foregoing idea in mind the writer proposed the use

of the nitrification method as a standard test for the availability of fertilizer nitrogen. This test has of course been used by many investigators in connection with various researches on soil microorganisms, but the proposition has never been made to employ it as a standard method for the purpose above mentioned as was the case with the ammonification method. The proposition in question is based on the idea that nitrates constitute the end product of nitrogen transformation in normal soils, that they are always found in more or less considerable quantities in soils, whereas ammonia is usually found only in traces, and because all experimental data now at hand point to nitrates as the form of nitrogen which plants generally will absorb from soils by preference over any other form. I had also suspected for some time that, at least in certain groups of soils, there might be no parallelism between the ammonifiability and the nitrifiability of organic nitrogen. It should be added before proceeding with the discussion farther, that the strongest support which I possessed for the idea of using the nitrification method as a standard method for nitrogen availability lay in the experiments of Vogel at Bromberg and others in Germany, England, and in this country which pointed to a fairly accurate correlation between a soil's nitrifying power, other things being equal, and its crop-producing power. With these ideas as a basis, the writer, with the assistance of Prof. P. S. Burgess, carried out a series of investigations with a large variety of California soils and a considerable number and variety of nitrogenous fertilizers. In these investigations the ammonifying as well as the nitrifying powers of the soils in question for the fertilizers tested were determined. The nitrification studies have been reported in *Bulletin 260* of the California Agricultural Experiment Station and the comparison between the ammonification and nitrification data will soon appear in *Soil Science*. The method employed for the nitrification studies was an adaptation of the well-known ammonification method proposed by J. G. Lipman and consisted chiefly in mixing 1 g. of the organic nitrogenous fertilizer to be tested with 100 g. of soil, making up to optimum moisture content and incubating for 1 mo. at 28 to 30° C. At the end of the incubation period nitrates were determined by the colorimetric method. In brief, the results of these studies seemed to show the following:

- 1.—That the nitrogen in an organic nitrogenous fertilizer like dried blood, high-grade tankage, or fish guano may be readily ammonified, but not necessarily readily nitrified by soils.
- 2.—That the nitrogen in low-grade nitrogenous organic fertilizers like steamed bone meal, cottonseed meal, sewage sludge, and garbage tankage, while ammonifying slowly, might be readily nitrified by the soils in question under the conditions described.
- 3.—That most truly arid soils nitrify the organic nitrogen of low-grade nitrogenous fertilizers well, but that the converse is true with respect to the high-grade nitrogenous materials.
- 4.—The opposite is true of soils with plenty of organic matter and large internal surface which resemble the humid soils.
- 5.—That the excess of ammonia elaborated from the high-grade nitrogenous fertilizers by arid soils is toxic to the nitrifying bacteria and that therefore no nitrates are formed.
- 6.—That sulfate of ammonia is readily nitrified by the truly arid soils but only relatively feebly by the soils of a more humid nature.
- 7.—That relatively speaking, the low-grade organic nitrogenous fertilizers and sulfate of ammonia are better suited for application to arid soils than the high-grade materials.

The foregoing conclusions were further strengthened by another series of investigations carried out by the writer and Prof. Burgess

and Dr. Klein which is soon to be reported in the *Journal of Agricultural Research*. In these investigations about 50 Eastern soils representing the different states in the Union were compared with about 150 California soils representing four soil survey areas, in regard to nitrifying powers. The results of these investigations indicate that in general, and contrary to the teachings of Hilgard and others, the arid soils, so far from possessing more intense nitrifying powers than the humid soils, are actually more feeble than the latter in that respect. This is true whether the soil's nitrifying powers be determined by means of the soil nitrogen alone or by means of added fertilizer nitrogen. It appears moreover that nearly all humid soils nitrify dried blood nitrogen satisfactorily and sulfate of ammonia nitrogen relatively feebly and that the obverse is true of arid soils.

The results of the investigations above described have been called in question by Kelley on the basis that our methods of determining the nitrifying powers of soils by admixing with soils such large proportions of fertilizers as 1 per cent, were not valid, because the concentration of nitrogen in the soil was made too high and therefore abnormal as compared with field practice. Kelley claims that by using very small quantities of dried blood (approximately such as are used in field applications) with soils he was able to obtain good nitrification in cases in which large quantities of dried blood would give no nitrification at all. That this is beyond question we have no desire to deny. Our only claim has been and is that the relative ratings we have accorded to soils in the direction of nitrifying powers for different fertilizers would still hold true by whatever arbitrary method was adopted for their determination. In other words, I believe that soils are correspondingly strong or weak in nitrifying power, according as they behave in tests such as we made, so long as any one method is used consistently throughout. This seems to me to be true still by further confirmatory experiments of the vegetation order which will be described below, and despite the fact that I believe in all probability we shall have to adopt nitrification methods in general like those proposed by Kelley. I desire to repeat again, however, that I cannot as yet see how the method which we employed militates against the validity of our conclusions. If it does so at all it operates in the direction of the degree of accuracy in our results, and not against their character and kind. Many of the theoretical considerations concerned with the results briefly discussed above cannot for lack of time be given here, and my hearers are referred to the papers above mentioned and to others soon to appear for a full discussion of our views and those of others.

CONFIRMATORY VEGETATION EXPERIMENTS

On learning of the objections to our methods and conclusions, which are discussed above, the writer and Prof. Gericke determined to choose an arid soil which by our method showed no power to nitrify dried blood nitrogen and which was known to be in need of available nitrogen, and by vegetation tests to establish the availability of various fertilizers therein. Accordingly, we chose an and blow sand from near Oakley, Cal., for the experiments. Pot cultures were employed in the greenhouse and all treatments were run in triplicate. Barley was the crop tested. Moreover, in order to meet the objections in question, the fertilizers were applied on a field basis in one part of the experiment and on our laboratory basis on the other. Where the fertilizers were employed on the field basis an equivalent of all fertilizers to an 850 lb. per acre application of dried blood was applied, the equivalent being calculated to equal quantities of nitrogen in all pots. The fertilizers were thoroughly mixed with the soil before the planting was done and the following materials were used: dried blood, steamed bone meal, cottonseed meal, sulfate of ammonia, nitrate of soda and nitrate

of calcium. The nitrifying powers of the soils in question were determined for all non-nitrate fertilizers used by our regular laboratory method above referred to. According to this it was found that dried blood yielded no nitrates and that sulfate of ammonia, cottonseed meal and steamed bone meal were about equal in nitrifying power. From the very start the growth of the plants in the different pots indicated clear differences in availability of the nitrogen. At first the steamed bone meal was slightly superior to the cottonseed meal and sulfate of ammonia nitrogen, but the latter two forms soon manifested as high an availability as the former and toward the end of the growing season slightly surpassed it. The dried blood showed itself from start to finish to be distinctly inferior to all the other materials as did also the sodium and calcium nitrates. The sodium nitrate, however, was considerably better than the calcium nitrate. When the total weights of dry matter were considered, it was found that the sulfate of ammonia stood first, the cottonseed meal was a close second, and the steamed bone meal a good third. The others were all considerably inferior, but the dried blood nitrogen and nitrate of soda gave similar results and the calcium nitrate was the lowest on the list. So far as the yield of grain alone is concerned, the sulfate of ammonia again stands first and the cottonseed meal and steamed bone meal are about equal and close seconds. The other fertilizers are about equal as regards grain production and distinctly in the third class.

These results will all be presented in full in a forthcoming publication, but enough has been stated above to show that a distinct correlation exists between the nitrifiability of fertilizers in the Oakley soil and their availability to barley plants in that soil. Whether or not the correlation could be drawn more closely by another method is beside the point. Our main thesis is that the nitrifiability of fertilizers as determined by some laboratory method is a reliable guide to the determination of their availability; that soils of different climatic regions differ markedly in that respect; and that the standards on the availability of nitrogen in different fertilizers as previously established under humid soil conditions will probably have to be revised, for arid soils at least.

Without any intention to introduce anti-climatic considerations I cannot refrain from emphasizing again, to obviate possible misunderstandings, the position taken by me in regard to the subject in hand. I do not claim the nitrification method to be much less arbitrary than the ammonification method. But I do claim that it can be correlated more closely with field effects of nitrogenous fertilizers than the ammonification method and much more so than either of the permanganate methods. This is especially so in the case of arid soils in which ammonifiability seems to fall far short of the nitrification method in usefulness. Again, in saying all this, I am not unaware of the satisfactory correlations drawn by Brown at Iowa, by J. G. Lipman at New Jersey, and by others between ammonifying powers of soils and their crop-producing powers. I am merely pointing out that such correlations do not hold for soils in general as do those based on the nitrification method. It should be added, moreover, that some of the laboratory methods can be expected to furnish absolute results, but only relative ones, but if they indicate the latter, they serve their purpose admirably.

In view of the foregoing, I would urge the adoption by the fertilizer and soil chemists of the method of nitrifiability of nitrogen fertilizers for the determination of their availability. Whether the nitrification method be adopted in one form or another is a secondary question that can probably be settled in without difficulty.

PERKIN MEDAL AWARD

The Perkin Medal for 1917 was conferred on Ernst Twitchell, Ph.D., for his distinguished services in the field of fats and their saponification, at the regular meeting of the New York Section of the Society of Chemical Industry held at the Chemists' Club, January 19, 1917. Dr. Jerome Alexander, Chairman of the Section, presided and delivered the introductory address; the presentation address was made by Prof. C. F. Chandler, Senior American Past President of the Society of Chemical Industry. The acceptance of the medal by Dr. Twitchell was followed by addresses by Dr. A. C. Langmuir, Dr. Martin H. Ittner and Mr. H. B. Schmidt. A telegram from the Cincinnati Section of the American Chemical Society, congratulating Dr. Twitchell, was read by the chairman. The addresses are printed in full below.

Previous to the meeting a reception was held in the Club's rooms at which the members had opportunity to meet Dr. Twitchell, this being followed by an informal dinner in the Club dining room.—EDITOR.

INTRODUCTORY ADDRESS

By JEROME ALEXANDER

The Jubilee of the Coal-tar Color Industry, being the 50th anniversary of the discovery of the first aniline color by Sir William Henry Perkin, was celebrated on July 26, 1906, by a large meeting at the Royal Institution in London, which was attended by representative chemists from all over the world.

The epoch-making nature of Perkin's discovery was referred to by one of the visiting German scientists, who quoted from a recent speech of Adolf von Bayer the statement that Sir William Henry Perkin was the man who lit the torch "which enlightens the path of the explorer in the dark regions of the interior of the molecule."

On October 8, 1906, it was our good fortune to have Sir William Henry Perkin with us in New York as our guest at a large banquet given in his honor. There are many of us here who recall with pleasure his charming and modest personality.

Subsequent to the banquet the happy idea was suggested by the committee in charge, that a Perkin Medal be established to be awarded annually for the most valuable work in applied chemistry.

The award may be made to any chemist residing in the United States of America for work which he has done at any time during his career, whether this work proved successful at the time of execution or publication, or whether it became valuable in the subsequent development of the industry.

The first impression of the medal was presented to Sir William Henry Perkin himself, and we are now met to make the 11th Annual Award of the medal. It is but natural, therefore, that we should review briefly the awards of the past decade, mentioning, however, only the principal inventions of the respective medalists. You will soon hear details of the work of the eleventh recipient of the Medal, Dr. Ernst Twitchell.

Awarded to	Date of Award	PRINCIPAL FIELDS OR INVENTIONS
Sir W. H. PERKIN	1907	Discoverer of First Aniline Color
J. B. F. HERRESHOFF	1908	{ Metallurgy { Contact Sulfuric Acid
ARNO BEHR	1909	{ Corn Products Industry
E. G. ACHESON	1910	{ Carborundum
CHARLES M. HALL	1911	{ Artificial Graphite
HERMAN FRASCH	1912	{ Metallurgical Aluminum
JAMES GAYLEY	1913	{ Desulfuring Oil and { Subterranean Sulfur Industry
JOHN W. HYATT	1914	{ Dry Air Blast { Celluloid and Flexible Roller Bearings
EDWARD WESTON	1915	{ Electrical Measurements { Electro-deposition of metals { Flaming Arc
L. H. BAERKELAND	1916	{ Velox Photo Print paper { Bakelite and Synthetic Resins { Caustic Soda Industry

Although we are a relatively young nation, we have certainly furnished our full share of inventions, as may be seen from the following list of epoch-making inventions by people of the United States during the last fifty years.

INVENTIONS BY PEOPLE OF THE U. S. DURING THE LAST FIFTY YEARS (Taken from the National Geographical Magazine)

INVENTION	INVENTOR	DATE
Air Brake.....	Westinghouse.....	1869
Celluloid.....	Hyatt.....	1870
Wet Machine.....	Goodyear.....	1871
Block Signals for Railways.....	Robinson.....	1872
Automatic Car-coupler.....	Janney.....	1873
Water Gas.....	Low.....	1875
Machine for Making Barbed Wire.....	Clidden.....	1875
Telephone.....	Bell.....	1876
Typewriter.....	Sholes.....	1878
Talking Machine.....	Edison.....	1878
Electric Lamp.....	Brush.....	1879
Automatic Knot-tying Harvester Machine.....	Appley.....	1880
Incandescent Lamp.....	Edison.....	1880
Buttonhole Sewing Machine.....	Reece.....	1881
Chain-stitch Shoe-sewing Machine.....	French & Myers.....	1881
Chrome Tanning.....	Schulz.....	1884
Trolley Car.....	Van Depoele & Sprague.....	1884-7
Type-bar Casting.....	Mergenthaler.....	1885
Electric Furnace Reduction.....	Cowles.....	1885
Cash Register.....	Patterson.....	1885
Rotary Converter.....	Bradley.....	1887
Single-type Composing Machine.....	Lanston.....	1887
Split-phase Induction Motor.....	Tesla.....	1887
Transparent Photograph Film.....	Eastman.....	1888
Calcium Carbide.....	Wilson.....	1888
Continuous-process Match Machine.....	Beecher.....	1888
Recording Adding Machine.....	Burroughs.....	1888
Electric Welding.....	Thomson.....	1889
Electrolytic Alkali Production.....	Castner.....	1890
Harveyed Armor Plate.....	Harvey.....	1891
Carborundum.....	Acheson.....	1891
Motion-picture Machine.....	Edison.....	1893
Dry Air Process for Blast Furnace.....	Gayley.....	1894
Artificial Graphite.....	Acheson.....	1896
Disk Flows (modern type).....	Hardy.....	1896
High-speed Steel.....	Taylor & White.....	1901

It is interesting to note that many of these inventions are chemical inventions, and that four of them have been recognized by the award of the Perkin Medal. The list of course is not complete, for there are missing among others, the aeroplane and submarine boat, which are American inventions.

As compared with the above list, note the following list of important inventions that have been made during the same period by foreigners:

INVENTIONS BY FOREIGNERS DURING THE LAST FIFTY YEARS (Compiled from information furnished by the 43 examining divisions of the Patent Office)

INVENTION	INVENTOR	NATIONALITY	DATE
Dynamite.....	Nobel.....	Swedish.....	1867
Artificial Alizarine (dye).....	Graebe & Lieberman.....	German.....	1869
Siphon Recorder.....	Thompson.....	English.....	1874
Gas Engine: Otto Cycle.....	Otto.....	German.....	1877
Centrifugal Creamer.....	De Laval.....	Swedish.....	1880
Electric Transformer.....	Gaulard & Gibbs.....	English.....	1883
Manganese Steel.....	Hadfield.....	English.....	1884
Smokeless Powder.....	Vielle.....	French.....	1886
Cyanide Metal Extraction Process.....	Arthur & De Forrest.....	English.....	1888
Mantle Burner.....	Weissbach.....	Austrian.....	1890
By-product Coke Oven.....	Hoffman.....	Austrian.....	1893
Diesel Oil Motor.....	Diesel.....	German.....	1900
Wireless Telegraphy.....	Marconi.....	Italian.....	1900
Electric Steel.....	Héroult.....	French.....	1900

The eleventh presentation of the Perkin Medal will now be made by one we all love, revere and honor. Although a little tardily, we extend to him our heartiest congratulations on the eightieth anniversary of his birth, with the assurance that if it

were within our power, no one else would ever present the Perkin Medal. I have the pleasure of presenting, rather than introducing, the Dean of the American chemical profession, Professor Charles Frederick Chandler.

NATIONAL GUM AND MICA COMPANY
NEW YORK CITY

PRESENTATION ADDRESS

By C. F. CHANDLER

MR. CHAIRMAN AND BROTHER CHEMISTS:

It is my privilege and very pleasant duty as Senior Past President of the Society of Chemical Industry, residing in this country,

to present to Ernst Twitchell, B.S. and D.Sc., the eleventh impression of the Perkin Medal, in recognition of his most original and valuable work in Applied Chemistry.

Dr. Twitchell was born in Cincinnati, on February 26, 1863. He graduated in 1886 from the University of Cincinnati with the degree of B.S., and in 1915 received from his *alma mater* the honorary degree of Doctor of Science. On his graduation in 1886, he was appointed chemist to the Emery Candle Co., of Cincinnati, and has been connected with that firm ever since.

At present he is Chemical Director to the Emery Candle Company, President of the American Oil Treating and Hardening Company, and Chairman of the Board of Directors of the Twitchell Process Company.

Dr. Twitchell has devoted the past thirty years chiefly to the chemistry of fats. His investigations and discoveries have been given to the chemical world in the form of articles in various chemical journals and in letters patent of the United States and other countries.

In 1891 he published his method for the determination of rosin in the fatty acids of soap. The method is based on the fact, observed by him, that the fatty acids, when dissolved in absolute alcohol, are readily and completely converted into ethyl esters by the action of dry hydrochloric acid gas which, absorbing the water set free, acts to reduce the reaction. On the other hand the rosin acids, under the same treatment, remain unchanged, and may be determined volumetrically with standard alkali solution, or gravimetrically.

Lewkowitch, in his comprehensive work on "Oils, Fats and Waxes," remarks: "Of all the methods for determining rosin acid in the presence of fatty acids, the Twitchell method gives the best results."

Dr. Twitchell's most important contributions to Industrial Chemistry involve new and improved methods for the hydrolysis of oils and fats for the production of the free fatty acids and glycerin. These methods have very largely superseded the old methods such as that of Chevreul and Gay-Lussac (in 1825), who saponified in open kettles with alkali. This process was improved by Milly in 1831, who substituted milk of lime for alkali, and later by conducting the saponification in closed vessels, under pressure, reduced the amount of lime required from 14 per cent of the fat to as low as 2 per cent. Then came the process of Dubrunfaut, first applied practically in 1842 by Jones and Wilson, in which the fat was saponified by sulfuric

acid, and the fatty acids subjected to distillation.

Wilson and Gwynne later applied the discoveries of Bertholet and Melsens in a process in which the fat was decomposed by superheated steam and subsequent distillation, which was practiced at the works of the Pricis Candle Co., Battersea. Finally in 1854, Tilghmann introduced his process in which the fat, emulsified in water, was forced through a coil at a temperature of 320° C. Marix found that by adding a little calcium or magnesium carbonate to the water, the temperature and pressure could be very materially reduced to as low as even 3 to 5 atmospheres.

The art of saponifying the fats had reached this stage of development when Dr. Twitchell made an entirely new departure by the application of new reagents, which by acting as catalyzers, even when used in such small proportions such as 1 to 2 per cent, are able to saponify the fats completely. The operation may be conducted by simply boiling the fat with water and the proper quantity of the saponifier. The agents first employed by Dr. Twitchell were the sulfonates of the fatty acids, such as sodium stearate and

sulfo-oleic acid, etc. Later Dr. Twitchell found that by introducing an aromatic sulfonic acid into the solution a much more satisfactory catalytic action could be brought about. Such aromatic sulfonates as are furnished by benzene, phenol, and naphthalene are successful in effecting saponification and being a former catalyst.

The aromatic sulfonates may also be used in a different manner, catalyzing saponification, etc., may be produced in a dry condition, to be used with a suitable proportion of water, and so be readily used to make these esters.

It would now be most desirable to have a list of these



ERNST TWITCHELL, PERKIN MEDALIST, 1916

DR. TWITCHELL'S U. S. PATENTS

March	29, 1908	601,603	Process of Decomposing Fats or Oils into Fatty Acids and Glycerin.
July	11, 1909	628,503	Fatty Aromatic Sulfo Compound and Process of Making Same.
January	19, 1907	844,426	Process of Effecting a Combination between Selected Members of the Alcohols and Fatty Acid.
April	20, 1909	918,612	Process of Separating Liquid from Solid Fatty Acids.
December	30, 1913	1,082,662	Process of Manufacturing Fatty Acids and Glycerin.
February	1, 1915	1,170,468	Sulfo-Fatty-Aromatic Acid Salt.

interesting inventions and improvements made by Dr. Twitchell, but inasmuch as you are to hear from the Doctor himself, and also from Dr. Langmuir and Dr. Ittner on the subject, I will limit myself to the following statements:

The Twitchell process has made possible the large scale saponification of fats for the production of crude glycerin free from salt and of fatty acids for direct combination with soda so as to make soap instead of using the more expensive caustic lye on the neutral fat.

Low-grade fats, such as garbage grease, cottonseed oil foods, etc. were formerly with difficulty used in the soap or candle industry. Such materials can now be readily worked up by the Twitchell process, the fatty acids being distilled to remove color before use. This releases a large quantity of the higher grade fats for use as food products.

The bulk of the soap used in Belgium, Holland, Germany and Scandinavia is said to be prepared from fatty acids direct, and 75 per cent of these acids are made by the Twitchell method. Millions of pounds of fats are saponified yearly in the United States by this process, and practically all of the larger soap factories have Twitchell plants.

All of the recent books in German and English on the soap and fat industries discuss the Twitchell process in full.

DR. TWITCHELL'S PUBLICATIONS

"The Determination of Rosin in Its Mixtures with Fatty Acids," *J. Anal. and App. Chem.*, Vol. 5 (July, 1891).

"The Separation of Solid and Liquid Fatty Acids," *Journal of the American Chemical Society*, Vol. 17 (April, 1895).

"Sulfuric Acid as a Reagent in the Analysis of Fatty Acids," *Journal of the Society of Chemical Industry*, Vol. 16 (December, 1897).

"Benzene-Stearo-Sulfonic Acid and Other Sulfonic Acids Containing the Stearic Radical," *Journal of the American Chemical Society*, Vol. 17 (January, 1900).

"A Reagent in the Chemistry of Fats," *Journal of the American Chemical Society*, Vol. 28 (February, 1906); Vol. 29 (April, 1907).

"The Melting and Solidifying Points of Mixtures of Fatty Acids, and the Use of These Points to Determine the Composition of Such Mixtures," *Journal of Industrial and Engineering Chemistry*, Vol. 6 (July, 1914).

"Unsaponifiable Matter in Greases," *Journal of Industrial and Engineering Chemistry*, Vol. 7 (March, 1915).

CONFERRING THE MEDAL

ERNST TWITCHELL, BACHELOR OF SCIENCE AND DOCTOR OF SCIENCE;

It gives me the greatest pleasure, as the representative of the Affiliated Chemical and Electrochemical Societies of America, to place in your hands this beautiful Perkin Medal, as a token of the appreciation and affection of your fellow chemists.

COLUMBIA UNIVERSITY
NEW YORK CITY

ADDRESS OF ACCEPTANCE

By ERNST TWITCHELL

The first suggestion which led to my discovery of a special catalyst for hydrolyzing fats came to me in studying the so-called *Acidification Process*. This was one of the oldest methods used in candle factories for separating glycerol from fatty acids. It consisted in treating the fat at a fairly high temperature, over 100° C., with a small amount of concentrated sulfuric acid; 4 per cent or considerably less could be used; the product was then boiled with an excess of water. The result is a layer of fatty acids floating on the acid water containing the glycerol.

This reaction could not be explained by the assumption that there is a combination of sulfuric acid with the fat or fatty acid and glycerol, which decomposes during the subsequent operation of boiling with water, because there was not enough sul-

furic acid to combine with all of the fat. I have seen various theories given to explain the Acidification Process, some quite absurd. For instance, in one text-book it is stated that fats consist of minute globules surrounded by membranes and that the function of the sulfuric acid is simply to char and destroy these membranes, leaving the fat in a condition to be hydrolyzed by water at 100°. Another theory I have frequently seen even in recent articles, is that compounds are formed which cause the fat to emulsify with water, and the idea evidently is that if a good enough emulsion is obtained, hydrolysis will take place even at 100°. I have seen this theory given to account for the action of my hydrolyzing reagent. As a matter of fact, fats do not hydrolyze at 100°, practically speaking, with water alone, even though they may be perfectly emulsified. At higher temperatures than 100°, and under pressure, hydrolysis takes place, as is illustrated in the autoclave process of separating glycerol.

In the course of practical experiments with the Acidification Process I found that I could reduce the amount of sulfuric acid used very considerably and yet obtain complete decomposition; but often the boiling with water had to be decidedly prolonged. It seemed clear that there was some catalytic agent which caused the reaction between the fat and the water in this process of boiling, and it would naturally occur to any one that this catalyst was probably some sulfur compound produced by the action of sulfuric acid on fat. I found that compounds of this nature could be roughly separated from the fat which contained them by treating with petroleum ether in which they were insoluble. They could be further purified by solution in ether and extraction with water and were easily identified as sulfonic acids by their acidity, the formation of potassium sulfate on fusion with caustic potash, and other characteristics.

It occurred to me to prepare this catalyst outside of the body of the fat, thus avoiding the action of the sulfuric acid in forming with the fat undesirable compounds, in charring, discoloring, and partially destroying it.

As these sulfonic acids were probably produced by the action of the sulfuric acid on the oleic acid constituent of the fat, I first studied the results of the action of sulfuric acid on pure oleic acid under various conditions of temperature, quantity, etc.

The action of sulfuric acid on oleic acid at low temperatures, as was known, produces a compound of sulfuric acid, stearo-sulfuric acid, an acid sulfuric ester. This was not the catalyst that I was seeking. It very probably has all the properties of a catalyst for the hydrolysis of fats except one; it is decomposed on boiling with water, and as the hydrolysis of a fat hardly takes place at all under any circumstances at a lower temperature than 100°, it is plain that this compound would not serve my purpose.

The compounds obtained on treating oleic acid with sulfuric acid at a temperature of 100° or over are not sulfuric acid compounds but are true sulfonic acids. The principal one seemed to be derived from two molecules of oleic acid and contained one sulfonic acid group and one carboxyl group.

I have never seen this sulfonic acid described, but believe that I had in my hands a fairly pure compound of the composition $C_{17}H_{34}(SO_3H)COO.C_{17}H_{33}COOH$. This was my first hydrolyzing reagent or "Saponifier." But as it was difficult to prepare commercially in fair yield and of any degree of purity, I dropped further investigation along this line on the accidental discovery of the fatty aromatic sulfonic acids, described in the *Journal of the American Chemical Society*, January, 1900.

In this research the most important question was: What properties must a substance have to act as a catalyzer to accelerate the hydrolysis of fats? My views on this subject I have partially expressed in my paper, "A Reagent in the Chemistry of Fats,"¹ where I say that it must be a strong acid, one dissociated strongly in water giving a considerable concentration of hydrogen ions, and then it must be soluble in both fat and water and cause the one to dissolve in the other.

The only bodies that I can at present conceive to have the desired properties are sulfonic acids containing higher fatty radicals. They have the physical character of fats or oils, yet are soluble in water forming soapy solutions, and are strong acids.

As I have said, the discovery of the fatty aromatic sulfonic acids was made by accident. I had a mixture of oleic acid and benzene which I treated with an excess of sulfuric acid and then poured the mass into water. I was not surprised to find an oily layer floating on the acid water, and when I found this oil to be soluble in pure water, that also did not surprise me, as I supposed I had simply stearosulfuric acid; but when I found that after boiling for half an hour with water it still remained soluble, I felt sure that I had a sulfonic acid, and the analysis of the product confirmed my conclusion. This is the compound which has been put to practical use in the separation of glycerol and fatty acids. Instead of benzene, naphthalene is used with oleic acid in the manufacture of the commercial article. This "Saponifier," when added in the proportion of half a per cent or less to fat boiling with water in an open tank, will cause the separation of the glycerol.

Besides the compound containing the stearic radicals and a sulfonic group, the first which I found to have the catalytic property, and the fatty aromatic sulfonic acids, I have also prepared hydrolyzing reagents by treating oleic acid at 200-220° C. with sulfur, or in the cold with sulfur chloride (S_2Cl_2), and then oxidizing with nitric acid, potassium permanganate, bromine, or other oxidizing agent. The resulting compound contained one sulfonic and one carboxyl group and its molecular weight and other properties showed it to be a sulfonic acid of the stearic radical.

Belonging to this class of substances is a compound, cetyl sulfonic acid, described by A. Reyckler two or three years ago. When I saw this description I was sure that it was also a catalyzer of the same type as my reagent, although Reyckler does not mention this as one of its properties.

As this is a typical compound, it may be interesting to describe how it was prepared, partly following directions given in Reyckler's paper. Cetyl alcohol, prepared by saponifying spermaceti with caustic potash and extracting the soap with petroleum ether, was converted into the iodide by dropping iodine into a heated mixture of the alcohol and red phosphorus. This iodide, after purification, was converted into the sulphydrate by treating with alcoholic potassium sulphydrate and the cetyl sulphydrate converted into cetyl sulfonic acid by oxidizing with potassium permanganate, the excess of which was reduced with sodium sulfite. The cetyl sulfonates could be freed from most of the foreign matter by taking up with hot water from which sodium cetyl sulfonate crystallized on cooling. This was dried, extracted with petroleum ether, then dissolved in water and treated with hydrochloric acid. The salted out cetyl sulfonic acid was dissolved in ether and remained in a nearly pure state as a residue on evaporating the ether. It can be further purified by crystallizing its sodium salt from dilute alcohol and there can be no doubt of its composition. It is a simple sulfonic acid of a hydrocarbon of the paraffine series.

Reyckler explains some peculiar properties of this compound in this way: "the sulfonic radical tends to make it very soluble in water, while the long hydrocarbon chain has just the reverse effect. The result is that it forms colloidal solutions." Fahnson,

in reviewing Reyckler's article, calls the cetyl sulfonic acid, "Reyckler's hydrogen soap" and that term, *hydrogen soap*, is as good a definition as I can think of to cover the whole group of compounds which catalytically induce hydrolysis of fats on the principle of my discovery. An alkaline soap plus hydrogen ions would no doubt have the same effect if it were possible to have such a combination.

Besides its use in hydrolyzing fats, my catalytic agent has been applied to other less important ones. A catalyst, which would accelerate the hydrolysis of an ester in the presence of an excess of water, would also accelerate the esterification of a fatty acid and an alcohol on the removal of the water formed. Fatty acids can be made to combine with glycerol and other alcohols of high boiling point by simply treating a mixture of the two with a small quantity of the reagent and evaporating the water formed at 100° C.

The solubility of sulfo-fatty acids in both fat and water leads to a method of separating solid and liquid fatty acids of which I have made some application. If a small quantity of the sulfonic reagent is dissolved in melted mixed fatty acids and the mixture allowed to cool, the solid acids will crystallize out pure and the liquid acids will contain the sulfo-fatty acids, being thus rendered slightly soluble in water, and on treating with water, can be washed out from the mixture, partly in solution but mainly as an emulsion.

Patents have recently been obtained by Grigory Petroff of Russia on a reagent obtained as a by-product in refining petroleum with fuming sulfuric acid. This is a sulfonic acid of hydrocarbon radicals, probably not of the paraffine series. It is a very efficient catalyzer in the hydrolysis of fats, for which purpose it is now largely used.

WYOMING, OHIO

THE TWITCHELL PROCESS AND THE GLYCERINE TRADE

BY A. C. LANSBURY

Some years ago a manufacturer asked my assistance in developing a chemical process. He wanted a process which would "cost nothing to work, would take nothing out of the product and would put nothing in." This man had heard nothing of catalytic methods, but his conception of the ideal chemical process which he was requiring corresponded closely to the modern catalytic methods such as the platinum contact process for the manufacture of sulfuric acid, which costs nothing to operate, once the contact mass is prepared, and which brings about the combination of sulfur dioxide and oxygen without adding an impurity which must be subsequently taken out and without removing something, which would lower the yield.

The Twitchell catalytic process goes far toward meeting this ideal in the saponification or breaking up of fats and oils into their constituents—glycerine and fatty acids. Twitchell's invention, U. S. Patent 661,000, July 17, 1897, was made at a time when catalysis was not the universal subject of attention it is to-day. The Badische process for the catalytic production of sulfuric acid had not been published and catalysis was a new thing in chemical industry.

Twitchell's work has been characterized by a sound appreciation of the work of physical and organic chemists and by analytical and technical methods, have been worked out, not remarkably, but from theoretical premises. That the Twitchell method for the determination of saponification numbers with fatty acids, as in soap analysis, rests upon the principle of the esterification of the fatty acids, when treated with hydrochloric acid and in presence of absolute alcohol and his discovery that when made when so treated, soaps, in combination with the alcohol and water subsequently be separated as pure glycerol. Additionally, provided in use, this method gives a basis for the most accurate means for the determination of saponification numbers of fatty acids.

Again in use, we find him bringing out a method for the

¹J. Am. Chem. Soc. 39 (1916): 196.

separation of saturated and unsaturated fatty acids based upon the solubility of fatty acids with double bonds, such as oleic acid, in concentrated sulfuric acid at ordinary temperatures with the formation of sulfo-fatty acids soluble in water; the saturated fatty acids such as stearic acid are unacted on. In 1914 Twitchell makes use of the principle of the equal depression of the freezing point for equal molecular proportions and determines the composition of mixtures of fatty acids by the observation of the freezing point in the Beckmann apparatus. To test whether a given sample of fatty acid is identical with a fatty acid of known character he adopts the novel plan of adding a portion of the known acid and noting whether there is any change in the melting point of the mixture.

Possibly his investigation of the action of concentrated sulfuric acid on fatty acids led to his discovery of the catalytic action of these sulfo-fatty acids in bringing about the decomposition of fats by water, as little as 0.5 per cent splitting up the fats almost completely on digestion with water.

The prevailing method for the manufacture of soap consists in the saponification of the fat by boiling with caustic soda lye. The fatty acids combine with the soda as soap, which is separated by the addition of salt and comes to the surface in the molten condition. The glycerine is set free and remains dissolved in the spent lye. It is contaminated by the presence of the salt used to render the soap insoluble. During the concentration of the spent lye for the recovery of the glycerine a large quantity of salt is thrown out, making the evaporation somewhat difficult, although this difficulty has been largely eliminated of late years by the use of properly designed evaporators working *in vacuo*. The final crude glycerine is a saturated solution of sodium chloride and some sulfate together with sodium salts of the lower fatty acids in glycerine and water. The crude averages about 80 per cent glycerine and contains about 10 per cent mineral salts.

The glycerine refiner distills this crude soap lye glycerine with superheated steam *in vacuo* for the production of dynamite glycerine and chemically pure glycerine. The presence of so large a quantity of salt raises the boiling point of the glycerine and reduces its vapor tension so that the output is reduced. Furthermore, the salt accumulates in the still, producing finally a semi-solid mass of salt and glycerine together with tarry matter which constitutes the "foots" of the glycerine trade. It is a difficult matter to extract all the glycerine from this residue without undue loss. The treatment of the "foots" is one of the problems of the glycerine trade.

The glycerine distiller therefore prefers a crude glycerine which is free from this large admixture of salt. Up to the early nineties all the crude glycerine refined consisted of what is termed "saponification" or "candle crude." It was the by-product of the candle factory and was produced by the breaking up of fat in autoclaves by heating under pressures of 200 lbs. and more with water and a little lime. The fat was split into fatty acids and glycerine directly and the latter was a product of considerable purity, containing about 88 per cent glycerine and less than 1.0 per cent of mineral matter. With the greatly increased demand for glycerine for explosives, the soap makers, who formerly discarded their spent lyes, found it profitable to work them up and to-day scarcely a soap plant can be found that does not recover its glycerine as a by-product. This change in the business compelled refiners to develop methods for distilling soap lye crude glycerine and eventually the larger refiners were working mainly on soap lye rather than candle crudes although there were still a number of glycerine refiners who worked exclusively on candle crudes. Saponification crudes free from salt have always been in greater demand and have commanded a higher price per unit of glycerine. For several years before the advent of the Twitchell process it looked as if saponification glycerines would practically disappear as

a raw material in glycerine refining, but with the success of this process, the Twitchell saponification crudes made their appearance and are now a factor of very considerable importance.

The ideal of the glycerine refiner has thus been the production of a saponification rather than a soap lye crude by the soap manufacturer. It has also been the hope of the soap trade to obtain directly by the deglycerinizing of the fat a relatively pure glycerine as a by-product and free fatty acids which could be combined with the cheap alkali, carbonate of soda, to make soap instead of the relatively expensive caustic soda. To meet this need have been developed the Twitchell process, the Krebitz lime saponification method and the Connstein ferment process.

The Twitchell process is characterized by its simplicity, and the low cost of the plant. Prior to Twitchell's discovery free fatty acids could be obtained only by the autoclave process, involving a heavy capital outlay for copper apparatus, which could be used only in small units and at a high temperature and pressure, making the operation expensive and somewhat dangerous. The autoclave saponification was used only in the preparation of fatty acids for candle manufacture as the process was too costly to be used in the production of fatty acids to be used in soap. The Twitchell process is effected in loosely closed wooden tanks by digestion with water and as little as 0.5 per cent of the reagent and at a temperature not exceeding that of exhaust steam. The reaction may be carried out on a scale limited only by the size of the tank. The Twitchell process has made possible the saponification of fats on a huge scale for the direct production of free fatty acids and saponification glycerine. When combined with the distillation of the fatty acids for the improvement of their purity and color it has opened up for the soap trade the use of low-grade fats such as garbage grease and cottonseed oil foots, the distilled fatty acids being combined directly with carbonate of soda to produce light colored soaps, and the glycerine being made available for the manufacture of dynamite glycerine. In this way the Twitchell process has benefited the glycerine trade in these days of glycerine scarcity by opening up new sources of supply which were previously unavailable.

In Germany, Austria, Belgium, Holland and Scandinavia the larger soap plants prepare soap from fatty acids directly and it is stated that in most of them the Twitchell process is used for the saponification of the fats.

The crude glycerine prepared by the Twitchell process comes to us from all parts of the world in normal times. There is no evidence that it is any less pure than the saponification glycerines prepared by other processes provided the fat used as a raw material is reasonably pure. Of course a crude glycerine manufactured from a low-grade fat will fall behind a crude made from good tallow, but this is the fault of the fat and not of the Twitchell process.

9 VAN BRUNT STREET
BROOKLYN, NEW YORK

THE TWITCHELL PROCESS IN THE SOAP AND CANDLE INDUSTRY

BY MARTIN H. TENCER

It is essential in the candle industry to have a satisfactory method for separating the fatty acids, as such, from fats and oils. In the soap industry such a method, although it may be considered highly desirable, is not absolutely essential since very satisfactory methods of direct saponification by alkali with the formation of soaps have long been utilized.

In recent years there has been an ever increasing demand for fats and oils and for glycerine, resulting in greatly increased market prices for these articles. The market for soap and candle materials is directly related to the market for fats and oils for edible purposes, and an increased demand from either source usually results in higher prices for all fatty materials.

High costs of fatty materials have made the practice of economy in the soap business essential. This economy may manifest itself in several ways. We will assume at the outset that the soap manufacturer wishes to maintain the quality of his products and therefore does not wish to make any sacrifice in this direction. His economy must therefore direct itself in one of the following directions. He must be able to utilize the fats and oils which give the greatest soap-making value at the lowest cost per unit, whether these materials are of the better, or of the poorer grades, and he must so utilize his raw material that his final product will be of the same high quality no matter which grade is used. This means that he must have a method for getting good results out of poor material when poor material gives him the greatest value. It is also essential that he have some method whereby he may realize the maximum yield of glycerine at a low expense for recovery. This will readily be understood when I explain that at present market prices for fats and glycerine, which are both abnormally high, the value of the glycerine which can be obtained from one pound of neutral fat is about one-third of the cost of the fat. Another possible way of economizing is by quicker and easier methods of manufacture.

All of these advantages have been realized in some degree by the advent of the Twitchell Process. This process has given a quick and easy method of obtaining fatty acids and glycerine from the better grades of fats so that the fatty acids are at once ready for making into better grades of soap, and the glycerine is in a condition suitable for easy refining. With care of operation the yield of glycerine may be made to approximate closely that theoretically obtainable. When one operates on fats of poorer quality, and this may include black greases, the Twitchell process furnishes a most satisfactory method for saponifying. It renders the glycerine available even from such material and gives acids in good condition for refining by means of distillation. Such acids when carefully distilled yield a product of light color suitable for making good soaps of light color.

The use of fatty acid as such, has made it practicable to use soda ash very largely in the place of caustic soda. The former will combine direct with fatty acids making soap from which the glycerine has already been recovered, whereas caustic soda is necessary for the direct saponification of fats into soap, and tedious methods must be used for recovering the glycerine, and, except with the greatest care, the yields will be poor. It will thus be seen that in the use of fatty acids a saving may be effected even in the alkali employed, as soda ash is considerably cheaper than caustic soda per unit of alkali.

Fatty acids suitable for making into soaps are also suitable for making into candle material. Partial-solidification on cooling, will, with the aid of pressing, separate the solid from the liquid acids. The former yields commercial stearic acid so extensively used in candle manufacture and the liquid portion yields the oleic acid, or red oil of commerce. Red oil is used for many purposes, one of the most important being in the manufacture of soaps for washing wool. The manufacture of stearic acid and red oil did not originate with the Twitchell process, but the advent of the Twitchell process gave a new and satisfactory method for the saponification of fatty materials at atmospheric pressure with advantages over methods formerly used. Saponification by means of the Twitchell process may be carried out on a larger scale, with less danger and with greater ease than is obtainable by other methods of acid saponification.

Twitchell's first process in which he recommended the use of sulfonaphthene acid was soon very much improved by the use of naphthalene along with the oleic acid during sulfonation. Whatever the chemical action in the formation of this reagent, it is my observation based on many experiments that satisfactory saponification will result from saponifier made as Twitchell recommends, whereas, poor results only are obtainable when separate sulfonation and subsequent mixing are tried. I may

say that I was among the first to have an opportunity to become acquainted with the process, and that this acquaintance has become closer with added years.

This process has been put to extensive use not only in America but also in European countries.

Twitchell later devoted himself to a method of manufacturing his reagent which would enable him to produce it in a more concentrated form. He accomplished this by methods of washing, extraction, precipitating as an insoluble salt readily convertible into an active reagent, and drying.

Twitchell and others allied with him have been busy in trying to perfect still further the process of atmospheric saponification of fats into fatty acids and glycerine with the result that a new sulfonated reagent with increased efficiency has recently been put upon the market.

The Twitchell process has been so simple in use that one is almost inclined to look upon it as nothing out of the ordinary. On careful thought one is forced to conclude that it is this simplicity, which has become almost commonplace, that commands it most to the many who have become familiar with it in operation.

COLGATE AND COMPANY,
JERSEY CITY, NEW JERSEY

AN APPRECIATION OF DR. TWITCHELL

By H. B. SCHMIDT

Thirty years is a span of life; practically a generation has passed. In these thirty years there has been marked in this country profound changes, unparalleled growth and vast development. The bankers may tell you that the bank deposits have increased maybe ten times in this span of life. The iron people tell us the production of iron has increased about ten times, but what measure of increase can be put upon the developments that increased the chemists' opportunity; how many times—surely hundred-fold at least.

Only a generation ago when the industrial chemist started on a career, what had he before him? Simply the obligation to create an opportunity. As an example, going back to conditions then in Chicago, it was hard work to gather together a dozen men at a meeting. There were two iron and steel chemists, two railroad chemists, two metallurgical chemists, one soap chemist, one packing house chemist, two assayers and two professors.

The audience will get an idea of how inadequate the conception was of what a chemist's work consisted. One day in walking across the Stock Yards in Chicago I was stopped by one of the then partners of what to-day is one of the largest institutions of its kind in this country, who said: What do you do over at Fairbanks? Explaining what the routine duties consisted of, what new things had been taken up by the laboratory, he finally said he did not think his institution could employ a man full time at that kind of work and yet three months after that interview that institution employed its first chemist. I dare say that that institution to-day has at least fifty in its employ.

In Cincinnati the conditions were similar and if we look back on the chemist's equipment and the supply of reagents at that lot of practice with no gas, no electric light, coal oil lamps and gasoline torches to work with, and with a furnace on some severe conditions. I am always amazed when I think of the difficulties of nitric acid determinations at that time compared with the Kjeldahl method of to-day. There was no rapid glass combustion tube and charged furnace and a box to fire the coals. If he failed to find the final time, instead of 15 he did not run hard enough, the acid then was poured and you could not titrate it. I have just such conditions now in my personal quiet studio.

Comparing these meagre facilities with the magnificent equipments that every college laboratory has to-day, reminds me of Dr. Wolcott Gibbs, when one day in his research laboratory the inadequacy of the equipment came up and he said, why—do you know how the great Berzelius got his results? Why, all he had were some bottles, a sink and a cook stove. The present generation hardly realizes the huge advantages it enjoys.

Away out in a field, in a lean-to to a still building, Dr. Twitchell also had to create his opportunities, and there seeds of progress were sown. There were no fixed lines to work on; every step was capable of researches and these had to be made, in order to find the ways in which the chemist could make himself valuable and gradually the structure grew. Twenty-four years ago next July, there was a meeting of the Society of Chemical Industry at Liverpool. One morning while riding on the second story of a tram car, the two-story horse car affair that was a characteristic of English streets, reading the itinerary of the meeting, a party slapped me on the back and said: Are you a chemist? Yes. Oh! he said, you are from the States; where from? Chicago, but expected to go back to Cincinnati to live. Well, he said, Cincinnati—why, do you know Mr. Twitchell? Yes; we went to school together. Well, he said, he has made the best contribution to the chemistry of soaps that I know of. His method of determining the percentage of rosin in a soap is the only method that gives us the means of determining what

a competitor had in his soap and then my party said, here is my card, I am Dr. Lewkowitch and I had the experience of Mr. Twitchell's method in a soap works at Warrington. So our honored guest early in his career had made a valuable contribution to chemistry and was known to every chemist that was in fat and soap lines.

Only a few more years elapsed when Mr. Twitchell was able to announce the working out of the Twitchell Process of Glycerine Recovery. The means employed were so novel that when the German Patent Office was asked to pass upon the patentability of the Twitchell Reagent, they doubted that a compound described by Mr. Twitchell could exist. It is needless for me to dwell on what the process has done. You have heard that told to-night.

Just one more word. The young chemists will appreciate much more what Mr. Twitchell has done. His methods, employed in hundreds of factories throughout the world, have necessitated chemical control of operations and so have afforded just that many more opportunities for the employment of skilled chemists in those works. So what one man has done benefits one hundred or one thousand men through a new opportunity and this is only one example of where the opportunity has grown a hundred-fold.

CINCINNATI, OHIO

CURRENT INDUSTRIAL NEWS

VOLCANIC HEAT HARNESSSED

The idea of utilizing volcanic heat to drive an electric power house of 15,000 h. p. might seem as being out of the realms of possibility, but Prof. Luigi in an interesting article published in *Engineering* for November 17, 1916, shows that this has been realized in Italy. In Central Tuscany, near Volterra, there are numerous cracks in the ground from which powerful jets of very hot steam spout high in the air with great violence and constancy, bringing up boric acid and other mineral substances. These substances were found to have a corrosive effect on the engines in earlier experiments and the difficulty has been overcome by applying the steam, not directly in the engine, but to a boiler instead of fuel. Steam is produced in the boiler and then passed to a superheater after which it is utilized in the steam turbine for driving electric generators.

The undertaking has been financed by Prince Ginori-Conti and three large installations on this system have been made; one, of 3000 kw. units, was started in January, 1916, the second in April, and these seem to be giving satisfactory results. The third system has been started quite recently. These installations are said to be a great boon to the industries of Tuscany, where coal is scarce and very expensive and, since the region available is a large one, it seems likely that the system may be developed in such a way as to produce hundreds of thousands of horse-power.—A. McMILLAN.

RUSSIAN MANGANESE ORE

The Board of Trade, London, is in receipt of a memorandum by a Russian mining engineer dealing with the subject of Russian supplies of manganese ore. The memorandum discusses the manganese ore industry in Russia, the production and exportation of the ore and the market values of the same. Tables are also given showing the production of steel in certain countries and the imports of manganese ore into these countries distinguishing the proportion of ore of Russian origin, etc. It is stated that the output of manganese ore in Russia has increased from 396,324 tons in 1904 to 681,424 tons in 1909 and to 1,255,175 tons in 1913.

ADULTERATION OF COD-LIVER OIL IN NORWAY

According to an article in the *Oil and Color Trade Journal*, 50 (1916), 1815, the oils of exotic fishes used for the adulteration of cod-liver oil by some merchants are mostly those obtained from the so-called "coal-fish," "cusk" and haddock. It is asserted that the Lofoten merchants do not practice adulteration during winter fishing and that the oil then made is extracted exclusively from cods' livers because no other fish is caught at that season there. Chemicals are not used for purposes of adulteration as far as is known, excepting perhaps a very small percentage of sulfuric acid during the steaming process in order to facilitate the extraction of the oil. If cod-liver oil be mixed with oils from the livers of fish akin to the cod (such as mentioned above), the mixture is never more than 10 per cent or less. It is very difficult to prove this adulteration by methods of analysis. Medically pure genuine cod-liver oil is of a bright yellow color with a slight odor only. The adulteration of this oil is said to have started in Norway just about 1900.—M.

ON SOYA-BEAN EXTRACTION BY TRICHLOROETHYLENE

During recent years, says *Nature*, 98, 235, trichloroethylene has been used to a limited extent for the extraction of the oil of soya beans. The residual meal has been disposed of as food for stock and, as trichloroethylene is not poisonous when given in comparatively large doses to cattle, little risk would appear to be involved in the use as food of the extracted meal. Cases of poisoning of cattle attributed to soya meal have, however, been brought to the notice of the Board of Agriculture and the results of their investigations which are summarized in the October number of the *Journal*, throw strong suspicion on the meal obtained by the use of trichloroethylene. The cases of poisoning, both on the farms and in the investigations, were limited entirely to cattle and, in no case, was a sudden effect produced. Experience with soya extracted with naphtha makes it very improbable that the poisonous principle could have been inherent in the meal. It would appear more probable that it was either a non-volatile impurity present in the trichloroethylene, or a product of interaction between the trichloroethylene and some ingredient of the soya beans.—M.

BRITISH DEPARTMENT OF SCIENTIFIC AND INDUSTRIAL RESEARCH

A numerous and influential deputation was received by Lord Crewe on Friday, December 1, in connection with the work which is being done by the Committee for Research appointed some time ago. An important announcement as to the Government policy was made in the following terms: The Government has decided to establish a separate Department of Scientific and Industrial Research for Great Britain and Ireland under the Lord President of Council and with President of the Board of Education as Vice-President. They have also decided, subject to consent of Parliament, to place a large sum of money at the disposal of the new department to be used as a fund for the conducting of research for the benefit of national industries on a coöperative basis. To enable the department to hold the new fund and any other money or property for research purposes, a Royal Charter has been granted to the official members of the Privy Council for Scientific and Industrial Research under the title "The Imperial Trust for the Encouragement of Scientific and Industrial Research." The Trust is empowered to "accept, hold or dispose of money or personal property in furtherance of the objects for which it has been established, including money voted by Parliament."—M.

BRITISH BOARD OF TRADE

During the month of December the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply of the following articles. Firms which may be able to supply information regarding these articles are requested to communicate with the Director, Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.

Advertising novelties such as treasury-note cases
Amethysts, rough
Brushes, paint

CHEMICALS

Fatty acids, especially linseed and palm kernel
Formaldehyde, commercial 40 per cent in barrels
Toluidine
Zinc oxide
Naphthol yellow

CHINA AND EARTHENWARE

General earthenware
Toy china
China marbles
Fancy pottery
Combs, amber
Cork, agglomerated
Dental supplies

DRESS

Cimicifuga
Fengfleck

DYES

Powdered color for soap and confectionery manufacture

GLUES: Adhesive, similar to "Syndetkon"
Gramophone accessories
Kapak for filling cushions
Lemon and egg tints for coloring Italian papers

MACHINERY AND PLANT FOR

Cutting veneer out of blocks
Cutting and perforating toilet paper
Making black bottom paper bags
Cutting fiber for trunks
Cutting and planing whalebone
Making buttons from celluloid, horn, vegetable ivory, and similar composition
Small horizontal three roller mill for crushing lime
Magnets, permanent
Mirrors
Porcelain lining, hard
Push-buttons
Pens, fountain
Paints, dipping paints for paper machine articles
Paint, luminous
Wagons, pedrail

—M.

SANDALWOOD OIL

The action of the Mysore Government has resulted in the price of this indispensable oil being forced up to \$10 per lb and within a month the price may reach \$18. There are hardly any sellers. According to a report in the *Madras Weekly News*, the Mysore Government are preparing to distil the whole of the wood produced and may also, in the near future, take over the supplies from Coorg and Madras. The *Oil and Color Trade Journal*, 50 (1916), 1963, states that the Germans, who had a large share in the industry, have selected a neutral country, Spain, to continue their operations and that Schimmel & Co., Leipzig, are said to have started a factory there and are offering Spanish sandalwood oil at 100 fr. per kg. The report has not been confirmed, but it would seem that representations have been made in the Government as to the prospects of the wood being able to be so treated in Spain in behalf of German interests.—M.

BOLIVIAN MINERAL EXPORTS

The following taken from the report issued by the Minister of Finance to the Bolivian Congress, gives the quantity and value of the mineral exports of Bolivia in 1915 as compared with 1914:

	1914		1915	
	Kilograms	Value	Kilograms	Value
Tin ore.....	37,289,617	\$18,142,168	36,492,358	\$17,056,471
Copper ore.....	4,793,166	1,821,403	17,944,954	3,661,082
Copper bars.....	3,874,272	1,472,223	5,867,844	1,672,335
Wolfram.....	276,316	105,000	792,511	569,181
Lead ore.....	1,554,570	590,736	2,207,753	144,230
Antimony ore.....	186,077	70,709	17,923,048	5,108,068
Bismuth ore.....	437,751	166,345	662,547	1,394,772
Molybdenum ore.....	5,191	7,279

It will be seen that owing to the high price, the value of the exports of tin increased in spite of a decrease in quantity. In 1914 the consuming countries were the United Kingdom, Germany, France and Belgium, but last year new markets were found in the United States, Argentina and Uruguay. The large increase both in the quantity and value of wolfram is due to the war conditions which have caused a demand for tungstic acid in the New York market. The increase in antimony export is continued in the present year. Molybdenum appears in the list for the first time. It is being obtained from the Illampu Range.—M.

BURMESE MYROBALANS AS TANNING MATERIAL

The *Chemical Trade Journal*, 59 (1916), 508, quoting from a report on Burmese myrobalans as a tanning material, which has been drawn up by the chemical adviser to the Forest Research Institute, states that Burmese myrobalans are different from the Indian chebulic myrobalans in points of tanning and non-tanning content and color. In the air-dried Burmese material the tannin varies from 16 to 32 per cent; the general average may be taken to be 20 to 25 per cent, which is about one-half the tanning content of the Indian myrobalans. The non-tanning content ranges from 25 to 34 per cent and the general average may be taken to be 27 to 30 per cent, which is three times that of the Indian myrobalans. The color is high. The maximum red and yellow recorded for the Indian product is 2.5 red and 7.4 yellow while the Burmese myrobalans in general have 4.9 red and 18.35 yellow. The excess of non-tanning material is a disadvantage and all tanning substances having non-tanning constituents in excess must be classed as somewhat inferior, although they give fairly good results. To form some opinion as to actual tanning properties of Burmese myrobalans, experiments were undertaken which disclosed that leather made with this material alone is spongy and tough like the leather produced by the Indian product, that Burmese myrobalans can be used in the preparation of butts for making army boots and shoes and also for making black uppers of inferior quality and, further, that they will be useful in conjunction with babul bark for making sole leather.—M.

JAPANESE LACQUER INDUSTRY

It is reported that a Japanese Lacquer Committee has recently considered measures for promoting the lacquer industry in Japan. The demand for this product in Japan is increasing each year and has attained an annual volume of 1,000,000 lbs. during the last three years. It is estimated that the total requirements of the country will, over some years, amount to 1,500,000 lbs. annually. The Japanese output of lacquer in 1914-15 was valued at about \$4,000,000 and it is expected to be increased after the war. Thirty per cent of the quantity of lacquer consumed in Japan is produced at home, the remainder being imported from China. The Government is now considering making further investigations with a view to promoting the industry in Japan.—M.

OIL PRODUCTION FOR JAPAN

According to the annual report, the production of crude oil in Japan was 3,015,327 barrels in 1915, an increase of 272,807 barrels over that of the preceding year. The following table shows the production by districts in 1915 compared with 1914:

	1915	1914
Toyama.....	1,975,443	2,009,603
Akita.....	1,008,863	706,588
Enshu.....	2,098	2,455
Yokohama.....	471	435
Sagami.....	195	138
Hokkaido.....	9,287	5,987
Japanese Possessions.....	18,970	17,814
Total barrels.....	3,015,327	2,742,520

—M.

WATTLE EXTRACT MANUFACTURE IN NATAL

The manufacture of extract from wattle bark grown in Natal has become an accomplished fact. One firm is already treating 50 tons of green bark daily. A first consignment of extract was recently sent to the United Kingdom. Another company expects to commence work in a few months' time. The utilization for extract of a proportion of the bark grown in Natal will considerably improve the market position of this material. During 1915 the total quantity of wattle bark shipped was 40,027 tons, which, owing to difficulties as to cargo-space, was some 18,000 tons less than in the previous year.—M.

TRANSPORT OF HOT FLUID PITCH FOR BRIQUETTE MAKING

The *Zeitschrift für angewandte Chemie*, 29 (1916), 549, has an article dealing with the transport of hot fluid coal-tar pitch in tank-wagons for briquette making. The factory mentioned is at a Silesian colliery that obtains a supply of pitch direct from a neighboring coal-tar distillery. The pitch is delivered in fluid form and is conveyed in tank-wagons. The system has already been tried at Bochum, where wagons holding 15 tons each are filled direct from the retorts with pitch at 250° C. In this instance, the rail distance is 4 km., the time between filling and emptying is 7 hrs., and the pitch in the fluid state is readily discharged by compressed air. It is intended to work this system in conjunction with the Fohr-Kleinschmidt method of briquetting. The pitch is brought into a mobile condition by heating to 130–170° C. and then sprayed by a steam-heated atomizer worked with steam or compressed air in a mixing drum where the pitch spray solidifies while still in the air to a very fine soot-like dust. It is then passed to the kneading apparatus by suitable transporting arrangements and finally pressed into briquettes at 50 to 80° C. By this process the proportion of pitch in the briquettes is reduced by fully 1 per cent and the costs of manufacture are decreased by the tank-system; the wagons can be emptied in 15 minutes and the necessity of handling, breaking and melting the pitch is avoided.—M.

NEW JAPANESE ANILINE DYE FACTORY

According to *Oil and Color Trade Journal*, 50 (1916), 1903, the Japanese Government having decided to grant state aid to the color industry, an enterprise has now been started in Japan under the title of the Japan Dye Manufacturing Company. As, so far however, no agreement has been come to between this group and the government as to the exact interpretation of subvention law (which fixes the subvention at 8 per cent of the paid up capital), it has not yet been possible even to commence the erection of the factory building. Apparently the project has been carelessly handled and the great difficulties have been disregarded as well as the question whether Japan possesses sufficient experience to enable her to take up this branch of industry and compete successfully with Germany in the dye trade after the war.—M.

ELECTROLYTIC DISINFECTING FLUID

An interesting reference, says the *Chemical Trade Journal*, 59 (1916), 482, to the development of the application of electrolytic disinfecting fluid on board hospital ships is made in the second annual report of the Medical Research Committee. A suitable electrolytic cell, under Dr. Dakin's instructions, has been made by Messrs. Mather and Platt, Manchester, which was found to furnish disinfecting fluid at a cost of less than 6 cents per 100 gallons and could be operated by an unskilled attendant. The first test of the method was made on the "Aquilania" with highly satisfactory results, no significant damage to any of the ship's structure following the free use of the suitably diluted solution. The hypochlorite solution from sea-water was used as a general disinfectant and deodorant and also with good results for the purification of the ship's water and as an antiseptic dressing for infected wounds. It should be mentioned that the saving of expenditure upon carbolic acid and cresol during this experimental trip was estimated to exceed the whole cost of the manufacture and maintenance of the electrolytic cell. In consequence of the results, the War Office has caused the installation to be made in various capacities.—M.

MAGNETO APPARATUS

A method of testing magneto apparatus is described in a recent issue of *La Revue Électrique*. The magneto to be tested is caused to produce sparks between platinum points in an atmosphere of nitrogen enclosed in glass bulbs across which also extends a resistance wire in an independent circuit. The expansion of the enclosed gas due to the heat generated by the sparks is measured by the movement of a mercury column in a U-tube, one end of which opens in the bulb at the bottom. The apparatus is calibrated by means of the resistance wire. The results of experiments are given showing the variation in the energy per spark. This rises to a maximum and then decreases as the speed of rotation is increased.—M.

TURBO-ELECTRIC PROPULSION

In the United Kingdom, says the *Electrician*, 78 (1916), 306, there are two vessels being built to Lloyd's classification in which the Ljungstrom turbo-electric propelling plant will be fitted; one, a single screw vessel in which the power will be 1,500 shaft h. p., and the second, a twin-screw vessel with a total shaft h. p. of 5,400. In the Ljungstrom turbine, there are two stationary blades and the steam passes across two sets of blades which revolve with equal speeds in opposite directions so that the effect is similar to that which would occur with one set of blades stationary and the other set moving at twice the velocity. Each half of the turbine is directly coupled to its own alternator producing a three-phase current of about 50 alternations per second with a voltage of 800. The alternators of each set are electrically locked, ensuring exactly equal speed and consequently equal power on each rotating half of the turbine. In each vessel there will be two turbo-alternator sets so that the stoppage of one will not disable the vessel. The two alternators of each set work in parallel. They have each only one pair of poles and supply current to two motors each having five pairs of poles which will, therefore, rotate at one-fifth the speed of the turbines. These motors are connected to pinions with spiral teeth which gear, in the ordinary way, with a large gear-wheel secured to the screw-shaft. The combination of electrical and mechanical reduction gear will enable a speed of turbine of 3,600 r. p. m. to rotate the screw at 76 r. p. m. The reversing of the screw is effected by the motor, the steam always running in the one direction. Reduction of speed is effected down to about 80 per cent of the fuel speed by varying the steam supply to the turbine and for slower speeds, resistances are interposed in the circuit.—M.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS

The Ninth Annual Meeting of the American Institute of Chemical Engineers was held in New York City, January 10 to 12, 1917, at the Chemists' Club. The attendance was very satisfactory and reached a total of about 100. The meeting was called to order Wednesday morning by First Vice-President G. W. Thompson. President George D. Rosengarten was unable to be present as he is in Florida recuperating from recent illness. The out-of-town members and visitors were welcomed to the club and to New York City by Mr. Ellwood Hendrick with a characteristic cordial address.

The reports of officers and committees were read. The treasurer reported all bills paid and a substantial balance on hand, the financial condition of the Institute being very satisfactory. The Secretary reported a substantial growth of the Institute during the past year, 31 members having been elected, the present membership in the Institute being 250. Volume 8 of the Transactions has been issued during the year, also two bulletins. A report was also read from the Membership Committee with reference to action taken on the applications received during the year and the ballots canvassed.

COMMITTEE REPORTS

Professor James R. Withrow, chairman of the Committee on Chemical Engineering Education, reported that a joint meeting of the Engineering Societies was being arranged to discuss the question of engineering education, under the leadership of Professor Mann.

The Committee on Meetings reported invitations for the next meeting of the Institute from Chicago, St. Louis and Buffalo. By vote of the Institute the meeting in June will be held in Buffalo. The Institute also voted in favor of arranging for a meeting in New York in September, at the time of the Third Chemical Exposition.

The Committee on Patents reported that there was no prospect of improvement in patent laws on account of the urgency of other legislation and war conditions.

The Committee on Catalogs reported that the Chemical Engineering Catalog had been issued by the Chemical Catalog Company during the early fall under the editorial supervision of this committee. This arrangement had proved entirely satisfactory and a very large number of letters had been received from the users of the catalog expressing enthusiastic praise of the work and the great usefulness of the publication.

SOCIAL FEATURES

A subscription banquet was held at the Chemists' Club on Thursday evening. Fifty-nine covers were laid, a considerable number of ladies being in attendance. The after-dinner program was carried out under the direction of Mr. Maximilian Toch as toastmaster who proved to be an exceptionally genial and humorous master of ceremonies. The Secretary of the Institute, Dr. John C. Olsen, was first introduced and spoke on the Institute. He stated that one of the most important achievements of the Institute was the drafting of the Code of Ethics. Dr. Olsen thinks that the influence of the Institute could be of the greatest value in bringing about cooperation between the chemical industries which would be very essential in order to meet conditions following the war. Mr. Ellwood Hendrick responded to a toast entitled "Chemical Credit," and explained the methods by which chemical industries are financed. Dr. Leo H. Baekeland spoke on qualitative and quantitative thinking and showed how very erroneous conclusions are reached, especially by politicians, by drawing quantitative conclusions from qualitative statements. Dr. Chas. Baskerville responded to a toast upon education. He pointed out the great necessity of expansion of educational facilities to meet the increasing

demand of the industries for trained technical men, and emphasized the great difficulty under which the great educational institutions rest in securing adequate funds not only for expansion, but for the very necessary increase in salaries of the instruction staff. He, therefore, urged the cooperation of the industries with the educational institutions to remedy these conditions. President-elect G. W. Thompson responded to the toast, "The New Administration," and stated that the policy of this administration will be the rendering of service to the members of the Institute in every possible way, and the increasing of acquaintanceship and mutual helpfulness among members.

The Smoker was held at the Chemists' Club on January 10th. Mr. Theodore Bamberg was the entertainer who performed a great many very mysterious tricks after explaining fully how they were carried out, in spite of which the jugglery was as mysterious as ever.

A program for the ladies had been arranged under the chairmanship of Mrs. Maximilian Toch. This program included welcome to the visiting ladies at the Chemists' Club under the leadership of Mrs. H. R. Moody; a theatre party at the Hippodrome, chairman, Mrs. Frank Hemingway; musical afternoon at the National Opera Club of America, chairman, Mrs. Leo Baekeland; automobile trip to Metropolitan Museum of Art, chairman, Mrs. J. M. Matthews and Mrs. P. C. McIlhenny; luncheon at the Plaza Hotel, chairman, Mrs. D. L. Davoll; tea at the residence of Dr. and Mrs. Charles F. Chandler; a theatre party at the Strand, chairman, Mrs. Chas. Baskerville. The ladies also attended the subscription dinner at the Chemists' Club on Thursday evening.

PAPERS

Unpreparedness. By GEORGE D. ROSENGARTEN. This paper called attention to the urgent necessity for providing an ample supply of raw materials as cannot be obtained in the United States. [This paper appears in full below.]

Recent Developments in Chemical Engineering Equipment. By H. D. MILES, President of the Buffalo Foundry and Machine Company. [See THIS JOURNAL, page 161.]

Corrosion of Pure Iron Containing Cobalt, Nickel or Copper. By HERBERT T. KALMUS and K. B. BLAKE. In the absence of the authors, this paper was presented in the form of preprints. Extended criticism was made by Dr. A. S. Cushman because the test pieces used were so small that the conclusions reached were not in his opinion justified. [This paper appears in full in this issue, pp. 123-136.]

The Fixation of Nitrogen. By JOHN E. BUCHER. No formal paper had been prepared on this subject but an extended discussion of his methods and results was given by Prof. Bucher who described his experiments carried out at Providence, R. I. [Prof. Bucher is now working up a paper for THIS JOURNAL which he expects to complete in time for publication in the March issue.]

The Effect of Centrifugal Force on Colloidal Solutions. By EDWARD E. AYERS, JR., of the Staphylo-Specific Company. The theory of separation of small particles by centrifugal force was developed and the relation between molecular weight, concentration of the solution, and centrifugal force, and the time required for separation were described. The effect of centrifuging those at present employed in process from the point of view of the upper centrifuge, which is connected with the lower one, was shown.

Recent Developments in the Absorption and Distillation of Volatile Liquids. By GEORGE E. COOPER, of the C. O. Leitch & Son Company. Certain new ideas in which the

number of fractionations required for separating two given liquids can be determined. Numerous lantern slides of installations were also shown.

The Human Side of the Development of Chemical Industries. By G. W. THOMPSON. This paper emphasized the importance of a study of the operating force of chemical industries and adapting processes to the character of the labor available. [See This JOURNAL, pp. 181-186.]

The Recovery of Benzol from Coke Oven and Illuminating Gas. By F. W. SPEER, JR., of the H. Koppers Company. The methods in use for the recovery of benzol were described and installations shown by means of lantern slides.

The Fairlie Method of Control for the Chamber Process of Making Sulfuric Acid. By ANDREW M. FAIRLIE. This process, which is patented, consists of the determination of the sulfur dioxide content of the gas before entering and after leaving the acid chamber.

EXCURSIONS

Davis-Bournonville Co., Jersey City. Great interest was shown in the methods which have been developed for accurate following of tracings in cutting sheet steel, also in the demonstration of cutting a 9-in. steel bar which was cut through in about 4 minutes: this is the maximum thickness which can be cut through by the oxyacetylene flame (the maximum thickness for the oxyhydrogen flame is 28 in.). The construction and manufacture of a recently developed electrolytic cell for producing oxygen and hydrogen, also 500 and 1000 ampere cells were shown, also the method of use and control as demonstrated in a small experimental installation.

Pierre Lorillard Tobacco Company. The sorting, cutting, impregnating, weighing and packing of the tobacco was inspected with the greatest interest.

American Smelting and Refining Co., Maurer, N. J. This excursion could not be made on account of a strike at the plant of this company.

Didier March Co., Keasby, N. J. The method of manufacturing refractory brick was shown, especial interest being manifested in the continuous kiln, which is 200 ft. long, the maximum temperature being 2600° F. Interest was also shown in carborundum bricks which do not melt at 3600° F.

German-American Stoneware Works. A great variety of chemical stoneware was shown together with the process of manufacture, the method of making stoneware condensers involving the manufacture of the stoneware tubing and coiling of same being especially interesting. The trip was made especially comfortable and convenient by having available a special car furnished by the German American Stoneware Works.

The members watched with great interest on the return to New York the fire and explosions which destroyed the plant of the Canadian Car and Foundry Co. at Kingsland, N. J.

Commercial Acetylene Welding Co., Bound Brook, N. J. A great deal of interest was shown in the manufacture of cylinders, more particularly the process of filling the cylinders with a very light and porous mixture of charcoal, asbestos, kieselguhr and cement. After thorough drying, the cylinders are charged with acetone and then charged with purified acetylene gas under 200 lbs. pressure.

J. C. OSLEN, *Secretary*

COOPER UNION, NEW YORK CITY

UNPREPAREDNESS¹

By GEORGE D. ROSENGARTEN

When by unforeseen circumstances a nation is suddenly plunged into conditions depriving it of materials necessary for

its welfare, it becomes an eminent duty of such a people to take immediate steps to attempt to restore the supply of the wanting essentials. Since history ever repeats itself, the assumption can at once be made that such conditions must have been taken under advisement long before there was any evidence of their becoming actualities, but the presumable optimistic trait in human nature and without which we would not be able to live through a happy existence, will procrastinate the evil day, with the intention of relying on the strength of the country when the necessity arises.

Recent events, however, have proved that this is no easy matter and the effort made in this direction, by making an inventory of our supplies, brings us to face the question of crude material, a question which is of the utmost importance in order that our stocks may be sustained. The United States is a country of immense resources, but owing to territorial advantages or seasonal conditions, it follows that some of the basic needs are entirely wanting or so limited that they may be considered a negligible quantity. No matter if we are surrounded by a high protective duty or laboring under a tariff for revenue simply, at least that in name, which obviously means nothing at all, instances will always remain where desirable commodities are lacking. Among the various expedients suggested, the consideration of the question of crude material has been, to a large extent, neglected, and a very serious condition confronts us if the very material from which the finished goods must be manufactured is placed beyond our reach. The eternal slogan "preparedness" is the real foundation for the prevention of such conditions or at least to reduce them to a minimum. It is so easy to preach, but this is not sufficient; it is the practice we need. There are not only the much-mooted coal-tar dyes, but other articles which have not had the publicity but are just as deserving. The coal-tar dyes of course derived all their fame from the fact that we were dependent for them on Germany and when the source of supply was shut off the prominence afforded them was amazing. Presuming that sulfur had not been obtainable in this country during the European crisis, can we for a moment believe that we would have enjoyed anything like the opportunity offered for prosperity—a forced prosperity in truth and due to no cause of internal workings, but entirely and absolutely to European conditions? The very contemplation of the thought of what might have been, had we been dependent for sulfur on foreign sources, is sufficient to bring horror to any chemical manufacturer. Fortunately we were not compelled to combat this situation, but the grave consequences are prominently brought to mind as to our situation if we were to be deprived from enjoying foreign commercial intercourse. The basic reflection is the problem how crude material is to be obtained to sustain our industries and the secondary consideration is the inventoring of our supplies.

It is quite evident that the New Tariff Commission must be deeply involved in the consideration of the question of crude material and that the industries must assist in this respect, since they are much more cognizant of their necessities. Under the condition existing, while hostilities in Europe endure, it would seem doubtful if any commission can really approximate the need of protection for American industries. The present exaggerated situations do not offer a stable basis for even a shrewd surmise towards consequent events and certainly are far from lending themselves as a solid foundation for the establishment of what really may be necessary for the future and lasting prosperity of this country. The prominent need is that the new ventures which have been brought about by the war must receive sufficient nursing and that the industries already established must enjoy protection in the same measure to insure our independence and security from foreign inroads.

¹ Read at the 9th Annual Meeting American Institute of Chemical Engineers, New York City, January 10, 1917.

NOTES AND CORRESPONDENCE

TWO LETTERS ON OUR NITROGEN DEMAND AND SUPPLY IN THE EVENT OF WAR

Editor of the Journal of Industrial and Engineering Chemistry:

The editorial in the December 1916 issue of *THIS JOURNAL*, pages 1088-1089, on the subject "Our Nitrogen Demand and Supply in the Event of War," contains a number of errors, and is seriously misleading both on that account and by reason of unwarranted assumptions and conclusions. Without any desire to belittle the importance of adequate preparedness for this country, and merely for the sake of a true understanding of the nitrogen situation on the part of the public, I ask that you will grant space in your columns to the facts presented in this letter.

The most serious error in the editorial lies in the presentation of the 1916 abnormal consumption of nitrates and other inorganic nitrogen with the assumption that these figures serve as a basis for the future "imperative" needs of our own country. There can be no question that the chemical industries of this country using sodium nitrate and ammonia are now greatly expanded for export purposes. It is estimated by one of the large explosive manufacturers (in a private communication) that fully 900,000 tons of nitrate of soda have been made into explosives in this country during the year 1916; and that the average annual consumption for this purpose for several years preceding the war was about 180,000 tons.

A reasonable estimate of our imperative future needs, say in 1918, for nitrate and ammonia for home consumption should be based on the 1914 consumption with addition of an annual percentage for growth derived from the statistics of previous growth. Such an estimate is made in a later paragraph.

NITRATE IN THE CHEMICAL INDUSTRIES

It is not justifiable to estimate the consumption of nitrate or of ammonia in the chemical industries by difference; i. e., to assume that all of that portion of the total imports and production which is not reported as used in agriculture goes into the chemical industries. A press bulletin of the Bureau of the Census, Department of Commerce, issued in August 1916, and quoted in the *Oil, Paint and Drug Reporter* of August 28th (p. 26) and September 4, 1916 (p. 56), gives the statistics of the consumption of nitrate of soda in the acid and chemical industries, the explosive industry and for fertilizer in 1914, as follows:

	1914	1909	% Increase
In the sulfuric, nitric and mixed acid industries and the chemical industries...	59,604	56,597	5.3
In the fertilizer industry:			
For acid manufacture.....	15,134	89,836	81.1
For mixed fertilizers.....	147,030		
In the explosives industry.....	190,960	188,889	1.1
Totals.....	412,748	335,332	

These statistics place the amount of nitrate used in the chemical and explosives industries in 1914 at 250,564 tons, or 30,088 tons of nitrogen. The corresponding figure given in your editorial is 60,600 tons of nitrogen.

The imports of nitrate of soda in 1914, viz., 541,715 tons, were in excess of the total of the above quoted census figures of distribution by 128,967 tons. A large portion of this amount unaccounted for was no doubt consumed in direct sales to the farmer for unmixed fertilizer. The Federal Trade Commission Report on The Fertilizer Industry, August 1916, p. 30, estimates this item for 1913 at 900,000 tons. The only other item of importance not included in the above quoted census figures is the glass industry which in 1914 may have used 21,000 tons of nitrate of soda, based on the 1909 consump-

tion and assuming same percentage growth as in chemical industries).

The total consumption then for the explosives, chemical and allied industries in 1914, was 271,564 tons (190,960 + 59,604 + 21,000) of nitrate, or 42,464 tons of nitrogen,—less by 18,136 tons than the amount given in the article in question.

AMMONIA FOR THE CHEMICAL INDUSTRIES

Similarly for ammonia, the amount used in the industries cannot accurately be estimated by difference.

In the absence of statistics of the chemical industries showing directly the use of ammonia therein, it is reasonable to estimate the amount of sulfate consumed in agriculture (or stored) at 60 per cent of the total coke oven production plus the total imports of sulfate (this assumption used in The Federal Trade Commission Report on the Fertilizer Industry, August 19, 1916, pp. 43-44). On this basis the production and imports of sulfate of ammonia in 1914 amounted to (0.60 × 139,500) + 83,377 = 167,077 tons (equivalent to 34,417 tons of nitrogen). (Ref.: "American Fertilizer Handbook," 1916, p. 43.) By difference then the amount of ammonia used in 1914 in other forms than sulfate, or for all purposes other than agriculture, would be 56,050 — 34,417 = 21,633 tons of nitrogen, instead of 25,150 tons as given in the editorial.

AMMONIA FOR REFRIGERATION

Your estimate of the use of ammonia for refrigeration is greatly exaggerated. The editor of "Ice and Refrigeration" (in a private communication to The Barrett Company, New York) estimates this at 7,000,000 lbs. of NH_3 per year (equivalent to 284 tons of nitrogen). Estimates, also made by refrigeration experts, for the Nitrate Supply Committee of the National Research Council, lead the latter to estimate the probable annual consumption of ammonia for this purpose in 1916 at 3500 tons as nitrogen. (Private communication from the Committee.)

Your editorial places this consumption (in 1916) at 12,600 tons of nitrogen, based on "Mineral Resources of the U. S.," 1914, p. 408. This reference does not give the consumption of ammonia for refrigeration. It states that the ammonia produced at by-product coke plants and reported as anhydrous ammonia was in 1914, 25,370,509 lbs. (equivalent to 10,450 tons of nitrogen), but explains in a foot-note that this figure refers "mainly to ammoniacal liquor sold on pound basis of NH_3 ."

TOTAL IMPORTS, NITRATE OF SODA, 1914

Imports of nitrate of soda in 1914 were 541,715 net tons (equivalent to 84,550 tons of nitrogen, on basis of 15.6 per cent). (Ref.: "American Fertilizer Handbook," p. 81.) The editorial gives this figure as 101,200 tons of nitrogen, which is the figure for 1913, a year of abnormally large imports. Statistics of annual imports since 1909 follow:

(Ref. Federal Trade Commission Report on the Fertilizer Industry, August 1916, p. 30)		
	Short tons	Per cent variation from average
1909.....	116,735	100.00
1910.....	128,967	110.40
1911.....	128,967	110.40
1912.....	485,947	416.30
1913.....	606,000	523.50
1914.....	541,715	464.30
Average.....	200,000	

RATE OF GROWTH OF NITRATE AND AMMONIA CONSUMPTION IN THE INDUSTRIES

The growth of the consumption of sodium nitrate in industrial explosives and for the chemical industries has been as fol-

1914 is shown in the census figures quoted in the first table given on page 203.

For explosives the increase has been small (1.1 per cent). In the chemical industries the growth was larger (5.3 per cent). For future growth, on account of a more rapid development of the chemical industries occasioned by the war, it is proper to estimate probably a 20 per cent increase in imperative demand for nitrate during the 5 years following 1914. For industrial explosives it would seem that a 5 per cent increase in imperative demand is probably a liberal estimate.

For ammonia in the industries (including refrigeration) reliable figures of growth are not at hand, and the estimate in Reference 17 of your editorial of an annual increase of 1300 tons of nitrogen may be accepted provisionally. This is an increase of 9 per cent per year on the basis of the 1914 consumption, or for the period 1914 to 1918 a total increase of 36 per cent.

ESTIMATE OF THE IMPERATIVE DEMAND FOR INORGANIC NITROGEN IN 1918
(Exclusive of Export Products and Fertilizers)

	Tons of Nitrogen
Ammonia for the chemical industries and refrigeration, 21,633 (1914 consumption) $\times 1.36 =$	29,421
Sodium nitrate for the chemical and allied industries (not including explosives), 12,674 (1914 consumption) $\times 1.16 =$..	14,702
Sodium nitrate for industrial explosives, 29,790 (1914 consumption) $\times 1.05 =$	31,279
Total industrial demands for ammonia and nitrate.....	75,402

ESTIMATE OF THE AMMONIA-PRODUCING CAPACITY OF COKE AND GAS PLANTS IN 1918

The reference quoted in your editorial, viz., Ref. 20, W. H. Childs (President of The Barrett Co., New York), as authority for the estimate of ammonia to be produced in 1918, was made on a conservative basis early in the year 1916 and later developments warrant its modification. Since this estimate was made several more plants have been placed under construction and the known capacity of those plants now actually in operation or under construction exceeds the estimate of Mr. Childs by 140,000 tons of ammonium sulfate. (Ref.: H. C. Porter, *Met. & Chem. Eng.*, Oct. 15, 1916, p. 473; with addition of the capacity of 135 coke ovens since contracted for, making a total of 513,400 tons of ammonium sulfate from both coke and gas plants, or 105,760 tons of nitrogen.)

In support of this estimate there may be cited the actual production during 1916 (given out recently by The Barrett Co., New York) at both coke and gas plants, which was 325,000 tons of ammonium sulfate (272,000 tons at coke plants and 53,000 tons at gas plants). This production at coke plants is 94.4 per cent of the actual capacity of completed plants given in the article above cited, September 1916, allowing for four new plants or 557 ovens which operated only a part of the year (H. C. Porter, *Met. & Chem. Eng.*, Oct. 15, 1916, p. 473).

With the probable addition during the next two years, of new plants, both for coke and gas, not yet contracted for, the capacity for ammonium sulfate in 1918 may reasonably be expected to reach 580,000 tons, or 119,500 tons of nitrogen.

The probable capacity, therefore, for ammonium sulfate in 1918 will supply the probable demands of the industries for ammonia and also meet the Government's estimated demand for nitrogen in munitions. It will not entirely meet in addition the probable demand for nitrate in the industries, although a considerable part of this can be met, as well as a part of the demand for fertilizer (using the Government's own estimate for munitions). The private manufacturers using nitrate for industrial purposes may be expected to take steps toward supplying, in an emergency such as war, at least a part of their own demands through synthetic or fixation methods.

In conclusion, it is important to note in this connection that Germany, a military nation, was prepared, just prior to the outbreak of the war, with an annual capacity for inorganic nitrogen of only about 120,000 tons (98,000 tons from coal

plus 22,000 from fixation processes). That Germany had to increase this supply greatly through nitrogen fixation was due to her large and imperative demands for fertilizer nitrogen, demands which do not exist in this country.

H. KOPPERS COMPANY

PITTSBURGH, December 22, 1916

HORACE C. PORTER

Editor of the Journal of Industrial and Engineering Chemistry:

I beg to acknowledge copy of a letter addressed to the Editor of THIS JOURNAL, by Mr. Horace C. Porter of the H. Koppers Company, dated December 22, containing comments on and criticisms of the editorial in the December 1916 issue of THIS JOURNAL on "Our Nitrogen Demand and Supply in the Event of War." Mr. Porter's contentions and attitude as set forth in his letter are evidently due to a misunderstanding of the purpose and the conclusions reached in the editorial.

Mr. Porter says: "The most serious error in the editorial lies in the presentation of the 1916 abnormal consumption of nitrates and other inorganic nitrogen with the assumption that these figures serve as a basis for future imperative needs of our country. * * * * A reasonable estimate of our imperative future needs, say in 1918, for nitrate and ammonia for home consumption should be based on the 1914 consumption, with addition of an annual percentage for growth derived from the statistics of previous growth." It is clear that Mr. Porter had in mind *normal peace requirements* of the United States in laying down this postulate of his argument. The title of the editorial is "Our Nitrogen Demand and Supply in the Event of War." The first paragraph ends with, "insure the country a dependable supply of nitric acid for military explosives in the event of war." The second paragraph ends with, "a forecast of what may be expected in the event of war." The third paragraph ends with, "by reason of enemy attack at sea, by the scarcity of ocean craft, or for other reasons the country is cut off from importations of nitrogenous materials." The fifth paragraph begins with, "The figures show unmistakably that in the event of war the United States will face an imperative demand for over 309,000 tons of nitrogen."

It is not easy to understand how Mr. Porter in quoting the word "imperative" from this sentence can make it apply to the peace requirements of the country instead of the specifically stated situation set forth in the same sentence that it applies to "the event of war." However, he may have fallen into this mistake by reason of the fact that the diagram itself applying to the year 1918, does not state that it is based upon assumed war conditions. To one reading the editorial critically no other interpretation of the 1918 diagram is possible, for the reason that the diagram for 1918 shows a demand for exactly the 309,000 tons mentioned in the preceding quoted sentence. Furthermore, the diagram includes nitric acid for Government military explosives enormously greater than any possible peace-time requirements, and specifically referred to in the editorial as equivalent to Germany's estimated military explosives requirements. Therefore, Mr. Porter's contention in the whole matter might be discharged as having no value in controverting or modifying the conclusions of the editorial.

It is, I believe, worth while to consider certain specific statements which Mr. Porter offers in substantiation of his estimate of the country's peace-time requirements. He states in the third paragraph of his letter: "There can be no question that the chemical industries of this country using sodium nitrate and ammonia are now greatly expanded for export purposes. It is estimated by one of the large explosive manufacturers (in a private communication) that fully 900,000 tons of nitrate of soda are being made into explosives in this country during the current year, and that the average annual consumption for this purpose for several years preceding the war was about 180,000 tons."

It is fair to presume from the facts in the case and from the context of this statement in Mr. Porter's letter, that he assumes that the difference between the two figures mentioned of 720,000 tons of nitrate of soda, equivalent to 111,600 tons of nitrogen, is consumed in making explosives for export.

Numerous estimates of the proportionate amount of explosives which this country is furnishing to the Entente Allies, vary between 10 and 20 per cent of the Allies' requirements. From the latter figure it is indicated that the minimum annual Allied demand for nitrogen in the making of military explosives to meet its present war needs approximates 558,000 tons per annum. It is pertinent to compare this figure with the assumed war requirements of the United States as shown on the 1918 diagram in the editorial, where our demand, inclusive of every possible use to which nitrogen is placed except the moderate quantity of 59,000 tons of inorganic nitrogen in fertilizers, is given at 250,000 tons. Exactly what part of this 250,000 tons would be exclusively military explosives demand in the event of war, the editorial does not pretend to say. Only 55,000 tons of it are assumed as a definite Government-controlled supply: 156,000 tons are for nitric acid for the maintenance of the present chemical industries, some of which are, of course, engaged in the manufacture of military explosives. Therefore, the net war demand as set forth in the editorial must appeal to a careful student of these figures, whether based upon a war demand or upon Mr. Porter's own figures, as extremely moderate.

Mr. Porter's figure of 900,000 tons of nitrate (equivalent to 139,500 tons of nitrogen) of soda "being made into explosives in this country during the current year" has another interesting significance. The editorial shows for the 1916 demand in this country for nitrate of soda for all chemical industries 155,600 tons of nitrogen. Therefore, this figure must appeal to Mr. Porter as being understated rather than overstated, and it is this figure of 155,600 tons, roundly 156,000 tons, that is moved up into the 1918 diagram as nitric acid for the maintenance of the present chemical industries. It is to the point to ask Mr. Porter how far it would be consistent with adequate preparedness for this country, the importance of which he states he has no desire to belittle, to reduce, in the event of this country being at war, the output of the present chemical industries, which, according to his own estimate, as compared with the statements of the editorial with which he takes issue, are now engaged to the extent of almost 90 per cent in the manufacture of military explosives.

Mr. Porter states under the caption "Nitrate in the Chemical Industries" that "it is not justifiable to estimate the consumption of nitrate or of ammonia in chemical industries by difference; *i. e.*, to assume that all that portion of the total imports and production which is not reported as used in agriculture goes into the chemical industries." Mr. Porter summarizes the figures of nitrate of soda consumption for 1914 for explosives, chemical and allied industries, by deductions drawn from a press bulletin of the Bureau of Census, Department of Commerce, issued in August 1916, and in this way he secures a figure of 42,464 tons of nitrogen consumed in those industries in 1914, in comparison with the figure in the 1914 diagram of the editorial of 60,600 tons. Whether one figure or the other is adopted is immaterial to the purpose of the editorial, for the reason that this 1914 figure is not used in projecting the 1918 war demand, but to Mr. Porter it has some significance because he employs the figure later for developing the 1918 peace demand. Even for Mr. Porter's purposes, however, the method of the editorial of securing the figure 60,600 tons of nitrogen as nitrate of soda used in the chemical industries for 1914, which is an estimate by difference, is preferable because the total consumption is known definitely, and the consumption by agriculture is well established by the Federal Trade Commission Inquiry. That the balance must have been used in the arts, providing the 1914

imports were all used in the year 1914, which Mr. Porter does not question, and in view of the fact that they were less than the 1913 imports, with the probability that something was carried over from 1913, is a reasonable conclusion.

Mr. Porter under the caption "Ammonia for the Chemical Industries" next quarrels with another 1914 figure, namely, the quantity of sulfate of ammonia used during that year as shown in the editorial diagram for all purposes exclusive of agriculture. The difference is only 14 per cent from the figure in the diagram. The editorial and Mr. Porter agree on the quantity of sulfate of ammonia produced in the country and the amount imported in 1914. The diagram deducts from this total of 56,050 tons nitrogen equivalent, the estimate of Bureau of Commerce Census of Manufacturers' Fertilizer Industry, released July 6, 1916, 30,900 tons of sulfate used in agriculture. The difference is 25,150 tons of nitrogen in the form of sulfate of ammonia consumed for other purposes than agriculture. While Mr. Porter enters into calculations to determine the quantity of sulfate of ammonia used in agriculture which gives results different from the figure given directly by the Bureau of Commerce Census, it would seem to be preferable to use the direct figure rather than the one calculated by Mr. Porter, notwithstanding that they may proceed from the same fundamental basis. The editorial develops the 1918 war demand for ammonia mainly upon the 1916 records, so that here again, to a considerable extent, Mr. Porter's comments do not apply to the question of developing an estimate of the war-time demand. Furthermore, it would seem that these fine distinctions are on the order of cheese paring, in view of the fact that in determining upon the Nation's military requirements in time of war, the estimates should be broadly based and an effort made to play safe and to discourage the use of a questionable figure which would minimize the amount of the imperative demand. Mr. Porter, under the caption of "Ammonia for Refrigeration," takes exceptions to the quantity set down in the editorial. The difference is chiefly a difference of definition. The ammonia produced and imported and not used in agriculture is necessarily used in the arts. What the relative quantities may be that are used in different branches of the arts is a matter of indifference so far as the purposes of the editorial are concerned. Mr. Porter does not take issue with the diagram statement of the amount of sulfate of ammonia produced and imported; nor does he question materially the statement of the amount of sulfate of ammonia used in agriculture, particularly in the case of the year 1916. Therefore, it is reasonable to infer, he accepts the difference between the two figures as the amount of sulfate of ammonia used in the arts. What he does quarrel with, however, is the subdivision of the quantity of sulfate used in the arts between the quantity used in the chemical industries and the quantity used for refrigeration. What this subdivision is, has no bearing upon the subject of the editorial nor upon the conclusions which it endeavors to draw. If we define "refrigeration" as used by the editorial as "Ammoniacal liquor sold on the pound basis of NH₃" as being practically the whole of Mr. Porter's contention on this point into substantial accordance with the editorial.

Mr. Porter states under the caption "Total Imports, Nitrate of Soda, 1914" that the imports for 1914 were actually short tons, equivalent to 81,330 tons of nitrogen. The record, however, is in long tons, and the quantity is therefore equivalent to substantially 68,000 net tons of nitrogen. The diagram in the editorial gave the quantity of nitrate of soda 50 per cent in excess of Mr. Porter's corrected figure. In view of the fact that the importations of 1914, the largest in the history of the country, were nearly 50 per cent in excess of the importations of 1913, and in view of the circumstances surrounding the use of nitrate of soda in those periods, it is entirely likely that part of the exceptionally large importations of 1914 were carried over into 1915, so which event the editorial figure would seem

to be conservative. Absolute facts in such matters, of course, cannot be determined, but differences of a few per cent one way or the other hardly constitute so strong an indictment of an estimate of the character which the editorial undertakes to develop, as to be, in Mr. Porter's words, "seriously misleading both on account of errors and by reason of unwarranted assumptions and conclusions."

Mr. Porter finally projects an estimate entitled "Estimate of the Imperative Demand for Inorganic Nitrogen in 1918 Exclusive of Export Products and Fertilizers." This very clearly is a peace-time estimate, as he includes nothing whatever for military explosives. The estimate whether right or wrong, reasonable or unreasonable, has no bearing upon the subject of the editorial. While comment upon the figures contained in this estimate would, therefore, have no practical bearing upon the subject under discussion, it may not be without interest to point out the fallacies, as I see them, of Mr. Porter's method of approaching even the special problem that he set for himself.

The first item in this estimate is ammonia for the chemical industries and refrigeration, which he takes on the basis of the 1914 consumption, plus an assumed annual increase. The quantity is equivalent to 29,421 tons of nitrogen for 1918, but his basic figure for 1914 (21,633 tons of nitrogen), plus the well-established quantity of sulfate of ammonia used in agriculture in 1914 (23,800 tons of nitrogen), will not add up to the total that was consumed in 1914 of domestic and imported sulfate (58,100 tons of nitrogen). His second figure in the estimate, for sodium nitrate for the chemical and allied industries, not including explosives, takes an assumed figure for the 1914 consumption for these purposes and adds an assumed increase, giving an amount in equivalent nitrogen of 14,702 tons. Again, he does not give, in his basic figures for 1914, enough uses to account for the actual imports in 1914. His assumed consumption in equivalent nitrogen for 1914 for this item of 12,674 tons is almost 12,000 tons short of the actual figure which comports with the import records. This appears from the fact that 94,648 tons of nitrogen were imported as nitrate of soda in 1914, and 40,600 tons of this quantity were used in agriculture, leaving 54,048 tons used in the arts. If from this we deduct the quantity assumed by Mr. Porter in the next item of the estimate to have been used as sodium nitrate for industrial explosives, namely, 29,790 tons, we have 24,258 tons of nitrogen as sodium nitrate that were used in the chemical and allied industries in 1914, which, as just stated, is nearly double the quantity assumed by Mr. Porter.

The fact is that the whole of Mr. Porter's letter up to this point has no real bearing upon the findings of the editorial. It does not meet the issue in any particular and so far as any inferences can be drawn from Mr. Porter's figures upon the imperative demand in time of war, they would seem to confirm the findings of the editorial rather than to deny them.

Mr. Porter then proceeds, under the caption of "Estimate of the Ammonia-Producing Capacity of Coke and Gas Plants in 1918," to swell the forecast of President W. H. Childs of The Barrett Company as to the amount of ammonia that will be produced in this country in 1918 from by-product coke ovens, notwithstanding Mr. Childs' forecast was made as late as July 1, 1916. Mr. Childs' estimate is the equivalent of 77,200 tons of nitrogen. This was the quantity used in the 1918 diagram of the editorial. Mr. Porter says that this should be increased by the equivalent of 140,000 tons of ammonia sulfate or substantially 28,000 tons of nitrogen. He states further that probable additions during the next two years of by-product plants not yet contracted for, may reasonably be expected to increase the capacity in 1918 to 580,000 tons of sulfate of ammonia, equivalent to 119,500 tons of nitrogen. In a discussion the conclusions from which affect the safety of the Nation, it is hardly to be expected

that the optimism of a manufacturer of by-product coke ovens should be taken as a guarantee of what the country may have at its disposal from coke oven plants not even yet under contract nor, so far as known, even contemplated. Mr. Childs' forecast, made only 6 months ago, would have to be increased over 50 per cent to attain the happy anticipations of Mr. Porter. Even if it were proper to enter Mr. Porter's expansive figure into the 1918 war-time supply of nitrogen it would decrease the deficiency in the country as shown by the editorial diagram from 232,000 tons of nitrogen to 190,000 tons of nitrogen. The practical difference between the two figures, as it would affect this country, would be in the nature of the difference to the dog as to whether he had one inch of his tail cut off or one and two-tenths inches.

In conclusion, it is interesting to note the logical situation into which Mr. Porter has argued himself, even on the basis of accepting what we believe to be a wholly inadequate figure for the total industrial demands for ammonia and nitrate and his exorbitant anticipations of what the by-product coke oven industry will be able to furnish in 1918. As matters now stand, the sole source of nitrogen that this country could rely upon in the event of war in 1918 would be the by-product coke ovens. Accepting the unsafe and inappropriate manner by which Mr. Porter makes his forecast of the potential capacity of the by-product coke ovens, and the extraordinary figure of 119,000 tons of nitrogen being available from by-product plants in 1918, and deducting therefrom his minimum estimate of the requirements for industrial demand in that year of 75,402 tons, we would have left 44,098 tons of nitrogen available in this country for all other purposes, including military explosives in the event of war. Is it to be assumed that no inorganic nitrogen would be required for fertilizers in the event of war? War conditions are notably those which by taking men away from agriculture and industry demand for the maintenance of the country's industry and food supply that the productive capacity of the remaining workers should be increased by labor-saving appliances. There is no greater labor-saver than artificial fertilizers, and if we used as little as approximately half as much inorganic nitrogen for this purpose in the event of war in 1918, as was used in 1914, we should have absorbed substantially the whole of the remaining 44,098 tons of nitrogen referred to above. We would then stand with all of our nitrogen gone and nothing provided for military explosives. How shall we determine the maximum rate at which military explosives must be manufactured in time of war? Is it Germany's consumption of military explosives estimated at about 200,000 tons of nitrogen per annum? Is it five times the rate at which we exported during 1916 to the Allied Nations, amounting to 500,000 tons? But whatever the amount may be Mr. Porter by his own figures must admit that that amount would be our shortage. The editorial, in a very conservative manner, in order to express a guide to judgment rather than an exact figure, expressed the figure of deficiency as 231,850 tons. But whatever figure within reason is taken, surely the paltry amount of 40,000 tons which the twenty-million dollar appropriation made by Congress will provide from the fixation of atmospheric nitrogen as a definite assured and controllable supply, solely for the use of the Government in the event of war, is as moderate a safeguard as anyone could possibly recommend were he, to quote Mr. Porter's own words, "without any desire to belittle the importance of adequate preparedness for this country."

Mr. Porter has evidently entirely overlooked the fact that the U. S. War College has outlined a safety zone for the United States within which must be placed war munition and supply plants in order to safeguard them from undue exposure to enemy attack. A very large proportion (70 per cent) of the existing coke ovens of the country, all of which were included in Mr. Porter's estimates, fall outside of this safety zone.

To sum up, I do not see anything in the deductions made by Mr. Porter which would justify his criticism of unwarranted use of such statistical data in regard to the nitrogen problem as are available and obtainable under the circumstances. Certainly nothing has been presented which would cause me to modify the generalized conclusions established in the editorial.

M. C. WHITAKER

27 WILLIAM STREET, NEW YORK CITY
January 13, 1917

TWO LETTERS ON SYNTHETIC PHENOL RESINS

Editor of the Journal of Industrial and Engineering Chemistry:

IN THIS JOURNAL, 8 (1916), 1171, Mr. Kirk Brown of the Condensite Company of America gave his view of the dry process phenol resins.

May we point out an error in Mr. Brown's communication: his claim that the Aylsworth patent application for February 11, 1910, was the basic patent on the anhydrous reaction? If so, why did it never come into interference with our application with date of conception of April 29, 1910!

It must seem strange to Mr. Brown that the Aylsworth application was at no time declared in interference on the anhydrous reaction, nor cited as reference against our application though both applications were in the patent office at the same time, and were under the consideration of the Chief Examiner.

The Aylsworth application was not considered by the Examiner as dealing probably with the anhydrous process and for that reason did not declare it in interference with other applications which were possibly in interference. (Interference is not elective by the applicant but is imposed on the applicant by the Chief Examiner in the patent office.)

Curiously enough Mr. Brown shows in his letter that Mr. Aylsworth's process is not anhydrous for he carefully describes the method used to get rid of the free and combined water.¹

Mr. Brown is mistaken when he suggests that we implied that Mr. Aylsworth was second and Dr. Baekeland an "also ran," as the discoverers of the anhydrous reaction between dry phenol and dry hexamethylenetetramine. We tried to state clearly that there was no second and no "also ran." We discovered the anhydrous reaction, described it from a purely scientific standpoint, isolated and described the intermediates and by-products, discovered and described the many forms of the end-products and to-day are manufacturing the results of the anhydrous reaction and process under the broadest basic patents.

REDMANOL CHEMICAL PRODUCTS CO.
636-638 W. 22ND STREET, CHICAGO
December 27, 1916

L. V. REDMAN
A. J. WEITH
F. P. BROCK

Editor of the Journal of Industrial and Engineering Chemistry:

In my letter in THIS JOURNAL, 8 (1916), 1171, I tried to make it clear, and believe I did so, that Aylsworth was the first to suggest a true anhydrous reaction, but did not attempt to explain in detail the scope of the Aylsworth patents, because that is a function of the court. My letter was intended to be historical, not prophetic. I felt that it was not proper to encroach upon your space in a discussion having to do solely with the boundaries of the intellectual property of which patents in the absence of final litigation are merely the deeds without the surveys.

The fact that no interference was declared between the Redman application and the application of Aylsworth assuming that they were pending contemporaneously does not indicate to the slightest degree that the Aylsworth claims may not include the specific modification suggested by Redman. Interferences are declared only when two rival inventors are asserting rights to claims of the same scope. Since Redman evidently did not

seek to claim an anhydrous reaction broadly, but restricted and limited his claims to his specific suggestion of reacting upon dry phenol, no interference was declared.

For instance, suppose A and B are rival inventors with competing applications. The same broad invention is disclosed by both, but specifically the inventions are different. If A present broad claims comprehensive enough to include the specific inventions of both cases, B, by presenting only limited claims covering his specific form, can avoid the declaration of an interference by the Patent Office.

Dr. Redman's statement that I have shown that Mr. Aylsworth's process is not anhydrous is in error. If he will more carefully read my letter of December, he will see that the Aylsworth process consists of two steps, first the making of a dehydrated gum from phenol and formaldehyde, in which of course a great deal of water is present, which, however, is entirely eliminated, and the second step a reaction between this dehydrated gum and hexa. As in this reaction there is no water present or produced, it is properly described as anhydrous.

I do not know by what reasoning Dr. Redman reaches the conclusion that I have shown the Aylsworth process is not anhydrous but he might apply it equally as well to his own process to show that it is not anhydrous because phenol at some stage in its manufacture contained water.

CONDENSITE COMPANY OF AMERICA
BLOOMFIELD, NEW JERSEY
January 9, 1917

KIRK BROWN

FELLOWSHIPS IN CHEMICAL ENGINEERING, 1917-18 GRADUATE SCHOOL, UNIVERSITY OF MICHIGAN

The following seven industrial fellowships in Chemical Engineering are to be awarded in the Graduate School of the University of Michigan for the academic year 1917-18:

MICHIGAN GAS ASSOCIATION FELLOWSHIPS IN GAS ENGINEERING—For studies in the manufacture and utilization of gas. Two fellowships of the value of \$400 each.

ACME WHITE LEAD AND COLOR WORKS FELLOWSHIP—For the investigation of problems in the manufacture and utilization of paint and varnish. Value \$500.

MICHIGAN PULP AND PAPER MANUFACTURERS' FELLOWSHIP—For studies in the manufacture of pulp and paper. Value \$500.

DETROIT EDISON COMPANY'S FELLOWSHIP—For the investigation of materials used in central station equipment. Value \$500.

DETROIT COPPER AND BRASS ROLLING MILLS FELLOWSHIP—For the investigation of methods to produce better copper and brass products. Value \$500.

DETROIT STEEL CASTINGS COMPANY'S FELLOWSHIP—For the investigation of methods to produce better steel castings. Value \$500.

Application for these fellowships must be made on appropriate blanks and returned to the Dean of the Graduate School by March 1, 1917.

Correspondence should be addressed to the undersigned.

ARTHUR H. WHITE

Professor of Chemical Engineering

UNIVERSITY OF MICHIGAN
ANN ARBOR, JANUARY 15, 1917

THE CHEMICAL ENGINEERING CATALOGUE

The first volume of the Chemical Engineering Catalogue, described editorially in the November 1916 issue of THIS JOURNAL, was concerned mainly with chemical manufacturing industries. In order to expand the field to take in all that may be implied in the name "Chemical Engineering Catalogue" it is necessary to incorporate material from the more generalized line of chemical manufacturing. The first step in this direction has been the organization of a Metallurgical section to include

¹ THIS JOURNAL, 8 (1916), 1172.

the raw materials, apparatus and products of the metallurgical industries. This section will be in charge of Prof. G. A. Roush, of South Bethlehem, Pa., who will push the extension of this new department, while still retaining his connection with the Metallurgical Department of Lehigh University, and the editorship of Mineral Industry. In order that the Catalogue may be of maximum value to those interested, its preparation is under the supervision of a committee on which are representatives of the American Institute of Chemical Engineers, the American

Chemical Society and the New York Section of the Society of Chemical Industry.

SPRING MEETING AMERICAN CHEMICAL SOCIETY

The Spring Meeting of the American Chemical Society will be held at Kansas City, Mo., during the week of April 9, 1917. The Council Meeting will be held on Monday, April 9th, and the opening meeting of the Society on Tuesday, April 10th. One day will be spent at the University of Kansas, Lawrence.

PERSONAL NOTES

The American Leather Chemists' Association have endorsed Mr. Ellwood Hendrick of New York City, for appointment as a member of the Tariff Commission created under the General Revenue Act during the last session of Congress. For the other societies which have joined in this endorsement see THIS JOURNAL, 9 (1917), 4.

Mr. George Weith, of the Redmanol Chemical Products Company, Chicago, has recovered from a serious injury to his face and eyes by the explosion of phenol vapors while melting out a gum of phenol.

Mr. Felix Dreyfus, vice-president of Herman & Herman, Inc., sailed for Genoa on January 23 to inspect the company's branches in Europe and Great Britain. On January 25, Mr. Henry Frankel sailed from Seattle to establish branches in the Far East for the same corporation.

Prof. Wilder D. Bancroft, of Cornell University, gave an illustrated lecture on "Colloids" before the Franklin Institute, on January 11, 1917.

Dr. Harry N. Holmes, professor of chemistry, Oberlin College, addressed the Franklin Institute, on January 25th, on "The Formation of Crystals in Gels."

Dr. John E. Teeple, Consulting Chemical Engineer, New York City, has been appointed Associate in Chemical Engineering, Columbia University, and will at once assume charge of the courses in Chemical Factory Management, Advanced Industrial Chemistry and Chemical Engineering.

Professor F. J. Metzger, of the Department of Chemical Engineering, Columbia University, has resigned his position to accept that of Manager of Chemical Development with the Air Reduction Company, 120 Broadway, New York. Professor Metzger will assume his new duties February 1st.

Professor D. D. Jackson has been designated acting head of the Department of Chemical Engineering, Columbia University, to serve in place of Professor M. C. Whitaker absent on leave.

A public opening and inspection of the new chemistry building of the University of Cincinnati will be held Saturday, April 7th, under the auspices of the University and the Cincinnati Section of the A. C. S.

Dr. G. W. Gray, formerly Chairman of the Refining Committee of the Texas Company, is now Manager of the Midland Refining Company, located at El Dorado, Kansas.

The United States Civil Service Commission announces the following open competitive examinations: *Junior chemist*, for men and women, on February 7-8, 1917; *assistant chemist (qualified in the chemistry of steel)*, for men only, salary \$4 per diem, on February 7, 1917; *chemical laboratorian (male)*, salary \$4.24 per diem, on February 7-8, 1917; *explosives chemist (male)*, salary \$3,300 a year, postponed from January 30 to February 20, 1917; *assistant chemist (male)*, salary \$1,350 to \$1,500 a year, on February 27-28, 1917; *junior chemist*, Departmental Service, and *laboratory apprentice (male)*, Bureau of Standards, on March 14, 1917; *laboratory assistant (male)*, Bureau of Standards, and *scientific assistant*, Department of Agriculture, on April 11, 1917.

The next meeting of the Society for the Promotion of Engineering Education will be held at the Northwestern University, Evanston, Ill., on June 27 to 30, 1917.

Mr. C. C. Ramsey, president of the Crucible Steel Company of America, died on January 11, in the Allegheny General Hospital, Pittsburgh, after a six weeks' illness of lobar pneumonia.

Mr. Arthur H. Thomas, the laboratory apparatus dealer, fell on the ice while skating on Lake Lenape, December 31, 1916, and sustained compound fractures of both arms above the elbow.

Dr. Edgar F. Smith, Provost of the University of Pennsylvania, addressed the Engineers' Club of Philadelphia on "Chemical Research in Philadelphia," on January 16th. The Philadelphia Section of the A. C. S. were invited to the meeting.

The American Institute of Mining Engineers will hold its New York meeting, February 19 to 22, 1917.

The One Hundredth Meeting of the Louisiana Section of the A. C. S., on January 20, was a "Jubilee" in celebration of the continued success of the Section.

Prof. James Brown, of Butler College, Indianapolis, announces the theft in Butler College, about the middle of December, of two platinum crucibles weighing with their covers about 15 g. each, and one platinum spiral electrode weighing about 5 g.

The Forty-fifth Regular Meeting of the Connecticut Valley Section of the A. C. S. was held in Springfield on January 13th, with the following program: "Earliest Alchemy," by Prof. Hopkins of Amherst College; "Ice Cream—Its Nutritive Value and Bacteriology," by Dr. Herbert D. Pease, of the Lederle Laboratory, New York City.

President Robert B. Sosman, of the Chemical Society of Washington, addressed the Washington Academy of Sciences on "Some Problems of the Oxides of Iron," at its January 11th meeting.

Mr. Herbert L. Marter, of the Chicago Section, has resigned from the Sears-Roebuck Laboratory to accept a position with the Newport Chemical Company of Milwaukee.

Mr. R. R. Bliss, of the Chicago Section, has left the Sears-Roebuck Laboratory to accept a position as chemist with the Rundle Manufacturing Company of Milwaukee.

Mr. Bernard Schaar, of Schaar & Company, sailed on December 14th from Vancouver for Japan. He will spend about three months in the Orient on business for his firm.

Messrs. A. B. Davis, Arthur W. Bromell and Ralph W. Morgan, formerly of the Indiana Section, have gone with the Ault & Wiborg Company, Cincinnati.

Mr. E. A. Wildman, formerly associated with the Rockefeller Institute for Medical Research, has taken Mr. A. B. Davis' place in the synthetic laboratory of Eli Lilly & Company, Indianapolis.

Mr. W. J. Cotton, formerly associated with the scientific staff of Butler College, is now with the patent office, Washington, D. C.

Miss Ethel Jones, head of the chemistry department of the Los Angeles High School and of the Los Angeles Junior College, has been elected vice-president of the Southern California Section of the A. C. S.

The National Association of Manufacturers of Medicinal Products will hold its Sixth Annual Meeting at the Waldorf-Astoria Hotel, New York City, February 6 to 7, 1917.

We learn from *Science* that Prof. M. I. Pupin, of Columbia University, has been elected president of the New York Academy of Sciences, which in 1917 will celebrate its Hundredth Anniversary.

The Burdett Oxygen Company completed the erection of their Pittsburgh plant, at 40th Street and Allegheny Valley Railroad, on December 1, 1916, and are now in a position to furnish oxygen to users in the Pittsburgh territory. This is the eleventh plant erected by the Burdett Company in the various industrial centers of the country.

Dr. Claude L. Wheeler, editor of the *New York Medical Journal*, died in Brooklyn on December 30, 1916.

The Department of Ceramic Engineering of the University of Illinois will issue shortly a new bulletin describing in detail the courses, both graduate and undergraduate, which it offers in Ceramic Engineering and Ceramic Chemistry. The bulletin will also contain an illustrated description of the new laboratory and its equipment, and a list of the names and addresses of the graduates of the Department since its establishment. Copies of this bulletin can be obtained upon request from the Department of Ceramic Engineering, University of Illinois, Urbana.

A Joint Meeting of the New York Section of the American Electrochemical Society and the American Institute of Mining Engineers was held on January 26, the program consisting of a Symposium on the Electrical Precipitation of Smoke and Dust.

At the January 19th meeting of the New York Section of the Society of Chemical Industry, the retirement of Dr. P. C. McIlhenny from the secretaryship of the Section was announced. Dr. Allan Rogers, of Pratt Institute, Brooklyn, has been elected as his successor. A rising vote of thanks was extended Dr. McIlhenny for his efficient services to the Section during the past six years.

A Joint Meeting of the New York Sections of the American Chemical Society, the American Electrochemical Society and the Society of Chemical Industry will be held on February 9. The program will be a symposium on "Porcelain Manufacture in America—Chemical and Electrical Properties."

The general outline of the Spring Meeting of the American Electrochemical Society at Detroit has been sketched as follows: May 2—Visits to automobile plants with a "get-together" roadhouse dinner in the evening; May 3—Sessions on electric steel, ferro-alloys and general papers, with a "smoker" in the evening; May 4—Session on non-ferrous metals and low-temperature electric processes, followed by visits to Electric Steel Plants and Power Houses in afternoon, and addresses by President Fitzgerald and Mr. Alexander Dow in evening; May 5—Session devoted to electrodeposition of metals, theory and prevention of rusting of iron, and other papers. The Publication Committee announces that papers for this meeting should be in by March 1st.

The DeCamp Glass Casket Company has decided to locate its plant at Kingsport, Tenn., and will start immediately on the construction of their plant, designed for the production of glass burial caskets and other glass articles.

The British Dye Company, Ltd., have announced that they have placed on the market indanthrene blue under the name of chloranthrene blue.

GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

NATIONAL MUSEUM

Notes on Alunite, Psilomelanite, and Titanite. EDGAR T. WHERRY. Proceedings of the U. S. National Museum, Vol. 31, 81-8 (October 16); also Reprint No. 2145

INTERNAL REVENUE COMMISSIONER

Exemptions Applied to Distillers of Brandy. Treasury Decision 2472, from Vol. 31, No. 14. This decision makes certain exemptions for distillers of brandy from grape cheese, to which sugar solution has been added after manufacture of wine, in accordance with the exemptions which have been made for distillers of brandy from other authorized fruits.

Temperance Beer. Treasury Decision 2370, from Vol. 31, No. 14. This decision places the responsibility on brewers, manufacturers of beverages, and dealers who place on the market untempered beverages which are found to contain more than one-half of 1 per cent of alcohol by volume.

Regulations Relating to Domestic and Imported Wines, Liqueurs, Cordials, and Similar Compounds, taxable under the

Act approved September 8, 1916. Regulation 28, Supplement 2, 22 pp. Paper, 5 cents.

BUREAU OF SUPPLIES AND ACCOUNTS

Contract Bulletin Regarding Tool Steel. 6 pp., issued October 12. This bulletin of the Navy Department gives information for the guidance of commandants, commanding officers, constructing and engineering officers, inspecting officers and others, regarding contracts for tool steel.

NAVY ADVISORY COMMITTEE FOR AERONAUTICS

The first Annual Report of this committee includes the following four reports, three of them in 2 parts that are of some chemical interest:

(1) **Investigation of Pitot Tubes.** BUREAU OF STANDARDS. Part 1—Pitot Tubes and other Anemometers for Aeroplanes, by W. H. Henschel. Part 2—Theory of Pitot and Venturi Tubes, by E. Buckingham.

(2) **Relative Worth of Improvements in Fabrics.** GOOD YEAR TIRE AND RUBBER COMPANY.

(3) **Investigations of Balloon and Aeroplane Fabrics.** UNITED STATES RUBBER COMPANY. Part 1—Rubber and Aeroplane Fabrics, by Willis A. Gibbons and Chas. H. Smith. Part 2—Skin Friction of Various Surfaces in Air, by Willis A. Gibbons.

(4) **Thermodynamic Efficiency of Present Types of Internal Combustion Engines for Aircraft.** COLUMBIA UNIVERSITY. Part 1—Review of Development of Engines Suitable for Aeronautic Service. Part 2—Aero Engines Analyzed with Reference to Elements of Process in Operation, by Charles E. Tucker.

CONGRESSIONAL COMMITTEES

Sisal Hemp. Report of hearing before the House of Representatives committee on agriculture and forestry regarding importation of sisal and manila hemp, particularly in reference to United States Senate Resolution 94. This is a two volume report covering about 2,000 pages. It is available only through members of Congress.

DEPARTMENT OF AGRICULTURE

The Effect of Cultural and Climatic Conditions on the Yield and Quality of Peppermint Oil. FRANK RABAK. Bulletin 454, 16 pp. Paper, 5 cents.

Chemical Composition of American Food Materials. Bulletin 28 of the Experiment Station Office. A reprint giving analysis of animal and vegetable foods, showing chemical composition and nutritive value of food per pound. Paper, 10 cents.

Tests of Wood Preservatives. Department Bulletin 145. Reprint. Paper, 10 cents.

GOVERNMENT PRINTING OFFICE

Government Publications on Agricultural Chemistry. Price List 40, 8th Edition. This lists the publications for sale by the Superintendent of Documents.

INTERNAL REVENUE COMMISSIONER

Regulations and Instructions Relating to the Manufacture, Redistillation, and Denaturation of Domestic Alcohol. A reprint of regulations No. 30, revised. Supplement 2, 16 pp. Paper, 5 cents.

BUREAU OF MINES

Vapor Pressures of Various Compounds at Low Temperatures. G. A. BURRELL AND I. W. ROBERTSON. Technical Paper 142, 26 pp. Paper, 5 cents. "Among the compounds for which the pressures at low temperatures either had not been determined, or had been determined only within limited ranges of temperatures were ethylene, propylene, isobutylene, ethane, propane, isobutane, sulfur dioxide, nitrous oxide, ammonia, and acetylene. This paper presents the results of vapor-pressure measurements of the compounds mentioned at temperatures below the normal boiling point and at pressures ranging from 760 mm. to 1 mm."

List of Publications. A revised list of publications (to November 1916) giving those available for free distribution and those that may be obtained only through the Superintendent of Documents. 27 pp.

Operating Details of Gas Producers. R. H. FERNALD. Bulletin 109, 63 pp. Paper, 10 cents. This is a discussion of the various operating characteristics of the types of producers commonly used in this country, including a detailed summary of the reports received from a large number of plants.

Annual Report of the Director of the Bureau of Mines. 90 pp. This report covers the fiscal year ended June 30, 1916 and summarizes the administrative work, publications, and investigations of this Bureau. A brief résumé of the character and status of each problem under investigation is included.

BUREAU OF STANDARDS

Annual Report of the Director of the Bureau of Standards. 155 pp. This report covers the fiscal year ended June 30, 1916, and summarizes the administrative work, publications, and investigations of this Bureau. A brief résumé of the character and status of each problem under investigation is included.

Durability of Stucco and Plaster Construction. R. J. WIG, J. C. PEARSON AND W. E. EMLEY. Technologic Paper 70, 72 pp. "In 1915 the Bureau of Standards in cooperation with a committee which includes representatives from the Supervising Architect's Office of the Treasury Department, the American Concrete Institute, and three contracting plasterers of wide experience and from as many large cities, as well as representatives from the industries, undertook a comprehensive investigation of stucco construction. On the Bureau's grounds was erected a test structure containing 56 experimental stucco

panels, each approximately 15 feet long and 10 feet high. These panels, which were completed in November, 1915, represent practically all of the common types of stucco construction, a variety of mixtures being used on metal lath, wood lath, hollow tile, brick, concrete block, plaster board, gypsum block, and concrete bases.

"In April, 1916, a careful inspection of the condition of the panels was made, and the present progress report and full description of the test structure was prepared. Only 2 of the 56 panels were entirely free from cracks six months after the panels were erected, and a number of them were in very poor condition. On the other hand, about 40 per cent of the panels were rated as satisfactory. It should be mentioned that the smooth type of finish employed is well adapted to the bringing out of the small defects, such as cracks, blotches, uneven texture, etc. Further experimental work is needed before general conclusions can be drawn."

Investigation of Cartridge-Inclosed Fuses. By Board of Referees: E. B. ROSA, H. B. BROOKS, BURTON MCCOLLUM, W. J. CANADA, F. W. GLADING. Technologic Paper 74, 194 pp. Paper, 55 cents. This is a report of the Bureau of Standards in the case of Economy Fuse and Manufacturing Company vs. Underwriters' Laboratories (Inc.), concerning the fire and accident hazard of the Economy refillable fuse as compared with approved fuses.

Constitution and Microstructure of Porcelain. A. A. KLEIN. Technologic Paper 80, 35 pp. Paper, 25 cents. "The investigation consisted in the microscopic petrographic examination of kaolin, feldspar-quartz, feldspar-kaolin, and feldspar-quartz-clay bodies burned at various known temperatures. Furthermore, commercial bodies of various grades ranging from white ware to hard fired porcelain were investigated. The end in view was to obtain data as to the constitution and microstructure of porcelains and the changes in these involved by burning at various temperatures. Subsequently it was found possible to correlate to a certain degree the constitution and microstructure with the burning temperature of bodies whose composition lay within the limits of white ware and hard fired porcelains."

Thermoelectric Measurement of Critical Ranges of Pure Iron. GEORGE K. BURGESS AND H. SCOTT. Scientific Paper 296, 7 pp. Paper, 5 cents. "There is described a sensitive method for the measurement of the change of true thermoelectric power with temperature, by means of which observations may be taken *in vacuo* at 2° intervals.

"The thermoelectric power of the iron-platinum couple has been determined for the temperature range 0° to 1000° C., using iron of 99.968 Fe purity."

Specifications for and Methods of Testing Soaps. ANONYMOUS. Circular No. 62, 22 pp. Paper, 5 cents. This circular includes a general discussion of the composition of soap and the varieties of toilet and laundry soaps and cleansing powder for which specifications are suggested. Seven sets of specifications are proposed for milled toilet soap, white floating soap, liquid soap, salt-water soap, special grade laundry soap, ordinary grade laundry soap and chip soap. The methods described include those for sampling deliveries for preparations of the laboratory sample and for the following tests and determinations: Matter volatile at 105° C.; free alkali or acid (method for all except liquid soaps); free alkali or acid (method for liquid soaps); alkali as alkaline salts; silicate; sulfate; matter insoluble in water; unsaponified saponifiable matter; preparation of total fatty acids (method for milled toilet, white floating or salt-water soaps); preparation of fatty and rosin acids (method for ordinary or special grade laundry or chip soaps); titer test; acid number of fatty acids; total alkali (method for all except liquid soaps); total alkali (method for liquid soaps); chloride; rosin; total soap (method for liquid soaps); sugar—qualitative test.

BUREAU OF FOREIGN AND DOMESTIC COMMERCE

Artificial Dyestuffs Used in United States: Quantity and Value of Foreign Imports and of Domestic Production during Fiscal Year, 1913-14. THOMAS H. NORTON. Special Agents Series, 254 pp. Price, 30 cents. Census of dyes currently employed in United States by textile, paper, ink, varnish, fur, leather, paint, and other industries. It gives in detail quantity and value of each of 5,674 brands of synthetic colors imported from Europe, fiscal year 1913-14, similar information on coal-tar crudes and intermediates imported in same period, and complete list of artificial colors manufactured in United States prior to 1915.

GEOLOGICAL SURVEY

Quicksilver in 1915. H. D. McCASKEY. Separate from Mineral Resources of the United States, 1915, Part I; published October 4th. "The quicksilver industry continued to be of more than usual interest throughout 1915, owing to the large consumption of the metal in the manufacture of war supplies and the generally prevailing high prices resulting from the great demand. . . . Prices for the metal became so high in February and March, 1916, that domestic contractors for the Allies induced the British Government to permit shipments of quicksilver to this country to complete contracts, and thus, to a small but important extent, competition in the home market between domestic and foreign supplies was reestablished and prices rapidly fell from \$300 per flask in February, 1916, to \$75, the price now (August, 1916). According to reports from the producers, 169,939 short tons of new ore were mined and available for treatment in 1915, a considerable increase over the quantity in 1914, due, of course, to increased development and prospecting as well as to more rapid exploitation of established mines to take advantage of high prices.

"Of new and old ore and old furnace material, 158,817 short tons were treated in 1915, averaging 0.4 per cent quicksilver, or 9.9 lbs. per ton, an increase in quantity of 33,819 tons but with a slight decrease in tenor, owing chiefly to the lower-grade ore worked in Nevada.

"A total of only 2,391 tons was treated in retorts, yielding 1,214 flasks of quicksilver, or 1.9 per cent of metal from the ore charged. On the other hand, 156,426 tons of lower-grade ore were treated in shaft furnaces, yielding 19,819 flasks of mercury, or an average of 0.48 per cent of metal."

List of Publications. A revised list (to December, 1916) of the publications of the Geological Survey including those still available for free distribution and those for sale by the Superintendent of Documents. 168 pp.

Analysis of Silicate and Carbonate Rocks. W. F. HILLEBRAND. Bulletin 422, 239 pp. Paper, 25 cents. This is a reprint making this important publication again available through the office of the Superintendent of Documents.

Geographic Tables and Formulas. S. S. GANNETT. Bulletin 650, 4th Edition. Paper, 25 cents. The earlier editions of these tables were numbered otherwise in the series of bulletins.

Anticlines in Central Wyoming. C. J. HARRIS. Bulletin 641 I, from Contributions to Economic Geology, 1916, Part II, pp. 233-279. Published December 16, 1916. "The examination of central Wyoming was undertaken to determine whether or not the region contains anticlines or other folds favorable for the accumulation of oil and gas and also the number and occurrence of oil sands. If favorable folds are present, the next important question is whether the oil bearing sands are sealed below impervious rocks in these folds so as to hold the oil and gas or whether those sands have been exposed by erosion, allowing the oil and gas to escape.

"The United States Geological Survey can not state positively that oil or gas in commercial quantities exists in any of these anticlines, but it does suggest that some of them appear, after field examination, to offer favorable conditions for the accumula-

tion of oil and gas. Drilling is the only method of ascertaining whether or not oil or gas can be found in these folds."

Oil Shale in Northwestern Colorado and Adjacent Areas. DEAN E. WINCHESTER. Bulletin 641-F, from Contributions to Economic Geology, 1916, Part II, pp. 139-198. Published December 18, 1916. "The results of the tests made in the field and in the laboratory at Washington are given and show variation from a maximum yield of 90 gallons of oil to the ton of shale to a minimum of 0.31 gallon. The yield of ammonium sulfate was not determined for samples tested during the early part of the first season's work, but those which were tested show a range from 18.3 pounds by dry distillation or 34 pounds by steam distillation to 0.4 pound to the ton of shale. Likewise the yield of inflammable gas ranges in the samples for which the amount was recorded from 4,549 cubic feet to the ton of shale to less than 500 cubic feet."

Mineral Products of the United States. Unnumbered publication. 1 large sheet, 24 X 30 in., tabulating the mineral products for the calendar years 1906 to 1915 and indicating the total value of products from 1880 to 1905. Available from the Geological Survey on request.

Gold, Silver, Copper, Lead, and Zinc in Colorado in 1915. (Mines Report.) CHARLES W. HENDERSON. Mineral Resources of the United States, 1915, Part I, pp. 421-484. Published December 12, 1916. This and the following four pamphlets regarding gold, silver, copper, lead and zinc are "Mines Reports" for the districts in question. The general summary for these metals throughout the United States will be prepared in consolidated reports abstracted in THIS JOURNAL as they are issued.

Gold, Silver, Copper, Lead and Zinc in Arizona in 1915. V. C. HEIKES. Mineral Resources of United States, 1915, Part I, pp. 485-521.

Gold, Silver, Copper, Lead and Zinc in Idaho and Washington in 1915. C. N. GERRY. Mineral Resources of the United States, 1915, Part I, pp. 523-575. Published December 26, 1916.

Gold, Silver, Copper, Lead and Zinc in Montana in 1915. V. C. HEIKES. Mineral Resources of the United States, 1915, Part I, pp. 577-612. Published December 9, 1916.

Gold, Silver, Copper, Lead, and Zinc in Nevada in 1915. V. C. HEIKES. Mineral Resources of the United States, 1915, Part I, pp. 613-654. Published December 26, 1916.

Annual Report of the Director. 185 pp. This report summarizes the work of the Survey for the fiscal year ended June 30, 1916.

Copper in 1915. (General Report.) B. S. BUTLER. Separate No. 21 from Mineral Resources of the United States, 1915, Part I, pp. 655-722. Published December 26, 1916. "After the beginning of the European war in August, 1914, many of the large copper companies of the United States curtailed their output by 30 to 50 per cent and many of the smaller companies ceased operations entirely. This condition prevailed through the last five months of 1914 and into 1915. Early in 1915 it became apparent that the requirements of copper for war materials would far exceed what had been generally anticipated; the price of the metal began to advance, and in consequence production increased. Both price and output continued to increase steadily and rapidly. Before the middle of the year most companies were operating at full capacity and in the second half of the year plants were pushed to the utmost, as some of them a high recovery of metal from waste had a large output. The total supply for the year was the largest in the history of the industry.

"The summary of statistics of the copper industry in the United States in 1915 is given as follows:

Production of copper:	
Smelter output.....	1,388,009,527 lbs.
Mine production.....	1,488,071,528 lbs.
Refinery production of new copper—	
Electrolytic.....	1,114,345,342 lbs.
Lake.....	236,757,062 lbs.
Casting and pig.....	36,603,119 lbs.
Total domestic.....	1,387,705,523 lbs.
Total domestic and foreign.....	1,634,204,448 lbs.
Total new and old copper.....	2,026,000,000 lbs.
Total ore produced.....	43,415,153 short tons
Copper ore produced.....	43,404,182 short tons
Average yield of copper.....	1.66 per cent
Imports.....	315,698,449 lbs.
Exports.....	681,953,301 lbs.
Consumption:	
Total new copper.....	1,043,461,982 lbs.
Total new and old copper.....	1,435,000,000 lbs.
World's production.....	
Value of production in the United States.....	\$ 242,902,000

"The average cost per pound of producing electrolytic and casting copper, as compiled from the annual reports of companies giving this item, was 7.86 cents. This compares with 8.62 cents in 1914, with 9.49 cents in 1913, and with 8.74 cents in 1912. The cost as indicated by these figures is doubtless below the actual average cost of all copper but probably represents the general trend of costs.

"The average cost per pound of Lake copper, as compiled from the annual reports of companies giving this item, was 8.23 cents. In 1914 the cost was 10.93 cents; in 1913, 13.44 cents; and in 1912, 10.28 cents.

"The decrease in cost in 1915 from 1914 was accomplished in spite of increase in wages and larger expenditures on development and construction in 1915. Not only were wages increased but there was doubtless a decrease in average efficiency of labor, as is common when it is in large demand. Notable improvement in metallurgical practice was made, but the effect of this will appear in the output for 1916 much more than in that for 1915. In 1915 such improvements as were installed were probably partly offset by the sacrifice of the best practices for large outputs.

"The average selling price of electrolytic copper, as compiled from the reports of companies giving that item, was 17.33 cents a pound in 1915 and that of Lake copper was 17.79 cents. It is probable that the average profit per pound of copper produced was at least 8 cents. This would mean a profit for the industry of over \$111,000,000. Several of the copper companies increased their dividends during the year, and practically all added largely to their reserve funds, so that most of them were greatly improved in financial position at the close of 1915.

"The most satisfactory feature of the industry during the last few years has been the great improvement in metallurgical practices. The blast furnace that was long so large a factor in copper metallurgy has been in large part replaced by the reverberatory furnace. The silica-lined converter has in many plants given place to the more efficient basic-lined converter. The great increase in concentrating ore treated during recent years has served to emphasize the lamentably large losses by the older concentration processes, and the great increase in recovery effected by later improvements is most important and gratifying. The added recovery resulting from finer grinding in the Lake Superior district has already been felt. The flotation process, which promises almost a revolution in concentrating methods, had some influence on production in 1915 but will be more important in 1916 and subsequent years. Leaching processes, which a short time ago promised to take a prominent place in the industry, will probably be restricted to classes of ore not readily susceptible of treatment by the flotation process as at present developed. There seems to be a field, however, for leaching processes in the treatment of low-grade oxidized and partly oxidized ores. Plants were in process of construction during the year and others will doubtless follow.

"Improved processes promise to add from 10 to 20 per cent to the recovery of metal from concentrating ores. This will be felt not only in the added production from the class of ores that could be treated by the less efficient methods but will doubtless lead to a lowering in the grade of material that can be treated and thus add largely to the ore reserves. It will also be possible to re-treat some of the tailings from earlier operations.

"No systematic attempt has been made to ascertain the proportion of the copper output of 1915 used in different industries, such as electric transmission, brass manufacture, and casting, but some idea of the quantities entering the different industries can be gained from the forms in which the output of the refineries was cast.

"It may be assumed that a large portion of the 37 per cent cast as wire bars was used in the electric industry and that the 9 per cent cast as cakes was used largely for rolling. The other forms are less easily classified. The 6 per cent cast as cathodes, together with a portion of the ingots, probably entered the brass industry, and a large quantity of copper ingots was used in casting."

Coal in 1915. Part A—Production. C. E. LESHER. Separate No. 24, from Mineral Resources of the United States, 1915, Part II, pp. 345-431. Published December 16, 1916.

"The bituminous coal industry in 1915 responded in a gratifying manner to the quickening in all lines of business, and the record for the year shows an increase in the total quantity produced of nearly 5 per cent over 1914. The returns to the producers were, however, lower, the average price per ton at the mines declining from \$1.17 in 1914 to \$1.13 in 1915, with the result that the total value increased less than 2 per cent. Pennsylvania anthracite, production and value, decreased about 2 per cent.

SUMMARY OF STATISTICS OF COAL PRODUCED IN 1915

	Quantity (net tons)	Value
Bituminous coal and lignite.....	442,624,426	\$502,037,688
Pennsylvania anthracite.....	88,995,061	184,653,498
TOTAL.....	531,619,487	\$686,691,186

"The proportion of machine-mined bituminous coal to the total output has increased each year. In 1915 the proportion was 55 per cent, twice that of 1903, 12 years before, and the number of tons so mined in 1915 was more than three times that in 1903."

Coal in 1915. Part B—Distribution and Consumption. C. E. LESHER. Separate No. 25, from Mineral Resources of the United States, 1915, Part II, pp. 433-513. Published December 28, 1916. "The object of this report is to furnish statistics showing the internal distribution of the coal produced in the United States, the principal purposes for which it is used, and the quantities consumed in each state.

THE ESTIMATED DISTRIBUTION OF BITUMINOUS COAL AND LIGNITE BY USES

	Quantity (net tons)	Percentage of total consumption
Railroad fuel.....	122,000,000	28.0
Steamship bunker fuel (Tidewater)....	9,245,914	2.0
Great Lakes.....	1,461,593	0.3
Manufacture of beehive coke.....	42,278,516	9.3
Manufacture of by-product coke.....	19,554,382	4.3
Manufacture of coal gas.....	4,563,579	1.0
Domestic and small steam trade.....	71,536,489	16.0
Industrial steam trade.....	143,765,300	33.0
Exported.....	18,773,782	4.0
Used at mines for steam and heat.....	9,798,681	2.0
Special uses.....	714,073	0.1
TOTAL.....	443,492,509	100.0 "

Metals and Ores in 1914 and 1915. J. P. DUNLOP. Separate No. 22, from Mineral Resources of the United States, 1915, Part I, pp. 723-733. Published December 27, 1916. "The production of metals given in the following table shows the output from plants—mills, smelters, and refineries—in the United States, and is essentially a measure of the metallurgical industry, as the ore, matte, and unrefined bullion treated in this country

METALS PRODUCED IN THE UNITED STATES IN 1915

METAL	FROM DOMESTIC ORES		FROM FOREIGN ORES, MATTE, AND UNREFINED BULLION		TOTAL	
	Quantity (short tons)	Value	Quantity (short tons)	Value	Quantity (short tons)	Value
Iron (pig)(a).....	32,972,200	\$388,397,654	1,058,424	\$13,011,950	34,030,624	\$401,409,604
Manganese (spiegeleisen and ferromanganese).....	125,819	2,376,544	164,055	9,280,449	289,874	11,656,993
Other ferroalloys(b).....	143,902	3,621,264	1,505	2,172,128	145,407	5,793,392
Nickel.....	560	448,222	28,283,445	22,626,736	28,843,445	23,074,978
Aluminum(d).....	49,903	17,985,500			49,903	17,985,500
Gold.....	167,575	101,035,700	29,339	17,689,500	196,914	118,725,200
Silver.....	2,570,094	37,397,300	1,748,132	25,437,500	4,318,226	62,834,800
Platinum and allied metals.....	0.055	88,341	0.242	390,347	0.297	478,685
Quicksilver.....	788,737	1,826,912			788,737	1,826,912
Tin(e).....						
Copper, stated as refined.....	603,853	242,848,550	123,349	43,137,150	817,102	285,985,700
Copper, stated as refined.....	507,026	47,660,000	43,029	4,045,000	550,055	51,705,000
Antimony.....	2,000	1,180,000	1,544	910,960	3,544	2,090,960
Antimonial lead.....	19,371	3,092,675	3,853	573,061	23,224	3,665,736
Zinc (spelter).....	458,135	113,617,000	31,384	7,783,232	489,519	121,400,232
		961,575,662		147,058,033		1,108,633,695

(a) Marketed production.

(b) Includes marketed production of ferrosilicon, ferrophosphorus, ferrovanadium, ferrotungsten, ferromolybdenum. No ferrotitanium reported for 1914 or 1915.

(c) Nickel content of imported matte and ore.

(d) Includes foreign. Figures are consumption not production.

(e) No report of any tin ore smelted other than experimentally in 1914 or 1915.

are derived from both domestic and foreign sources. The attempt is made, however, to show the production in marketable form of metals from both domestic and foreign mines wherever possible. The production of domestic ore is a measure of the metal-mining industry of the United States alone.

The following table shows the production of crude ores supplied from domestic mines to gold and silver mills, concentrating plants, and smelters, in 1915, in short tons:

Iron ores (marketed production).....	62,152,272	Copper-lead ore.....	10,951
Manganese ore.....	10,874	Lead ore.....	
Manganiferous iron ore.....	53,976	Western States.....	2,429,546
Chromic iron ore.....	3,675	Central States.....	5,067,800
Tungsten ore.....	2,736(a)	Eastern States.....	14
Titanium ore.....	6,250	Total.....	7,497,360
Aluminum ore.....	332,686	Zinc and zinc-lead ore:	
Gold ore.....	11,279,354	Western States.....	2,412,663
Silver ore.....	1,407,772	Central States.....	14,467,100
Quicksilver ore.....	158,817	Eastern States.....	1,296,305
Tin ore.....	41,000(b)	Total.....	18,176,068
Vanadium and uranium ore.....	47,000	GRAND TOTAL.....	144,738,606
Antimony ore.....	5,000		
Copper ore:		(a) Not all crude ore; includes marketed concentrates from unknown quantity of crude ore milled.	
Western States.....	30,349,560	(b) Estimated.	
Central States.....	12,334,700		
Eastern States.....	868,555		
Total.....	43,552,815		

Magnesium in 1915. FRANK L. HESS. Separate No. 23, from Mineral Resources of the United States, 1915, Part I, pp. 735-741. Published December 21, 1916. "So far as is known to the Survey magnesium had not been produced on a commercial scale in the United States until 1915, though experiments looking toward that end had been made by various firms at different times and especially after the beginning of the European war in 1914. The total production during 1915 was 87,500 pounds, valued at about \$440,000.

"Before the European war magnesium was quoted at about \$1.65 a pound for the imported (German) material. After the cutting off of the foreign supply prices rose to \$5 or even \$6 a pound for sticks, and powdered material sold at \$6.50 a pound; and prices remained at about these levels through the year."

There is included in this bulletin a discussion of the properties of magnesium, the history and methods of manufacture, the uses, the future of this metal, and the prices under different conditions.

Magnesite in 1915. CHARLES G. YALE. Separate No. 13, from Mineral Resources of the United States, 1915, Part II, pp. 1019-1026. Published December 19, 1916. "The crude magnesite produced and sold or treated in the United States in 1915, amounted to 30,499 short tons, valued at \$774,491, as compared with 11,293 short tons valued at \$324,223, in 1914. The domestic material continues to be derived from California exclusively.

"The value assigned to the domestic product in 1915 is based on a price of \$25 to \$25.5 a ton of ordinary calcined magnesite, not ground, in sacks at San Francisco, which is assumed to be

approximately equivalent to \$9 a ton for the raw or crude magnesite at the same point. The ground magnesite brings a somewhat higher price in California markets, but the imported magnesite sells at a price above that of the domestic product, the reason being that the imported magnesite is more finely ground, is put up in better packages, and may be purchased in smaller lots on longer credit than the domestic. These prices plus freight rates have made the use of domestic magnesite expensive to those who have been accustomed to purchase the imported material.

"The Austrian and Hungarian magnesite formerly imported contains 6 to 8 per cent of iron; it is therefore more available for furnace use than the purer magnesite obtained in many other parts of the world; moreover, it can be produced more cheaply and in larger quantities and is more readily manufactured into refractory brick than the purer material. Until the cutting off of this supply, more than 90 per cent of the magnesite consumed in the United States was derived from these countries.

"The California magnesite deposits carry a purer material than the Austrian and Hungarian, and their output is better adapted for making paper, tiling, flooring, and cements than for refractory use. There is one mine recently reported in the State, in Napa County, whose product carries iron and corresponds nearly in composition to the ore from Austria. The mine is equipped with a calcining plant, but its entire output is absorbed by local steel plants. The deposits at a few other mines have smaller percentages of iron but more silica and lime. Magnesite is not in demand when it carries more than 5 per cent of silica and 3.5 per cent of lime."

Stone in 1915. G. F. LOUGHLIN. Separate No. 28, from Mineral Resources of the United States, 1915, Part II, pp. 761-842. Published December 27, 1916.

Gems and Precious Stones in 1915. WALDEMAR T. SCHALLER. Separate No. 29, from Mineral Resources of the United States, 1915, Part II, pp. 843-858. Published December 11, 1916.

Borax in 1915. CHARLES G. YALE. Separate No. 30, from Mineral Resources of the United States, 1915, Part II, pp. 1017-1018. "In 1915 the production of crude borate material in the United States was 67,003 short tons, valued at \$1,677,000, compared with 62,400 short tons, valued at \$1,464,400, in 1914, and 58,051 short tons, valued at \$1,400,000, in 1913. All the crude borate material now used in this country is the mineral colemanite (calcium borate), and the output in 1915 came from a few mines in southern and southwestern California. The value of the product given is the value of the ore at the point of shipment estimated on a basis of \$2.50 per short ton (net) of anhydrous boron acid (boron trioxide). Borax is the raw material. All the ore shipped from California, however, was calcined or concentrated before being sent out by the rail to the mines."

Peat in 1915. JAMES S. TURP. Separate No. 34, from Mineral Resources of the United States, 1915, Part II, pp. 1027-1030. Published December 30, 1916. "The most successful industry based on peat so far attempted in the United States is that of preparing peat for use as a fertilizer or as a filler for chemical fertilizers. Black, thoroughly decomposed peat is most satisfactory for all fertilizer uses, as such peats are generally heavier and more compact and contain more nitrogen and less fibrous material than the brown types. Some of the peat sold during 1915 for direct use as fertilizer was enriched by the addition of beneficial soil organisms.

"The production of peat for fertilizer and fertilizer filler during 1915, as reported, was 38,304 short tons, valued at \$258,447, as compared with 37,729 short tons, valued at \$249,899, in 1914. The selling prices given varied widely according to the grade of the product, the uses to which it was to be put, the quantity and quality of the materials added, and the size of the selling unit. The lowest price per ton reported was \$3, the highest \$16, and the average \$6.75."

COMMERCE REPORTS—DECEMBER, 1916

Filbert oil expressed from the mito in Turkey, is being used there for cooking, lighting and soap making. (P. 834.)

Large quantities of **potato starch** are being shipped from Prince Edward Island, Canada, to the United States. (P. 843.)

Shortage of the **beet sugar** crop in Russia, has caused increased demand for sugar in the far East, where the price had been declining. (P. 867.)

Information regarding **coal mining** in Silesia, including labor conditions, etc., are given. (Pp. 888-92.)

Porcelain manufacturers in Germany have increased the price an additional 20 per cent, making an increase of 65 per cent over pre-war prices. (P. 897.)

Shipments of **manganese ore** from Russia are increasing, though still far below normal. (P. 904.)

While the **sugar beet** crop of Russia is nearly normal, the output of sugar will be low, on account of lack of labor, transportation, etc. (P. 904.)

The regulations regarding the cutting and sale of **pulp wood** in New Brunswick, Canada, provide for the manufacture in Canada of all the wood into pulp, etc. (P. 910.)

Efforts are being made by the United States Bureau of Fisheries to develop the production of **leather** from shark skins. (P. 913.)

The development of **chemical industries** in South Africa is urged, especially the manufacture of supplies for the mining industry and of iron and steel, cement, soap, coal by-products, etc. (P. 924.)

A **fiber** known as "sandade" which is similar to kapok, and suitable for mattresses, etc., is now obtainable in Brazil. (P. 949.)

Steps are being taken in Chile for establishing a **school of mines** at Antofagasta, to develop the numerous mineral products of Chile. (P. 956.)

Oil is to be used entirely as fuel on the railway in Costa Rico. (P. 997.)

The Chilean **nitrate** industry has just about reached the proportions existing before the war. (P. 1011.)

Large amounts of **coal briquets** are being shipped from Wales to France, Italy and Spain. (P. 1048.)

A large **sulfite pulp mill** is being built in Finland. (P. 1051.)

In the manufacture of **precipitated chalk** in Germany, the marble or limestone is dissolved in hydrochloric acid and the iron, manganese, and most of the magnesium, are precipitated by the addition of chloride of lime, and subsequently milk of lime to

alkaline reaction. After filtration of the solution, it is slightly acidified with hydrochloric acid, then heated to 60 or 70° C., and precipitated with Na₂CO₃ solution in excess. The product after being washed filtered, dried, and pulverized has a very low apparent density. (P. 1062.)

The **rubber industry** of Honduras is in very poor condition. (P. 1075.)

Among the substitutes for **rubber** in use in Germany for bicycle tires, are steel wire, wood, leather, and a composition having some of the properties of rubber. (P. 1078.)

The **mercury mines** of Almaden, Spain, are to be leased. (P. 1079.)

The American output of **mercury** in 1915, exceeded that of 1914 by 27 per cent in quantity and 125 per cent in value. (P. 1080.)

Several deposits of **talc** are being worked in Brazil, both for talcum powder and for cooking utensils, which are turned from solid blocks of talc. (P. 1081.)

Chemical plants have recently been constructed in Russia for the manufacture of the following substances: Superphosphate, celluloid, formalin, lanolin, naphthalene, benzene, tanning materials, sulfuric acid and glass. (P. 1122.)

Among the plant products now exported from Brazil are the following: Cassia fistula, quassia, copaiba oil, ipecac, matico, sarsaparilla, tonka and vanilla beans, cacao beans, manaca, pilocarpus, carnauba wax, and Brazil wood. (P. 1126.)

Exports of oil from Tampico to the United States show a marked increase. (P. 1127.)

The **tungsten** output of Burma shows a marked increase. Most of the product is now being shipped to England. (P. 1166.)

Exports of **cassia** and **cassia oil** from Hongkong to the United States show a marked increase. (P. 1171.)

Most of the **tin** exported from southern China is obtained by crude methods, the concentration of the low-grade ore being principally hydraulic; much of the product is shipped to the United States. (P. 1176.)

At the recent Chilean Industrial Exposition was a large display of **chemicals** made in Chile. One plant is manufacturing 400 chemicals, which are being exported to all parts of South America. Before the war, Chile was purchasing iodine compounds from Germany. (P. 1185.)

The output of **gambier** from China is increasing. This dye, obtained from the cunao plant, produces a brown color on both silk and cotton. (P. 1189.)

The Ladysmith Copper Smelter on Vancouver Island, has been purchased by Americans and will be remodeled to produce blister copper. (P. 1197.)

A national mining congress is to be held in Peru in July, 1917. (P. 1203.)

SPECIAL SUPPLEMENTS ISSUED IN DECEMBER

GREECE—7b	NICARAGUA—34a
AZORES—11b	FRENCH INDO-CHINA—54b
BAHAMAS—22c	MAURITIUS—65b
COSTA RICA—24a	MADAGASCAR—70a
HONDURAS—31b	

STATISTICS OF EXPORTS TO THE UNITED STATES

HONGKONG—1181	GREECE—Sup. 7b
Antimony	Cork
Chemicals	Opium
Earthenware	Gum mastic
Explosives	Herbs
Hides	Marble
Leather	Chromite ore
Peanut oil	Emery
Amiseed oil	Magnoite
Cassia oil	Licorice
Paper	Amyl alcohol
SUGAR	COSTA RICA—Sup. 24a
Tin	Hides
NICARAGUA—Sup. 34a	Rubber
Gold	SUGAR
Silver	MADAGASCAR—Sup. 70a
Hides	Mangrove bark
Rubber	Graphite
Sugar	Hides
	Vanilla

BOOK REVIEWS

Coal Tar and Ammonia. By GEORGE LUNGE, Ph.D. Fifth and Enlarged Edition (English), 1916. 1658 pp. D. Van Nostrand Co., New York. Price for the set, \$18.00.

The new fifth (English) edition of Lunge's "Coal Tar and Ammonia" consists of three volumes, two devoted to the production, nature, components and uses of tar, and the third to ammonia. The edition is very much enlarged over the preceding one in mere bulk; has had new matter added and scarcely anything eliminated; has been fully sub-headed; has had the references made more specific and many new ones added; but otherwise retains the same general form.

Lunge has been recognized as the authority on coal tar and ammonia, and the work still remains a comprehensive treatise; but it seems that the time has come to choose between being an historical work and compendium of almost everything that has appeared on the subject of coal tar and ammonia, or an up-to-date treatise on the present accepted practices and conditions of this industry. The history of coal tar is interesting, as are many of the historical facts connected with the gas and coke industry; but with an edition of some 1600 pages it is difficult, if not impossible, to pick out the accepted practice and facts from the discarded practice or theory. Unfortunately the work is now neither a complete reference work, an up-to-date statistical work, nor a practical hand-book. Most of the statistical matter is already at least 6 years old—too old to be of more than historical value in a rapidly expanding industry such as coal tar and ammonia.

As a practical hand-book and compilation of accepted practice it falls far short, and this we believe to be the most necessary field to cover. We cannot help feeling that the accurate sources of information which Dr. Lunge may have had 20 years ago are no longer open to him; and failing in information of more modern methods, he has repeated the old ones, in reality long since obsolete.

These are general criticisms which apply principally to Vols. I and II, Vol. III on ammonia having evidently received the greatest attention. Below we have been more specific in calling attention to the valuable new matter found in this edition which has been added since the previous one, and also to the lack of current data and description of current practice generally referred to above. Before proceeding to the review in detail, we cannot refrain from the comment that the coal-tar and ammonia industry in the United States has received but scant reference and to express our belief that any future edition cannot afford to overlook the leadership which the United States is assuming in the volume of production of coal tar and ammonia.

CHAPTER I—INTRODUCTION. This introduction has been doubled in the space allotted to it, the principal additional matter covering coal, its formation, properties and occurrence, is a very proper addition to this work, though necessarily treating the subject but briefly; it contains some interesting results on work on the real composition of coal, with tables of coal production and the percentage which is so used that coal tar results as a by-product.

There are also a number of pages added on the values of tar in the past and some speculative remarks on future values under the suggested developments in possible coal tar production.

CHAPTER II—PROCESSES FOR OBTAINING COAL TAR. This chapter has been but slightly altered, the new matter being principally history of the introduction of by-product ovens, which, however, for most countries does not go further than the year 1906, there are several pages giving production of benzol from coke oven gases from 1880 to 1915, and some data on potential production of benzol in many of the countries having by-product ovens. Several additional pages are also given to

water-gas tar, its production and characteristics, with special reference to the separation of water from it. There are also included several new references to methods of producing aromatic hydrocarbons from petroleum oils by cracking. This is gone into in some detail, the Rittman process so widely heralded in this country being one which is specifically mentioned. To the coal-tar separators described is added a cut of the Koppers Company's separator; on which, however, but a few lines of description are given, together with several references to the condensation of tar fog by electric discharge.

Under the description of methods of recovering benzol from coke oven gases only old type apparatus is described, no reference being made to the tower system which this country adopted universally in connection with all of the new benzol recovery plants, in view of the fact that this is at this time the accepted German practice. The author does, however, very carefully refer to a number of other publications which he states describe modern methods and plants, giving particular emphasis to Lunge-Kohler's work. It seems to us that the present type of plants warrants more attention in view of the fact that there is still retained a whole page describing a method for removal of benzol from gas in the form of dinitro-benzol, which was exhibited in London in 1885, but certainly was nothing more than a curiosity.

CHAPTER III—THE PROPERTIES OF COAL TAR AND ITS CONSTITUENTS: This chapter remains exactly the same in form and almost the same in substance as in previous editions. The enumeration of the compounds contained in coal tar has been revised as to melting points and boiling points of a number of the better known compounds, and a few additions have been made to this list. One may, perhaps, question whether there is anything to be gained by carrying from edition to edition such terms as "tetracoline," "octacoline," etc., for which no formula can be given. It seems that after such a long period, lack of confirmatory evidence destroys whatever claims some of these doubtful substances may have had to "reasonable presumption." With a few exceptions, not much new matter has been added to the descriptions of the individual compounds, although perhaps this portion of Lunge's work, more than any other, is generally and deservedly referred to as authoritative.

Under aromatic addition products (naphthenes) are a number of new references to some important discussions, which may have considerable bearing on the theory and formation of coal tar. The author, however, dismisses rather impatiently the work of Pictet and Bouvier along these lines, and makes no mention whatever of the work of Burgess and Wheeler, Porter and Ovizt, and Parr and Olin. These works would seem to merit at least passing mention.

Even in this portion of his work, the author quotes authorities, to some of whom it is evident that much higher credence should be given than to others, without indicating whether or not the work quoted should be considered authoritative.

Under "Phenol" is a reference to its synthetic production by means of the benzene sulfonic acid process. The author states that it is accomplished by treating tar acid with caustic potash. Later on in the chapter on "Catechol" the somewhat more common method of heating the sulfonated tar acids with caustic soda is mentioned, but although the author cites an article by Noy describing this process in detail he does not in this or in any other place make the broad reference to the tremendous increase in synthetic phenol production by means of water-gas demand.

At the beginning of the chapter reference is made to the personal production of coal tar, and generally the most reference is repeated at the end of the chapter, indicating that the author approves of society not, and has, to the common

is mentioned a British patent for removal of the substances tending to produce pitch-cancer. Neither in this chapter nor in the chapter on "pitch," do we find any mention of what is probably the most important work dealing with this problem, namely, the report of H. C. Ross, J. W. Cropper and W. J. A. Butterfield. This report, under the title "The Problem of the Gasworks Pitch Industries and Cancer," was published in London, in 1913, and with it was printed an article by Dr. H. Bayon on "Epithelial Celloproliferation Induced by the Injection of Gasworks tar."

Perhaps nothing in the chapter needs revision more than its opening paragraph, dealing with the specific gravity of tar from various sources. Surely, at this late day, "London tar," "country tar" and "cannel coal tar," can hardly be considered a representative classification of coal tars.

CHAPTER IV—THE APPLICATIONS OF COAL TAR WITHOUT DISTILLATION: It can hardly be said that this chapter has undergone revision since the 1909 Edition. Everything contained in the previous edition is retained in the new.

About 20 pages are devoted to "Burning Tar as Fuel," and many burners are illustrated by drawings and diagrams. There is, however, only the very briefest reference to any methods of burning that would be considered good practice to-day. On page 341 appears the following: "In 1902, Bruckmann reports (*Z. Verein deutsch. Ingen.*, 1902, p. 317) that the Great Eastern Railway of North America used Holden's plan in 88 locomotives, and consumed for this about 85,000 tons of tar—that is, about a quarter of the coal tar then produced in the United States." The reviewer has noticed the deplorable tendency on the part of our continental colleagues to glean much of their information regarding American progress from the columns of their own technical journals.

In contrast to the amount of space devoted to burning tar, which we of the industry like to consider only as a last resort, such an important field for the use of coal tar as pipe coating receives only the barest mention. Even the protection of large diameter steel and iron tubes with bituminous coating, in which is embedded a spirally wound membrane, is not even mentioned, although this system is to-day in use by several large companies in Europe, as well as in the United States.

The section on the application of coal tar to the manufacture of roofing felt (which, judging from American practice, should not appear at all in this chapter, as coal tar without distillation is entirely unsuited for such a purpose) sets forth at the expense of 4 pages, a description of "a complete modern plant for the manufacture of roofing felt," illustrated with pictures and diagrams. This same modern plant, which was illustrated in previous editions, includes saturating machines operated by hand-power. We read on page 359: "Many attempts have been made to do it mechanically, but without success, as the loosened felt is not sufficiently resistant, and the least irregularity causes it to tear, which is easily avoided by a careful man working by hand." Although the reviewer has been connected with the American coal-tar industry for 17 years, the last hand-power saturating machines were scrapped before his advent. In spite of the fact that American practice is far in advance of European practice in the department of tarred roofing manufacture, we must note, in justice to the roofing manufacturers of Hamburg, that they have for some years been operating their saturating machines by steam power, Lunge to the contrary notwithstanding.

The pages devoted to the use of tar for road-making are more numerous than in the previous edition, but are less numerous than the tremendous development along these lines warrants. The author has not been at pains to inform himself widely concerning modern practice in various countries. He refers, on page 362, to the resolutions adopted at the Second International Congress of Roads, held at Brussels in 1910, with reference to

surface tarring of roads, but does not refer to the much more important and comprehensive resolutions adopted at the Third International Road Congress, held in London in 1913. On page 363, the author states that "except in the United States, special prescriptions for the quality of tar for spreading on roads have not been issued by the public authorities;" although for a number of years past, the Road Board of England have been publishing and revising quite elaborate specifications for tar for this purpose.

CHAPTER V—FIRST DISTILLATION OF COAL TAR: This chapter has been expanded to 153 pages, from 122 in the former edition, and additional matter is mostly good so far as it goes. Here as elsewhere, the information given applies almost exclusively to European practice, especially German and English, and in numerous cases no reference is made to practice in the United States, which in some lines at least is far in advance of that given. The author seems not to be aware of the fact that nearly as much tar is produced and worked up in the United States as in Germany or England, and that according to present indications the United States will probably before long pass both countries in quantity. For example, in dealing with the carriage of coal tar from point of production to point of use the classic illustrations of the previous edition show the relatively small German tank cars, holding presumably 20 tons or about 90 barrels of tar, whereas modern practice here generally employs tank cars over twice as large. Mere increase in size of course does not prove better practice but comparison of notes with the manager of the largest German tar distilling factory showed they would rather use the larger cars but could not do so on account of the inability of the railroads to handle very heavy equipment. Possibly recent developments may be changing this condition. Attention might be called to the evident typographical error near the bottom of page 376, where the size of these German cars is given as 20,000 tons instead of 20 tons. Only casual mention is made of steam heating coils in these cars, which practical operators know is one of the most important and at the same time one of the most difficult features of tank car construction. The strains in railroad movement easily break the coils or start troublesome leaks unless they are very carefully designed and strongly constructed. No mention is made of the use of pressure safety valves common in the dome of tank cars to-day.

With regard to storage tanks at the plants, description is given of underground wells, formerly largely used but now rarely built and no details are given as to design, construction or equipment of ground level steel storage tanks now commonly employed. The author is also sadly deficient in knowledge of modern pumping equipment of large capacity and apparently favors the expensive and double arrangement of filling a small receiver by gravity and then blowing the contents by compressed air to the stills.

Over 2 pages are given to distillation of tar (in stills) by steam. This might be condensed to a few lines by saying the practice has been somewhat used in the past but is now practically unknown, although in a few small works superheated water is sometimes used in making dehydrated tar in stills to reduce the fire risk.

The general subject of dehydrating tar is given extended consideration. The statement is made that in Germany the quality standard of sale of coal tar is that it contains not over 4 to 5 per cent water, otherwise reduction is made for excess water. If this is correct the basis is unreasonably liberal. In the United States 2 per cent is the recognized standard and although with high carbon, viscous gas-works tar it is often difficult for the tar producer to reach this standard, on the other hand in the relatively greater production of coke-oven tar this standard is easily attainable. The author does not give adequate attention to the obvious point of having the water reasonably separated from the tar as a part of the operation of original con-

densation and collection of the tar in the gas-works or coke-oven plant.

Description is given of dehydrating by special type of centrifugal but no comment is made on the necessity and methods of avoiding excessive throwing out of the free carbon of the tar especially in handling by centrifugal high carbon gas-works tar which is more troublesome in regard to excess water. On page 388 is a questionable statement that moderate heating of tar "to a certain extent splits off the *chemically* combined water." Only passing mention is made at this point of the modern rational method of using for dehydrating purposes the waste heat from condensing oils and cooling pitch in connection with the regular distillation operation. Unnecessary space is given to the technical curiosity of dehydrating tar by chemical means.

In modern practice the purification of tar from free carbon is carried out to quite an extent in preparing coal tar creosote solution for wood preserving purposes. The author mentions this but his general treatment of the subject would lead the unwary reader to think the plan is used more or less generally commercially with tar for regular distillation purposes, whereas we doubt if this is ever done. Nearly all of page 395 is given to processes which even the easy going author indicates are valueless.

In the section on the construction of tar stills the author gives a very good description of the typical German vertical still and setting. Reference is made throughout to the use of "wrought iron" plates, presumably meaning steel plates as far as present practice is concerned. The treatment is too discursive, as usual, giving almost impartially all sorts of designs, good and bad. On p. 405 it is stated that the usual American tar stills are horizontal cylinders, holding about 2000 gallons. It is very doubtful whether even 5 per cent of American tar is handled in such sized stills, to say nothing of the fact that the details given of construction are incorrect for the comparatively few used. The author condemns the horizontal cylindrical stills of whatever size, claiming they use about three times as much fuel as the vertical type, but the figures given on p. 406 of coal used for such stills are absurdly high and have no relation to modern practice. On the same page is an illustration and description of the so-called "wagon-shaped" stills, said to be employed at the Paris Gas Works. Doubtless they may have been used there "once upon a time," but they had disappeared at the time of our visit five years ago.

The most important change in design of intermittent tar stills is the use of increased heating surface by flues through the still as in a horizontal tubular boiler (see p. 409). The author does not mention that the type shown has proved rather expensive in repairs to offset the fuel saving and that as a result a still later and simpler design is preferred.

The general description of auxiliary apparatus used in connection with the tar still is we think fairly accurate for German conditions but not as up-to-date as it might be. On p. 425 is another illustration of carelessness where the second and fourth paragraphs are practically duplications.

Attention should be directed to the paragraph at the bottom of page 431, referring to explosions which have resulted from using air pressure to remove these oils. Static electricity may be also suggested as a probable cause of similar explosions.

The general notes on fractioning and fractions of tar oils are quite good although troubled as usual by lack of simple co-ordination. At present anthracene is of considerable interest in this country in connection with the demand for dyes but it is not and probably never will be "the most valuable product of tar distillation" as mentioned at the bottom of p. 451, and furthermore, there is no evidence that it has been so in Europe for many years.

Numerous descriptions are given of apparatus for continuous tar distillation. It is difficult to assign any reason except laziness on the part of the author for carrying over in full some

descriptions from the older editions, while merely mentioning the patent number of more modern and rational processes.

On p. 507 the author includes some British statistics of 1885 which might have been considered rather aged when included in the last previous edition of 1909 but at any rate they are more modern than the test of Berlin Gas Works tar (p. 508) which is of 1879.

In the division on tar testing there is the usual mixture of mostly ancient practice, through which the reader plods wearily and finds at the end (bottom of p. 519) merely reference to "other ways of testing" which in reality include the present standards. Emphasis is laid on the importance of getting fair average samples for any testing. We might comment that this is most vital and at times it is appalling to think of the amount of work which has been and perhaps still is thrown away each year in various industries in testing carelessly taken samples which are not representative of the material in question.

CHAPTER VI.—PITCH: This chapter has a mixed value. In some divisions, as for example, briquetting, it is reasonably adequate. Considerable new matter has been added which is good, as for example, the comments and tests on the elementary composition of pitch, beginning at the bottom of p. 532.

It is natural for the author to give extended attention to the use of pitch as a binder in briquetting fine coal as this is and has been for years the main European outlet for pitch. Some day this industry will receive more attention in the United States on account of increasing cost of lump coal, unless the problem is otherwise solved by different methods of working up fine coal or better outlets are found for the increasing production of pitch in this country following the great increase in by-product coke-oven tar. Up to this time the coal-tar industry in the United States has had to find other outlets for pitch as briquetting has been practically negligible and it may be said the industry has developed very creditably in large use of pitch for roofing, waterproofing and road purposes. In the briquetting line many statistics as usual are given but there is practically nothing later than 1909.

Another use for pitch mentioned (p. 548) is in making black iron varnishes and paints. Very excellent paints are made, which compare favorably with most other metal paints, which use much more expensive materials and sell at much higher prices.

The use of pitch, etc., for paving and road purposes is but briefly referred to in this chapter, the subject being more fully covered in the chapter on "Applications of Coal Tar without Distillation," which heading is incorrect for road tar.

Practically no mention is made here of the important use of pitch in connection with tarred felt in making composition roofs so largely used as standard in this country for roofs which are flat or have only a moderate slope. The development in this line of the coal-tar industry has been very much greater here than in Germany.

Considerable attention is given, as in previous editions, to distillation of pitch to coke. Practically nothing new has been added, perhaps for the reason that until recently this outlet has been neglected. As the peculiar properties of pitch coke are better understood there will be increased demand for this product in this country as well as abroad.

In view of the present attention to occupational diseases, it is interesting to note the description (p. 574) of so-called "pitch cancer" and preventive measures. Arrangement should be made to prevent the fine particles of pitch dust getting lodged permanently in the skin and personal cleanliness on the part of the operatives is extremely important.

Considerable data, some new, is given on the testing of pitch, but as before, it is given more or less haphazard, leaving the reader in doubt as to the best practice. The impression rests that the author has not very clear and decided ideas when he presents so much data, often conflicting, without comment or indication of relative importance.

CHAPTER VII—ANTHRACENE OIL: A little revision has been made of this chapter, particularly on the purifying of anthracene, together with new tables on the percentage of anthracene in different fractions of the oil, new tables on the properties of bodies occurring with crude anthracene, and a description of the estimation of the commercial products obtained from filtered anthracene oil. The statistics do not go beyond the year 1909. The interesting statement is made that anthracene should only be recovered where it can be done on a large scale and in conjunction with the other products occurring with it. There is also mentioned a newer method for filtering out the anthracene crystals and a comparison of the usual method with the use of centrifugals. There is given a description of the well-known method of purifying anthracene from carbazol, and purifying the carbazol, which is already generally known. Several other methods of purifying are given, but seem to be old ones and really have had no practical application.

CHAPTER VIII—CREOSOTE OIL: Much attention has been given during the past 10 years to specifications for creosote oil for treatment of timber for various structural purposes. In so far as American practice is concerned, this chapter is almost entirely free from reference to recent developments. The author has evidently not availed himself of statistical data or technical information available in the Proceedings of the American Railway Engineering Association and the American Wood Preservers' Association. Most of the material in this chapter has been carried forward substantially unchanged from previous editions. The bibliography and patent references are fragmentary. The statistics are meager, and no attempt has been made to bring them up to date. Seeing that the industry of tar distillation has always depended for its success on the utilization of creosote oil in timber preservation, the inadequacy of Lunge's work in fulfilling the requirements of a practical reference work on coal tar is nowhere more clearly recognizable than in this chapter.

CHAPTER IX—CARBOLIC OIL: This chapter has been revised to a considerable extent, one of the new points brought out being the different methods of handling this oil depending on whether it has high or low acid content, and the fact that fractional distillation of this oil is advisable as well as the method of fractional distillation for the separation of phenol from cresols; all of which, however, has been pretty well recognized before its appearance here. A reference to the American practice is still retained which is undoubtedly many years old and has no basis in fact at present. Estimates of the per cent of constituents of carbolitic oil are given; as also the fractions and their properties obtained by redistillation of this oil.

In discussing carbolitic acid and its purification several new pages are given on the cause of reddening of this acid, together with a remedy. There is also description of methods for the separation of Meta and Para-Cresols, with separate description of Hoffmann-La Roche's French patent.

A section on methods for examination of carbolitic oil and carbolitic acid of various grades is particularly good, containing the German method of carrying out Lowe's solidifying point test. The specifications and properties of commercial forms of carbolitic acid and the cresols are also given. There is inserted in this chapter, which is certainly in the wrong place, reference to the work of Church and Weiss on testing creosote oils for paraffins, as also that of Cloukey on testing for carbon.

On the uses of carbolitic acid new matter is given on a formula for carbolitic soaps and similar preparations, and a section devoted to condensation products, which are certainly deservedly referred to, especially the work of Backeland. Several new methods are also given for the analysis of carbolitic preparations. The statistics in relation to phenol and cresols are only those of Germany up to 1910.

Under the sub-heading "Naphthalene" in this chapter the definite statement is made that the only rational way of removing

oils from crude naphthalene is by hydraulic pressure with the application of heat, of which fact we are somewhat doubtful. Several pages describing this process with its variations have been rewritten. Additional description has been given of the details of washing naphthalene with acid, and the apparatus used.

In the description of the distillation of naphthalene, and also its subliming, the same old matter is retained even to the cut and description of subliming the material into an inverted barrel, which seems to be exceedingly ridiculous in view of modern methods, one of which he also describes, the method being that of Rispler. It is also noted that the source of most of the new matter on naphthalene has been Rispler. Several new pages have been added on methods of naphthalene testing.

On the uses of naphthalene, the detailed description of the old Albo-Carbon light is still retained, although this undoubtedly is obsolete in Europe just as it has been obsolete in this country for twenty years. Naphthalene is also referred to in connection with motor fuel; and while this is properly discussed, yet the description would hardly be the basis for accepting the scheme as a practical one. Uses of naphthalene for treatment, in connection with sulfur, of plant diseases are given as well as a use for production of artificial resins. In the naphthalene statistics only the German statistics of 1909 and 1910 are given.

CHAPTER X—LIGHT OIL: The principal addition to this chapter is a six-page reference to the adoption of the fractional distillation of this oil, with reasons for such adoption, and typical results. A reference is also made to the handling of the light oil secured from the scrubbing of coke-oven gases and its separation into benzol and toluol with their purification.

An interesting addition is in the description of safeguards which are advisable for benzol plants, especially with respect to the methods of extinguishing benzol fires.

To the description of the recovery of the acid from the waste acid tar from coal-tar naphtha washing has been added more references; but a United States patent is quoted from, which is intended entirely for petroleum acid tars, which has no application in this case.

A few new notes are added regarding the recovery of pyridine bases, together with their testing, and a few lines on coumarone resin, which really deserves a little more attention than given. The statistics in this chapter again are only for the year 1911.

CHAPTER XI—WORKING UP THE LIGHT NAPHTHA INTO FINAL PRODUCTS: This chapter, in its description of stills used for this purpose, contains nothing new. The statement, however, is made that the diameter of a rectifying column must vary with the size of the still, which statement is obviously incorrect as the diameter of the column, other things being equal merely has to do with the rate of distillation and has no reference to the capacity of the tank constituting the still itself.

Several new pages have been inserted on removing thiophene from benzol. A new paragraph has also been inserted covering the removal of toluol from coal gas, which report has since been verified, the result being accomplished by washing the gas with the usual wash oil previously saturated with 5 per cent of benzol, which results in the toluol being taken out of the gas and the benzol left in it, the toluol substituting the benzol in the wash oil. The matter on xylois has been rewritten without noticeable change.

A number of new tables are given on the yields of commercial products from light oil and crude naphtha. Few dates are given in relation to these yields, and those only show the data to be old. Tables are also given on the composition of commercial benzois.

Under the head of testing methods at the end of this chapter, new matter is inserted giving typical results of the testing of light oil, and a page devoted to the determination of toluene in commercial toluol and solvent naphtha, which is evidently due to the efforts to recover all the toluene for war purposes.

A new section has been devoted to testing for pyridine and other bases. An interesting addition is the method of Spilker for esti-

inating the yields of the products obtainable from crude coke-oven benzol or coal-tar light oil. A number of new references are given on the storing and handling of benzols, etc., especially with respect to their inflammability; but, as usual in foreign practice, the units described are small.

Very considerable additions are made to the data on application of benzol, etc., with the principal uses being named, particular emphasis being laid on the description of carbureting water gas with benzol, which contains full explanation and cut of the apparatus used. Considerable addition has also been made to the notes on benzol as a motor fuel, in which is pointed out the necessity of a non-freezing specification and in which is given an idea of the wide use in Europe of benzol for this purpose, German figures of the quantity used being given from 1901 to 1910. German statistics of imports and exports up to 1905 are given at the end of this chapter of the various products of coal tar, and under the new German classification this continues to 1907. Benzol and toluol figures are given, however, including 1911.

CHAPTERS XII TO XVII—AMMONIA SECTION: The discussion of ammonia, as revised, has been extended from 342 to 574 pages, an increase of two-thirds, and in this amplified form has been deservedly accorded the dignity of a separate binding.

It may be said at the outset that as far as comprehensiveness, wealth of detail and timeliness go, the new volume easily surpasses its predecessor. Its rank as a compendium of information on ammonia is so high that it outclasses all the other books on the subject. Few industries that are as young as the recovery and treatment of ammonia, have had the benefit of so assiduous a biographer. The work is not, however, above merited criticism. It lacks notably on the side of well-digested comment.

To note the chapters in detail: The first, bearing the number XII and the title "Historical Notes," including a brief glance at the future, is practically new and decidedly interesting matter.

The following chapter, No. XIII, "Sources from Which Ammonia is Obtained," has been expanded to nearly twice its former dimensions, and constitutes a very complete description of the processes by which ammonia can be produced. Conspicuous among the additions is a discussion of the synthetic production of ammonia from nitrogen and hydrogen, including the Haber process and a list of patents taken out by Haber, Le Rossignol and by the Badische Anilin- und Sodafabrik, with a digest of them; an account of the Woltereck process for obtaining ammonia and other products from peat and of the controversy with Messrs. Frank and Caro as to the actual fixation of atmospheric nitrogen in the operation; the Frank-Caro peat process, using the Mond producer as a basis; a description of the original Mond producer and of the improved design as worked out by A. H. Lynn, and a discussion of the possibilities of cheap power production by the use of gas in the improved Mond producer and gas engines, as compared with water power.

In this chapter there are also some statistics given for the recovery of ammonia from coke ovens, in which the English Alkali Committee's reports are quoted. Among so much up-to-date data, it is rather surprising to find these statistics halt at the year 1907, when the Committee's report for 1914 was at least as easily available as the U. S. figures for coal carbonization for the year 1914, given in the line below. Apprehension is, however, allayed by finding the data given in detail up to 1914 on page 1520.

Chapter XIV treats of the composition and analysis of ammoniacal liquor and the properties of its constituents. One would not have expected to find the old English "Cume" test for gas liquor still quoted as being in use, although it is hardly conceivable that any up-to-date worker would admit that it was regarded as anything else than a historical curiosity.

Methods of analysis for ammonia liquor are employed by the British Alkali Committee up to 1909, and also given. It is to be noted, however, that a detailed and definite scheme for sampling and analysis of concentrated ammonia liquor and for

ammonium sulfate is not included, aside from a cursory description of the methods followed by the Deutsche Ammoniak-Verkaufs-Vereinigung for ammonia liquor, and farther on, an outline of the method for sulfate. From a commercial point of view, it is highly desirable that official methods of analysis be promulgated and adopted, not so much for the enlightenment of competent chemists, who indeed would find no difficulty in drawing them up for themselves, but in order to guide those of less experience and to avoid commercial disputes, to which lack of recognized official methods frequently gives rise. The carload unit of ammonium sulfate is 25 tons and of concentrated liquor, say, 7,000 gallons, which would be about the same amount of ammonia. A difference of 0.1 per cent in test, due either to sampling or analysis, would amount to about \$30.00. Larger differences frequently occur at present even in expert hands.

In Chapter XV the working up of crude ammoniacal liquor into concentrated liquor and pure ammonia is treated *in extenso*. The chapter does not include the production of sulfate, as formerly, this being reserved for the ensuing chapter.

In the first part of Chapter XV, devoted to the treatment without distillation and to the manufacture of concentrated gas liquor, the text has undergone slight revision and amplification. It is to be noted that in Fig. 265, p. 1355, the letters "C," "D," "E" referred to in the text, are still lacking in the diagram. The section on "Manufacture of Liquor Ammonia" is much the same, barring rearrangement, but under "Manufacture of Anhydrous Liquid Ammonia," some new illustrations and descriptive matter have been inserted. A few pages on the storage and carriage of anhydrous, the properties of commercial anhydrous, its application and analysis, have also been added.

Chapter XVI, on the "Manufacture of Sulfate of Ammonia," outside of a few new introductory paragraphs, is practically unchanged. The types of apparatus originated by different inventors are given as before. The mention of the Wilton saturator is given the same brief notice, as in the previous volume, although to the mind of the writer the use of the air lift or ejector for removing the finished salt from the acid bath solved at one stroke many of the existing difficulties of the sulfate maker, and made the continuous saturator a workable device. Previous to this use of the air lift by Wilton, elevated saturators with bottom outlets, mechanically operated bronze screws, or bucket conveyors, had been resorted to in continuous saturation with but indifferent success. Many times more space is given in the test to devices of far less practical importance. Additions have been made to the patent review together with new matter on the coloration of sulfate and on the treatment after removal from the saturator. Additional matter on the examination of commercial ammonium sulfate and the scheme or tests for it, as given by the D. A. V. V., has also been inserted here. Mention is made of the movement to establish the 25 per cent NH_3 grade as the standing in England, as it now is in Germany and the United States, but no reference is found to the appearance on the German market or elsewhere of a *ground* and *ground* sulfate carrying 25.25 per cent NH_3 , and practically moisture free, though the prices on this grade have been frequently quoted in Germany for years past.

The final chapter treats of the other technically important ammonium salts, including the chloride, carbonates, nitrate, phosphate and others. While the *strong* arguments are preserved, considerable new information has been added. It is followed by a brief Appendix and by several pages of addenda, including late data on coal tar as well as ammonia. The volume contains the index of names and one of subjects, the complete table of contents occupying only six volumes.

A new revision, making the *ammonia* and *nitrate* volumes, published by Messrs. H. C. Clarendon and W. P. Farrington, consists of certain of the chapters on Ammonia (part I), and on Nitrate, Sulfate, and Water (part II).
H. W. FARRINGTON

Transactions of the American Institute of Chemical Engineers.

Volume VIII (1915). Office of the Secretary, Cooper Union, New York, N. Y. Published by the Institute through D. Van Nostrand Co., New York, 1916. 8vo. iii + 309 pp. Price, \$6.00 net.

The eighth volume of these transactions is slightly larger than its predecessor through the use of heavier paper, there being the same number of pages in each volume. The high standard recently set by these transactions in its illustrations is largely maintained. The general make-up of the volume is as heretofore though the volume behaves upon handling as though the binding would not last. It is to be hoped this is not a sign amidst the general elevation of price and depression of quality, that our books are to be more poorly made. Committee reports which appeared in last year's volume after being omitted for three years are missing from this volume.

The frontispiece is a photogravure of Dr. J. C. Olsen who has served as Secretary of the Institute since the first year of its existence, and who has acted in this capacity from the first as editor of these Transactions.

The following papers and addresses presented before the Institute are contained in the present volume:

Resources and Possibilities of Chemical Industry in the Southwest. Edgar Baruch.

The Chemical Evidence of Smelter Smoke Injury to Vegetation. J. P. Mitchell.

Cottrell Processes of Electrical Precipitation. Walter A. Schmidt.

The Fleming Patent Dust-Collecting System. W. C. Hanna.

The Thiogen Process for Removing Sulfur Fumes. S. W. Young.

The Manufacture of Cream of Tartar. Otto Best.

Engineering Features of Wine Making. Arthur Lachman.

The Treatment of Sewage by Aeration in the Presence of Activated Sludge. Edward Bartow.

A New Electrolytic Method of Sewage Disposal. J. C. Olsen.

Costs as Applied to Professional Business. Ralph A. Gould.

The Improvement of High Boiling Petroleum Oils, and the Manufacture of Gasoline as a By-product therefrom, by the Action of Aluminum Chloride. A. M. McAfee.

Some American Contributions to Industrial Chemistry. Samuel P. Sadler.

The Development in the United States of the Manufacture of Products Derived from Coal. H. W. Jordan.

Notes on a New Process of Bleaching. S. F. Peckham.

Lutes and Cements. S. S. Sadler.

The Design and Operation of Ozone Water Purification Systems. Sheppard T. Powell.

Changes in the Volume and Specific Gravity of Linseed Oil Films on Drying. G. W. Thompson.

The Utilization of Wood Waste. Arthur D. Little.

The Production of Ammonia from Cyanamid. W. S. Landis.

These titles are typical of the broad field of chemical engineering. The collection of papers on phases of the smelter fume problem read at Leland Stanford Jr. University and not at "San Francisco," as might be inferred, in reality show clearly that the science of chemistry need not be divorced from usefulness to the community because its professors are not connected with a formal college of Engineering. It was a pleasure to note how every chemistry instructor one met at this institution seemed to have on his mind some phase of this important smelter problem, whereas too frequently in institutions where engineering and applied chemistry receive more formal recognition there is a profound coolness toward the "applied" man as though one became a sort of leper when he ventured into the field of problems from whose solution the community might benefit.

It seems too bad that the efficiency of the smelter's "legal department" renders it unnecessary to try out more thoroughly such processes as the Thiogen Process of Young. The article of Peckham and particularly page 222 should be read by every chemist who has not had experience with the brand of chemical logic with which our patent office suffers from time to time. Some remedy should be found for the type of injustice on the part of our patent office so mildly recounted in this article.

Other articles in the volume enrich the literature of this field

especially in the case of cream of tartar, sewage cost, petroleum refining, American contributions to industrial chemistry, ozone and ammonia from cyanamide.

It seems a pity in the Transactions of a select and small organization that better record cannot be kept of the discussions of papers. In the case of the Jordan paper on the coal-tar industry and its development in America it happened that there joined in the discussion a number of chemical engineers whose knowledge in this industry goes back farther than that of any American now living and the hitherto unpublished material brought out appeared unknown to the author of the paper, yet, for some reason it was omitted from the transactions.

JAMES R. WITHROW

The Analysis of Copper and Its Ores and Alloys. By GEORGE L.

HEATH, Chief Chemist, Calumet & Hecla Smelting Works. 292 pp., with 18 figures and 2 plates. McGraw-Hill Book Co., New York, 1916. Price, \$3.00.

A carefully written text by a leading authority on the subject is always welcome, more especially if material on the topic is widely scattered or altogether lacking. The present output of new copper in the United States is probably somewhere near 150,000,000 pounds per month, to which there must be added about one-fifth as much of secondary copper recovered. When it is remembered that this copper enters into an almost infinite variety of commercial products it is at once evident how important is the field to which Mr. Heath has addressed himself. To his task he brings the accumulated experience of years of practice and investigation, and the resulting volume seems likely to become, as the Confession of Faith phrases it, "the one infallible rule and guide to faith and practice" for chemists and assayers engaged in commercial work.

The introductory chapter is devoted to descriptions of equipment. Instead of describing all the wide variety of designs and patterns Mr. Heath contents himself with a brief but lucid account of those which he considers best, for which his readers will be grateful. The second chapter deals with sampling, and may therefore be considered the most important in the book. This is considered under five divisions: mine sampling, mechanical ore sampling, copper stamp mill sampling, smelter sampling, and copper-bearing products within the works. On the first two only a brief summary is given, with references to the recognized authorities, but the reader wonders why the practice at the Mansfield mines is described in some detail, unless Mr. Heath considers it representative of the best practice, which is at least open to question. It is interesting to learn from Division 3 that the Lake Superior stamp mills have a systematic method of sampling. The fourth and fifth divisions are those with which the author is chiefly concerned. The methods used in many different places are given in sufficient detail, with reference to the authorities. The third chapter deals with reagents and standard solutions. The next four chapters deal with ores, slags, metal and flue dust, furnace refractories, and the precious metals. This concludes the first part. Part II deals with the work of an electrolytic refinery, Part III with the analysis of refined copper, especially the detection of foreign metals, Part IV with the analyses of commercial copper alloys, and Part V with the metallography of copper and brass, and the electrical resistivity of copper. The volume concludes with a glossary, and, as frequently happens in glossaries, it is not difficult to find fault with some of the definitions. He also frequently uses the phrase "zinc spelter," as though there were some other kind of spelter that is not zinc. Such imperfections are only minor ones; it is fair to draw attention to them in a critical review, but it should not obscure the main point that Mr. Heath has done a tremendous service to analytical chemists in placing at their service so comprehensive and authoritative a work.

T. T. READ

NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

Agricultural College: A Study in Organization and Management and in the Problems of Teaching. F. A. WAUGH. 8vo. 260 pp. Price, \$1.10. O. Judd Co., New York.

Analysis: Elementary Practical Chemistry. Part 2. F. CLOWES and J. B. COLEMAN. 8th Ed. 8vo. 280 pp. Price, 3s. 6d. J. and A. Churchill, London.

Analysis: A Laboratory and Class Room Guide to Qualitative Chemical Analysis. G. F. WHITE. 12mo. 171 pp. Price, \$1.25. D. Van Nostrand Co., New York.

Analysis: Qualitative Chemical Analysis. A. B. PRESCOTT and O. C. JOHNSON. 7th Ed. 8vo. 436 pp. Price, \$3.50. D. Van Nostrand Co., New York.

Automatic Screw Machines, Construction, Design and Operation. D. T. HAMILTON and F. D. JONES. 8vo. 342 pp. Price, \$2.50. Industrial Press, New York.

Building Materials. G. A. T. MIDDLETON. 2nd Ed. 8vo. 430 pp. Price, 10s. B. T. Batsford, London.

Chemistry: La chimie est-elle une science française? PIERRE DUHEM. 16mo. 191 pp. A. Hermann et fils, Paris.

Chemistry: A Class Book of Chemistry. Parts 1-4. G. C. DONINGTON. 8vo. 546 pp. Price, 5s. The Macmillan Co., London.

Chemistry: Laboratory Manual of General Chemistry. A. B. LAMB. 4to. 166 pp. Price, \$1.45. Harvard University Press, Cambridge.

Chemistry: Synopsis of Introductory Lectures in General Chemistry. H. N. MCCOY. 8vo. 129 pp. Price, \$0.65. University of Chicago Press, Chicago.

Dyeing in Germany and America. S. H. HIGGINS. 8vo. 150 pp. Price, 5s. Longmans, Green & Co., London.

Engineering: Cyclopaedia of Civil Engineering. 9 Vols. 8vo. Price, \$29.80. American Technical Society, Chicago.

Engineering as a Career. P. MARSHALL and A. W. MARSHALL. 8vo. 51 pp. Price, 6d. Percival Marshall, London.

Foundry Work. B. L. GRAY. 8vo. 196 pp. Price, \$1.00. American Technical Society, Chicago.

Gas: Handbook of Casing-Head Gas. H. P. WESTCOTT. 16mo. 275 pp. Metric Metal Works, Erie, Pa.

Gas and Oil Engines and Gas Producers. L. S. MARKS and H. S. McDOWELL. 2nd Ed. 12mo. Price, \$2.00. American Technical Society, Chicago.

Gases: Measurement of Gases Where Density Changes. H. P. WESTCOTT. 16mo. 60 pp. Price, \$0.50. Metric Metal Works, Erie, Pa.

Hydraulics for Engineers. F. C. LEA. 3rd Ed. 8vo. Price, 15s. Edward Arnold, London.

Hydro-Electric Power—Vol. 1 of Electrical Equipment and Transmission. LAMAR LYNDON. 8vo. 498 pp. Price, \$5.00. McGraw-Hill Book Co., New York.

Hydraulic Development and Equipment—Vol. 2 of Electrical Equipment and Transmission. LAMAR LYNDON. 8vo. 360 pp. Price, \$3.50. McGraw-Hill Book Co., New York.

Industrial Chemistry: Cours élémentaire de chimie industrielle. D. TOMBRICK. 8vo. 335 pp. H. Dunod et E. Pinat, Paris.

Industrial Chemistry: Elements of Industrial Chemistry. An Abridgment of Manual of Industrial Chemistry. ALLEN ROGERS. 513 pp. Price, \$3.00. D. Van Nostrand Co., New York.

Industrial Electricity: Cours élémentaire d'électricité industrielle. P. ROBERTOT. 8vo. 353 pp. H. Dunod et E. Pinat, Paris.

Industrial Electricity: Leçons pratiques d'électricité industrielle. A. SOULIER. 8vo. 316 pp. G. Garnier frères, Paris.

Mechanics for Engineers. C. N. MILLER. 127 pp. Price, \$1.00. D. Van Nostrand Co., New York.

Metallurgy: Les Mines de fer et l'Industrie métallurgique dans le département du Calvados. JEAN DE MAULDE. 8vo. 272 pp. Price, 6 francs. Louis Jouran, Caen.

Milling: A Treatise on Milling and Milling Machines. 8vo. 409 pp. Price, \$1.50. Cincinnati Milling Machine Co., Cincinnati.

Minerals: The World's Minerals. I. J. SPENCER. Rev. Ed. 8vo. 327 pp. Price, \$2.75. P. A. Stokes & Co., New York.

Mining: A Textbook on Coal Mining Science. JOSEPH PARKER. 8vo. 422 pp. Price, 5s. Oliver & Boyd, Edinburgh.

Natural Gas. H. P. WESTCOTT. 2nd Ed. 12mo. 616 pp. Price, \$3.50. Metric Metal Works, Erie, Pa.

Oil-Field Developments and Petroleum Mining. A. B. THOMESON. 8vo. 692 pp. Price, 25s. Crosby Lockwood & Son, London.

Organic Chemistry: A Textbook of Organic Chemistry. F. V. MC-CORMICK. 14mo. 416 pp. Price, \$2.25. The Macmillan Co., New York.

Petrol Engine, the Magneto and the Carburettor. A. I. HERRIMAN. 2nd Ed. 8vo. Price, 7s. 6d. Methuen & Co., London.

Portland Cement Industry. W. A. BROWN. 8vo. 198 pp. Price, 7s. 6d. Crosby Lockwood & Son, London.

Refrigeration: A Practical Treatise on the Production of Low Temperatures. M. W. ARROWOOD. 12mo. 272 pp. Price, \$1.50. American Technical Society, Chicago.

Soldering, Brazing and Welding. B. E. JONES. 8vo. 156 pp. Price, 1s. Cassell & Co., London.

Starting, Lighting and Ignition Systems. V. W. PAGE. 8vo. 59 pp. Price, 1s. Hodder & Stoughton, London.

Steam Power. HIRSHFIELD and ULBRICHT. 8vo. Price, 8s. 6d. Chapman & Hall, London.

Stresses in Structures. A. H. HELLER. 3rd Ed. 8vo. Price, 11s 6d. Chapman & Hall, London.

Sulfitation in White Sugar Manufacture. FRANCIS MAXWELL. 8vo. 82 pp. Price, 7s. 6d. Norman Roger, London.

Switch Gear: Electric Switch and Controlling Gear. C. C. GARRARD. 8vo. 656 pp. Price, \$6.00. D. Van Nostrand Co., New York.

Tables of Physical and Chemical Constants. G. W. C. KAYE and T. H. LABY. 2nd Ed. 8vo. 153 pp. Price, \$2.00. Longmans, Green & Co., New York.

Water Flow: Tabulated Data with Explanatory Notes Relating to Flow of Water under Pressure through Clean Closed Pipes. G. T. PRINCE. 149 pp. Price, \$2.00. D. Van Nostrand Co., New York.

RECENT JOURNAL ARTICLES

Aluminum-Bronze Tests and Their Significance. W. M. CORSE and G. F. COMSTOCK. *The Foundry*, Vol. 45 (1917), No. 1, pp. 21-28.

Asbestiform Minerals: The Origin of Veins of the Asbestiform Minerals. STEPHEN TABER. *Proceedings of the National Academy of Sciences*, Vol. 2 (1916), No. 12, pp. 659-664.

Blast Furnace: The Future of the Iron Blast Furnace. J. E. JOHNSON, JR. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 1, pp. 11-21.

Boiler-Room Safety Pointers. M. A. SALLER. *Power*, Vol. 45 (1917), No. 1, pp. 14-15.

Calorimetry by Combustions with Sodium Peroxide. W. G. MINTER. *American Journal of Science*, Vol. 43 (1917), No. 283, pp. 27-34.

Castings: Making Non-Ferrous Castings in a Railroad Shop. E. I. SHANER. *The Foundry*, Vol. 45 (1917), No. 1, pp. 1-5.

Copper: Current Efficiency in Copper Refining. LAWRENCE ADDICKS. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 1, pp. 23-25.

Crane Operation Facilitated by Reflecting Mirror. WM. LAHLER. *The American Machinist*, Vol. 46 (1917), No. 1, p. 12.

Dyeing: Studies in Dyeing and Cleaning. D. B. LAKE. *The Journal of Physical Chemistry*, Vol. 20 (1916), No. 9, pp. 761-808.

Electrolytic Dissociation in Non-Aqueous Solutions. H. J. M. CREIGHTON. *Journal of the Franklin Institute*, Vol. 182 (1916), No. 6, pp. 745-761.

Electrolytic Refining at Trail. T. A. RICKARD. *Mining and Scientific Press*, Vol. 113 (1916), No. 26, pp. 903-907.

Gasoline Situation. V. H. MANNING. *Power*, Vol. 45 (1917), No. 1, pp. 29-30.

Low-Temperature Compression Systems. HARRY SLOAN. *Power*, Vol. 45 (1917), No. 1, pp. 28-29.

Magnesite: California Magnesite Industry and Production. W. A. SCOTT. *Mining and Engineering World*, Vol. 45 (1916), No. 27, pp. 1107-1109.

Molybdenum: Analysis of Molybdenum Ores. H. WESTLING and C. ANDERSEN. *Mining and Scientific Press*, Vol. 113 (1916), No. 26, pp. 912-918.

Petroleum: The Nature and Origin of Petroleum and Asphalt. CLIFFORD RICHARDSON. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 1, pp. 25-27.

Precipitation: Retarded Diffusion and Rhythmic Precipitation. I. STANSFIELD. *American Journal of Science*, Vol. 43 (1916), No. 283, pp. 1-36.

Scientific Research in Relation to the Industries. A. F. THOMSON. *Journal of the Franklin Institute*, Vol. 182 (1916), No. 6, pp. 731-739.

Segmental Block Sewers. I. F. NIKENY. *American Technical Society*, Vol. 51 (1916), No. 6, pp. 214-216.

Shrinkage and Contraction. H. I. MAXWELL. *The Foundry*, Vol. 45 (1917), No. 1, p. 5.

Stability in Paraffin Hydrocarbons. C. ELLERY and E. J. MACK. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 1, pp. 3-11.

Steel: A Method of Distinguishing Sulfides from Oxides in the Metallography of Steel. G. F. COMSTOCK. *Report of the National Bureau of Standards*, Vol. 1 (1916), No. 120, pp. 1-10.

Stresses in Impact. H. T. BERRY. *Transactions of the American Society of Mechanical Engineers*, Vol. 182 (1916), No. 6, pp. 1-17.

Sulfur's Effects on Low Carbon Steels. R. HAYWARD. *Steel and Iron*, Vol. 50 (1916), No. 1, pp. 101-103.

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON JANUARY 15

INORGANIC CHEMICALS

Acetate of Lime, 100 Lbs.	3.50	@	3.60
Alum. lump ammoniac, 100 Lbs.	4	@	4 1/4
Aluminum sulfate, high grade, Ton	60.00	@	70.00
Ammonium Carbonate, domestic, Lb.	13 1/2	@	14
Ammonium Chloride, gray, Lb.	12	@	14
Aqua Ammoniac, 26°, drums, Lb.	5 1/4	@	6
Arsenic, white, Lb.	8 1/4	@	9 1/2
Barium Chloride, Ton	90.00	@	95.00
Barium Nitrate, Lb.	10 1/2	@	12
Barytes, prime white, foreign, Ton	—	@	—
Bleaching Powder, 35 per cent., 100 Lbs.	4.00	@	4 1/5
Blue Vitriol, Lb.	11 1/4	@	12
Borax, crystals, in bags, Lb.	8	@	8 1/4
Boric Acid, powdered crystals, Lb.	12 1/2	@	12 1/2
Brimstone, crude, domestic, Long Ton	35.00	@	—
Bromine, technical, bulk, Lb.	1.40	@	1.50
Calcium Chloride, lump, 70 to 75% fused, Ton	23.00	@	23.00
Calcium Chloride, granulated, Ton	39.00	@	—
Caustic Soda, 76 per cent., Lb.	4 1/5	@	4 1/5
Chalk, light precipitated, Lb.	4 1/2	@	—
China Clay, imported, Ton	18.00	@	30.00
Feldspar, Ton	8.00	@	15.00
Fuller's Earth, foreign, powdered, Ton	\$35.00	@	—
Glauber's Salt, in bbls., 100 Lbs.	57	@	60
Green Vitriol, bulk, 100 Lbs.	1.10	@	1.15
Hydrochloric Acid, commercial, 18°, Lb.	1 1/4	@	1 1/4
Hydrochloric Acid, C. P., conc., 22°, Lb.	1 1/4	@	1 1/4
Iodine, resublimed, Lb.	4.25	@	4.30
Lead Acetate, white crystals, Lb.	12 1/4	@	13
Lead Nitrate, Lb.	15 1/2	@	15 1/4
Litharge, American, Lb.	9 1/4	@	9 1/4
Lithium Carbonate, Lb.	1.02	@	1.05
Magnesium Carbonate, U. S. P., Lb.	20	@	21
Magnesite, "Calcined", Ton	6.00	@	7.00
Nitric Acid, 36°, Lb.	4 1/4	@	4 1/2
Nitric Acid 42°, Lb.	5 1/4	@	5 1/4
Phosphoric Acid, sp. gr. 1.750, Lb.	34	@	36
Phosphorus yellow, Lb.	1.01	@	1.15
Plaster of Paris, Bbl.	1.50	@	1.70
Potassium Bichromate, casks, Lb.	39 1/2	@	40
Potassium Bromide (granular), 100 Lbs.	1.30	@	1.35
Potassium Carbonate, calcined, 88 @ 92%, Lb.	3.2	@	34
Potassium Chlorate, crystals, spot, Lb.	61	@	62
Potassium Cyanide, bulk, 98-99 per cent., Mixture	2.35	@	2.40
Potassium Hydroxide, 88 @ 92%, Lb.	84	@	86
Potassium Iodide, bulk, Lb.	3.45	@	—
Potassium Nitrate, Lb.	27	@	30
Potassium Permanganate, bulk, Lb.	2.75	@	3.00
Quicksilver, flask, 75 lbs., Lb.	\$80.00	@	—
Red Lead, American, dry, Lb.	9 1/4	@	10 1/4
Salt Cake, glass makers', Ton	14.00	@	15.00
Silver Nitrate, Oz.	46 1/4	@	—
Soapstone in bags, Ton	8.00	@	12.00
Soda Ash, 58%, 100 Lbs.	2.85	@	2.90
Sodium Acetate, Lb.	9	@	9 1/2
Sodium Bicarbonate, domestic, 100 Lbs.	1.65	@	1.75
Sodium Bicarbonate, English, Lb.	3 1/2	@	3 1/4
Sodium Bichromate, Lb.	17	@	17 1/2
Sodium Chloride, Lb.	24	@	26
Sodium Fluoride, commercial, Lb.	—	@	—
Sodium Hyposulfite, 100 Lbs.	1.50	@	1.65
Sodium Nitrate, 95 per cent, spot, 100 Lbs.	3.25	@	3.40
Sodium Silicate, liquid, 100 Lbs.	1 1/4	@	3
Sodium Sulfide, 30%, crystals, in bbls., Lb.	1 1/2	@	1 1/4
Sodium Bisulfide, liquid, 32 s. g., Lb.	.01	@	.01 1/4
Strontium Nitrate, Lb.	40	@	42
Sulfur, flowers, sublimed, 100 Lbs.	2.30	@	2.70
Sulfur, roll, 100 Lbs.	1.95	@	2.05
Sulfuric Acid, chamber, 66° Bé., Ton	27.00	@	30.00
Sulfuric Acid, oleum (fuming), Ton	35.00	@	40.00
Talc, American white, Ton	9.00	@	12.00
Terra Alba, American, No. 1, 100 Lbs.	85	@	90
Tin Bichloride, 50°, 100 Lbs.	13.50	@	—
Tin Oxide, Lb.	46	@	46 1/2
White Lead, American, dry, Lb.	8 1/4	@	—
Zinc Carbonate, Lb.	24	@	26
Zinc Chloride, commercial, Lb.	13	@	14
Zinc Oxide, American process XX, Lb.	11	@	11 1/4
Zinc Sulfate, Lb.	6 1/4	@	6 1/4

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls., Lb.	48	@	50
Acetic Acid, 56 per cent, in bbls., Lb.	7 1/4	@	7 1/4
Acetic Acid, glacial, 99 1/4%, in carboys, Lb.	28	@	25 1/4
Acetone, drums, Lb.	22	@	23

Alcohol, denatured, 180 proof, Gal.	64	@	64
Alcohol, grain, 188 proof, Gal.	2.70	@	2.72
Alcohol, wood, 95 per cent, refined, Gal.	1.00	@	1.02
Amyl Acetate, Gal.	3.80	@	4.00
Aniline Oil, Lb.	2 1/4	@	22
Benzoic Acid, ex-toluol, Lb.	8.00	@	9.00
Benzol, 90 per cent., Gal.	55	@	36
Camphor, refined in bulk, bbls., Lb.	85	@	86
Carbolic Acid, U. S. P., crystals, drums, Lb.	4 1/2	@	52
Carbon Bisulfide, Lb.	5 1/2	@	6 1/4
Carbon Tetrachloride, drums, 100 gals., Lb.	15 1/2	@	16
Chloroform, Lb.	60	@	61
Citric Acid, domestic, crystals, Lb.	64	@	66
Cresotee beechwood, Lb.	2.00	@	2.25
Cresol, U. S. P., Gal.	1.25	@	1.30
Dextrine, corn (carloads, bags), 100 Lbs.	3.90	@	1.95
Dextrine, imported potato, Lb.	12	@	13
Ether, U. S. P., 1900, Lb.	15	@	20
Formaldehyde, 40 per cent., Lb.	12	@	12 1/2
Glycerine, dynamite, drums included, Lb.	53	@	53 1/2
Oxalic Acid, in casks, Lb.	43	@	44
Pyrogallie Acid, resublimed bulk, Lb.	3.25	@	—
Salicylic Acid, Lb.	0.90	@	1.00
Starch, cassava, Lb.	—	@	—
Starch, corn (carloads, bags) pearl, 100 Lbs.	2.85	@	2.90
Starch, potato, Lb.	6	@	7
Starch, rice, Lb.	8 1/4	@	10
Flour, sago, Lb.	4.60	@	4.75
Starch, wheat, Lb.	5	@	6
Tannic Acid, commercial, Lb.	60	@	70
Tartaric Acid, crystals, Lb.	66	@	68

OILS, WAXES, ETC.

Beeswax, pure, white, Lb.	45	@	50
Black Mineral Oil, 29 gravity, Gal.	13 1/2	@	14
Castor Oil, No. 3, Lb.	14 1/2	@	17
Ceresin, yellow, Lb.	14	@	18
Corn Oil, crude, 100 Lbs.	11.25	@	11.50
Cottonseed Oil, crude, f. o. b. mill, Gal.	81	@	82
Cottonseed Oil, p. a. y., Lb.	12 1/2	@	12 1/4
Menhaden Oil, crude (southern), Gal.	68	@	69
Neat's-foot Oil, 20°, Gal.	1.20	@	1.30
Paraffine, crude, 120 m. p., Lb.	5 1/4	@	5 1/4
Paraffine Oil, high viscosity, Gal.	29 1/2	@	30
Rosin, "F" Grade, 280 lbs., Bbl.	6.80	@	—
Rosin Oil, first run, Gal.	38	@	—
Shellac, T. N., Lb.	40	@	41
Spermaceti, cake, Lb.	23	@	25
Sperm Oil, bleached winter, 38°, Gal.	1.02	@	1.03
Spindle Oil, No. 200, Gal.	24	@	25
Stearic Acid, double-pressed, Lb.	14 1/2	@	14 1/4
Tallow, acidless, Gal.	1.04	@	1.05
Tar Oil, distilled, Gal.	34	@	36
Turpentine, spirits of, Gal.	56 1/2	@	—

METALS

Aluminum, No. 1, ingots, Lb.	60	@	61
Antimony, ordinary, Lb.	14 1/4	@	14 1/2
Bismuth, N. Y., Lb.	3.05	@	3.10
Copper, electrolytic, Lb.	28	@	28
Copper, lake, Lb.	28	@	28
Lead, N. Y., 100 Lbs.	7.50	@	—
Nickel, electrolytic, Lb.	50	@	55
Platinum, refined, Oz.	90.00	@	—
Silver, Lb.	74 1/4	@	—
Tin, Lb.	42 1/2	@	—
Tungsten (WGs), Per Unit.	17.00	@	—
Zinc, N. Y., 100 Lbs.	9.25	@	—

FERTILIZER MATERIALS

Ammonium Sulfate, 100 Lbs.	4.35	@	4.40
Blood, dried F O B Chicago, Unit	4.05	@	—
Bone, 4 and 50, ground, raw, Ton	32.00	@	33.00
Calcium Cyanamid, Unit of Ammonia	2.75	@	—
Calcium Nitrate, Norwegian, 100 Lbs	—	@	—
Castor Meal, Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works, Unit	4.50	@	10
Phosphate, acid 16%, Ton	11.75	@	12.00
Phosphate rock; f. o. b. mine, Ton	2.00	@	2.10
Tennessee, 78-80 per cent., Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent., Ton	390.00	@	400.00
Pyrites, furnace size, imported, Unit	15 1/2	@	16
Tankage, high-grade; f. o. b. Chicago, Unit	3.90	@	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

AT EASTON, PA.

Volume IX

MARCH 1, 1917

No. 3

Editor: CHARLES H. HERTY

Assistant Editor: LEOLA E. MARRS

Advertising Manager: M. A. WILLIAMSON

ADVISORY BOARD

H. E. BARNARD, H. K. BENSON, F. K. CAMERON, B. C. HESSE, A. D. LITTLE, A. V. H. MORY, M. C. WHITAKER

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly

Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879

All communications should be sent to The Journal of Industrial and Engineering Chemistry,

35 East 41st Street, New York City

Telephone: Vanderbilt 1930

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

Chemists and the Country's Crisis.....	224
America for Americans.....	224
Investments for Wartime Profits of the Chemical Industries.....	226
Hail to Branigan!.....	227
Press and Publicity Committees for Local Sections.....	228
Announcement.....	228
No Nichols Medal This Year.....	228
Chemical Abstracts Again in the Saddle.....	228

REPORT OF AMERICAN INDUSTRIAL COMMISSION TO FRANCE. 229

A Survey of the Chemical and Allied Industries in France during the War. F. J. LeMaistre.....	229
---	-----

ORIGINAL PAPERS:

The Fixation of Nitrogen. John E. Bucher.....	233
The Volatilization of Potash from Cement Materials. E. Anderson and R. J. Nestell.....	253
The Effect of Temperature and Duration of Reaction on the Formation of Light Oils in Coal Carbonization at Atmospheric Pressure. M. C. Whitaker and W. R. Crowell.....	261
Inflammability of Carbonaceous Dusts. H. H. Brown.....	269
A Study of Commercial Beechwood Creosote. H. K. Smith and S. F. Acree.....	275
A Method of Producing Crude Wood Creosote from Hardwood Tar. R. C. Judd and S. F. Acree.....	276
Some Observations on the Influence of Humidity on the Physical Constants of Paper. Otto Kress and Philip Silverstein.....	277
Further Studies on a Numerical Expression for Color as Given by the Ives Tint Photometer. Otto Kress and G. C. McNaughton.....	282
The Chemistry of Wood Decay. Paper I. Introductory. Robert E. Heston, Rose and Martin William Lane.....	284
The Effect of Exposure on Commercial Limes. I. Clyde Whetzel.....	287
Studies on the Phenoldisulphonic Acid Method for Determining Nitrate in Soil. Charles W. Davis.....	290

A Note on the Detection and Estimation of Small Amounts of Methyl Alcohol. Elias Elvove.....	295
Relation of the Fat in Milk to the Solids-not-Fat. Lucius P. Brown and Clarence V. Ekroth.....	297
Chemical Quality of New York City Market Milk. Lucius P. Brown and Clarence V. Ekroth.....	299
Red Peppers. Frank M. Boyles.....	301

LABORATORY AND PLANT:

The Manufacture of Picric Acid from the Medical Standpoint. F. O. West.....	303
A New Direct Reading Precision Refractometer with Uniformly Divided Scale. G. W. Moffitt.....	305

REPORT OF THE JOINT RUBBER INSULATION COMMITTEE... 310

CURRENT INDUSTRIAL NEWS:

Corrosion and Electrical Properties of Steels; Cracking of Petroleum; New Proofing Material; Searchlight Projectors; Coke Industry of New South Wales; Iron Industry in Normandy; Vulcanization; Native and Artificial Asphalt; Electro-Metallurgy of Zinc; Shipbuilding Returns; Economic Utilization of Coal; Coke-Fuel for Electric-Power Stations; Glass Work Developments in England; New Paper-Making Material; Mineral Production of Spain; Articles Declared Contraband; Industrial Combine in Sweden; Cellulose from Spinach; British Board of Trade.....	318
--	-----

OBITUARIES:

Charles Marchand. Richard Bryant Esch.....	321
--	-----

NOTES AND CORRESPONDENCE:

Cooperation in Industrial Research Work. Abstracts and Fellowships in Chemistry. Pittsburgh University, Industrial Fellowship in Industrial Chemistry. Municipal University of Mexico. Study of Nitrogen Dioxide and Sulfur in the Exhaust of War Automobiles. The Sampling of Fertilizers. A Correction.....	321
---	-----

PERSONAL NOTE:

Government Publications.....	324
------------------------------	-----

NEW PUBLICATIONS:

Malting.....	325
--------------	-----

EDITORIALS

CHEMISTS AND THE COUNTRY'S CRISIS

On February 5th President Stieglitz sent the following telegram to President Wilson:

PRESIDENT WILSON, *The White House, Washington*

The American Chemical Society, with over eight thousand members, begs to place its services at your command, especially in matters facilitating preparations of munitions, supplies, medicinal remedies, and other chemical materials.

(Signed) JULIUS STIEGLITZ,
President, American Chemical Society

In reply the following acknowledgment was received:

THE WHITE HOUSE, WASHINGTON

The President deeply appreciates your very generous and patriotic proffer of your services, and he wishes in this informal way to express his grateful thanks.

On February 15th Secretary Charles L. Parsons, sent the following letter to the Secretary of War:

HON. NEWTON D. BAKER, *Secretary of War, Washington*

Professor Julius Stieglitz, President of the American Chemical Society, on behalf of the Society, requests me to offer to you, or to any of the Bureaus of the War Department, any assistance which the Society can render in the present international complications. The Society now has nearly nine thousand members covering all branches of chemical industry in all sections of the country. They are organized into forty-nine local sections. The American Chemical Society, its local sections, and, we believe, its individual members are at your service. It is already represented by two of its prominent members on the Naval Consulting Board, who are at liberty to call on the Society for any assistance which the Navy may require. We are equally anxious that the War Department shall feel that the chemists of this country represented by the American Chemical Society are placed at your service and your command, especially in matters facilitating the preparation of munitions, supplies, medicinal remedies and other chemical materials.

(Signed) CHAS. L. PARSONS,
Secretary, American Chemical Society

In this grave period of our country's history, the chemists of America pledge to President Wilson their undivided loyalty and untiring service. Our organization bears the proud title, "The American Chemical Society," and whatever America's call may be its chemists stand ready to respond.

Much has been said and written within the last two years of the important rôle of the chemist in modern warfare and the thought, broadened to include normal conditions, has gained firm lodgment in the national consciousness, bringing American chemists and the American people into closer and more cordial relationship. The thought carries with it no undue elation but rather a sober realization of the responsibilities which must be worthily met, responsibilities bearing not only upon the direct production of munitions and of other necessities for both the army and the navy but also upon the efficient operation of all industrial processes which will conserve to the utmost the resources of our land, the food and raiment of our people and the vigor of our race.

In this spirit we offer our services.

AMERICA FOR AMERICANS

On February 1, 1917, Germany began, without advance notice, the ruthless U-boat warfare on all merchantmen. This latest policy led to our severance of diplomatic relations with that country. With the conviction that events of the near future will inevitably draw us into active participation in the great world conflict, we have begun to clear our decks for action. Our representatives in Congress, laying aside all partisan feelings, have rightly stood squarely behind our President. Hundreds of millions have been appropriated for the navy and the army and for coast defense. Every effort is being made to coordinate all elements of national strength and to insure maximum efficiency in all lines when the fated day arrives.

In these busy days of "setting our house in order," there has been one abhorrent neglect. There still remains upon our statutes in Section 501 of the Dye-stuff Section of the General Revenue law an exception whereby the following classes of coal-tar compounds are relieved from the special duty of 5 cents per pound: "natural and synthetic alizarin and dyes obtained from alizarin, anthracene and carbazol, natural and synthetic indigo and all indigoids whether or not obtained from indigo, and medicinals and flavors."

To the average citizen—doubtless, indeed, to the average congressman—the enumeration of these peculiar sounding chemical terms has little significance, but to those who have followed closely the steps leading to this enactment the clause has a sinister meaning. Wherever the full measure of protection, both ad valorem and special was accorded these dyestuffs there has been remarkable industrial activity and development; where it was withheld, as in the excepted lines mentioned above, growth has been seriously hampered and in many cases completely prevented. Yet every new coal-tar dyestuff plant erected adds one more unit to the list of factories which can be quickly converted in time of war to munitions plants for the prompt manufacture of coal-tar high explosives. Furthermore, and of greatest importance, each such new plant would house operatives, foremen, superintendents and chemists who could serve as trained nuclei for larger groups in high explosives manufacture: this contention has been abundantly attested in public legislative hearings and in press accounts of the present activities of German dyestuff plants. Must our public interest be sacrificed, therefore, by the retention of this excepting clause in our dyestuff legislation? A thousand times we say, "No"! Every patriotic impulse demands that this clause, which has stamped upon its face in scarlet letters the words "Special Privilege," be removed from our statutes. The wording of that clause was never suggested by American chemical manufacturers. It was stricken by the Senate from the original House legislation at the earnest solicitation of American manufacturers but it was restored to the bill at the insistence of the House representatives in the Conference Committee. To be more specific, only one consumer has asked for special favors as to these

in the bill its classifications of last year and, having replaced them, stand by them to the end in the Conference Committee?

If Caesar Cone represents himself alone in this matter he has too much influence. How is it that he alone can negative a nation-wide demand for a complete American dyestuff industry? If he represents others will he or Mr. Kitchin publicly state who is so represented?

INVESTMENTS FOR WARTIME PROFITS OF THE CHEMICAL INDUSTRIES

The abnormal conditions of the past two years, with the excess of demand over supply of chemical products, has resulted naturally in a period of sunshine for the chemical industries of America. The ability of our manufacturers as financiers has been amply demonstrated by the fact that, although comfortable dividend payments have been made, other portions of profits have been devoted to plant expansions, to making better provision for plant depreciation, and to allowing good reserves for a future "rainy day." But are these lines of disposition of profits all-sufficient? Are there not other fundamental matters bearing on the future welfare of our chemical industry which stand closely related to these industries as a whole and which should therefore receive the general support of all industries individually and collectively? Two such items occur to us as urgently calling for the broad-minded consideration of our industrial leaders.

THE DECENNIAL INDEX OF CHEMICAL ABSTRACTS

Through *Chemical Abstracts*, the American Chemical Society places bi-monthly at the disposal of its readers a review of the world's chemical literature. For some time *Abstracts* has occupied the unquestionable position of being the greatest abstract journal ever published. The amount of material handled during the past ten years of its existence has been so enormous that the Council of the Society has felt compelled to publish a Decennial Index. The first ten volumes will thus be placed efficiently at the disposal of very busy chemists, who will have at hand complete bibliographies of each subject and author during the past decade. The industries have a very direct interest in this time-saving undertaking.

The members of the Society realized at once the value of the publication of such an index. The Editor had estimated that the cost of publication would not be more than \$10.00 per subscriber, in case 2000 subscribers were assured. While more than 2500 subscribers have been secured, the general advance in costs of materials and labor have combined to increase the expense as originally estimated. Furthermore, it has been found that the editorial work required to give the maximum efficiency to the volume is greater than the first estimate, and the adoption of the convenient entry-a-line form for the index has also added greatly to the original space requirements. More important than all of these considerations, however, is the fact that so valuable a publication should not be limited to the present actual subscribers but should furnish a considerable stock to be available for the constantly increasing membership of the Society.

A sum approximating \$10,000 above the subscrip-

tions is necessary to make this great work a complete success. Secretary Parsons has been authorized by the Directors to canvass the chemical industries for contributions to this fund. While only a few manufacturers have been approached, the response has been so cordial and hearty that it can be confidently predicted that the industries will stand squarely behind this noteworthy undertaking.

A CENSUS OF CHEMICAL IMPORTS OTHER THAN DYESTUFFS

The fundamental basis of the application of chemistry through industrial processes is the law of supply and demand. Our government furnishes through the Census and the publications of the Department of Commerce that which purports to be the statistical basis for our industries. This material is so lacking in detailed classification that its service is but limited in legitimate expansion under the hurry call of the present times. While ideal conditions demand a detailed census of productions, the more restricted and urgent need is for a detailed classification of imports of chemicals during a typical pre-war fiscal year. The compilation of such facts has already been partly accomplished by the publication of the Dyestuff Census by the Department of Commerce. Dyestuffs, however, constitute only a limited portion of imports of chemicals, and the same reasons which called it forth demand also a census of chemicals other than dyestuffs. In the December, 1916, issue of *THIS JOURNAL* an official of the Department of Commerce very clearly pointed out this need and stated that while the machinery for such a study was available in his Bureau, unfortunately adequate funds were not at hand. While such funds might be secured through the slow channels of congressional appeal, the situation from the chemical manufacturer's standpoint calls for prompter action. It was therefore suggested that the work be undertaken by co-operation of the American Chemical Society with the Bureau of Foreign and Domestic Commerce, the census to be published in *THIS JOURNAL*. The suggestion was so commendable that we, as President of the Society at that time, conferred with Dr. E. E. Pratt, Chief of the Bureau. At our request he prepared an estimate of the total cost of the undertaking. This amounted to \$4,000. It was further stated that there would be no objection from the Bureau's standpoint if private corporations aided in raising the \$2,000 expected of the American Chemical Society, the only stipulation being that the funds should be placed in the hands of the Treasurer of the Society and that the results of the study should be made known simultaneously to all manufacturers. In the Minutes of the Annual Meeting of the Directors of the Society on December 9, 1916, is the following record: "The Directors heartily approve of co-operation between the American Chemical Society and the U. S. Bureau of Foreign and Domestic Commerce in the compilation of a detailed statistical review of the imports of chemicals, other than dyestuffs, provided the necessary funds are furnished by the industrial chemical interests."

Several prominent chemical manufacturers were interviewed by us in this connection, and one of the

first acts of President Stieglitz was the appointment of a committee to raise the needed funds. This committee, consisting of Charles Baskerville, J. Merritt Matthews and Chas. H. Herty (*Chairman*), is now preparing to solicit funds.

It is sincerely to be hoped that the response on the part of the industries will be prompt and unanimous so that the actual work of compilation from the government records can be immediately begun. Only thus can we overcome the handicap under which we labor as compared with the chemists of Germany who have always been furnished by their government with the fullest possible detailed statistics on which to build the splendid chemical industry of that land.

HAIL TO BRANEGAN!

Have you ever met James A. Branegan of Philadelphia? If not, you have missed something. We had that pleasure a few days ago, for we looked him up, being anxious to learn something of the personality of the man whose name is so closely associated with the recent remarkable growth of the Philadelphia Section of the American Chemical Society, a Local Section whose membership has doubled within the past three years.

Genius displays itself in many forms and in the persuasive art of getting new members Branegan is a true genius. In him we found a remarkable combination. Just think of it—Widmann Medalist for his research on dyestuffs, salesman of "intermediates" for a great chemical organization, one-time feather-weight champion of Philadelphia, author of "The Scientist of Prehistoric America," and present holder of the championship of the world for getting new members for a chemical organization. This many-sidedness is not difficult to understand when one notes the aggressive air, the devotion to the matter in hand, the happy heartedness, the good judgment and sound common sense, and the fine sentiment which underlies his every thought.

We were, however, particularly anxious to learn how he managed to get so many new members, what were his methods of approach, his arguments, his general attitude in the matter. He talked freely and his answers to questions were illuminative.

"I never ask a man 'Don't you want to join the American Chemical Society?' that would give him a chance to say 'No,' and that would tend to end the interview." (There was the boxing instinct which had led to a championship; no defensive fighter, but aggressive through and through.)

"In the first place I always have a list of prospects with me. If they are very young men just starting out, I talk to their employers, otherwise to the man himself. Then I study my prospect just as I study the man to whom I want to sell something; I know him thoroughly before bringing up the subject." (There is the spirit of the investigator!) "Then when I do turn loose he doesn't have time to catch his breath; I tell him about the meaning of organization to men in any walk of life, of the great results accomplished by the Society through its publications and its meetings, how the presence near-by of its journals keeps one always brushed up on subjects

he has to handle, how one is sure to get into a rut and begin slipping backward if he doesn't know men and their work;" (Can't you see that uppercut with the left and that right-hand jab!) "how one fails to qualify for a better position if he fails to make use of such an opportunity, how already more than eight thousand men have banded themselves together to lift American chemistry and chemical industries to the very highest possible point. The prospect doesn't get a chance to say a word, but I am watching him closely and soon I see by his eye that the psychological moment has arrived—out from my pocket comes the ever present application blank and soon



JAMES A. BRANEGAN, *Chairman Membership Committee Philadelphia Section American Chemical Society*

the job is finished—and I get the \$10 membership dues too. Sometimes he doesn't have the amount with him; then I lend it to him and I never yet have lost a cent from such loans."

"Why do you do this, Mr. Branegan?" we asked.

"Because I love the American Chemical Society. I am grateful for all the good it has done me and I owe it something in return. A man who receives from and in turn contributes nothing to an organization gives a pretty good imitation of a leech. No man can get many members unless he truly loves the Society; if that feeling is in his heart his mouth will speak wisely.

"No, I don't want any position but Chairman of the Membership Committee. Perhaps I am a little 'nutty' on the subject. Well, it is my hobby. I get lots of fun and satisfaction out of it, and there's always plenty of work of this kind about."

We sat around at his talk. It put a new light. We felt inspired in our own way for the future. Oh, for a thousand like him! What possibilities suggest themselves! All hail to Branegan!

PRESS AND PUBLICITY COMMITTEES FOR LOCAL SECTIONS

In the February issue of the *Catalyst*, published by the Philadelphia Section, an account is given of the steps being taken for the appointment of a Local Press and Publicity Committee of members expert in different fields of chemistry who will supply the newspapers within the territory of that Section "with correct information and honest criticism" and who will "stand ready and willing at all times to be consulted by the press." One of the first fruits of that movement was the presence of Mr. M. D. Edmonds, Business Editor of the *Public Ledger*, at a local section meeting with consequent intelligent publicity of important papers presented at the meeting.

The Chicago Section has for some time had such a Committee. The Pittsburgh Section, on February 15th, took similar action, authorizing its chairman to develop a similar Committee for that section.

Such steps are heartening. Too long we have talked solely to each other and then wondered why our profession was not more highly appreciated by the general public. Too often we have cried out among ourselves against some of the travesties appearing in the daily press and purporting to be representative of what the public wished to read and therefore of what the managing editors were willing to publish. We are convinced that our criticisms of both the public taste and newspaper policies have been unjust. We have been selfishly lazy and neglectful in this important matter, and sometimes we have held ourselves aloof from popular presentation, though well qualified for such, assuming the snobbish attitude that such effort was the part of minds of lower order. Wherever the press has been approached in a spirit of true coöperation the response has been immediate: the collection of recent newspaper clippings presented to our office by the Press & Publicity Committee of the American Chemical Society furnish ample proof of these contentions.

In this connection we would suggest to President Stieglitz that the Chairman of each Local Section Press and Publicity Committee be appointed a member of the similar Committee of the Society. Through such connections the work of all of these Committees can be coördinated and their effectiveness largely increased.

ANNOUNCEMENT

While bringing to the office of Editor a mass of ignorance concerning technical details of the work, we also brought with us a deep-rooted conviction as to the undesirability of controversial communications being drawn out from month to month until the attenuation almost reaches the vanishing point. Our columns stand gladly open for communications in criticism of matter which has previously appeared, but we hereby announce that the future policy of THIS JOURNAL will be to submit copy of such communications to the authors so criticized with the request for their reply. Both communications will then be printed in the next earliest issue and it is hoped that this amount of discussion will suffice all parties concerned.

NO NICHOLS MEDAL THIS YEAR

This brief announcement, following the meeting of the Committee charged with the responsibility of annually awarding the Nichols medal for the best research in pure chemistry, gives pause for serious thought.

After careful consideration of American chemical literature and with the suggestions of the Secretaries of the Local Sections in hand, the Committee felt that during the year 1916 no research had been published which was of sufficient fundamental importance and intrinsic worth to justify the award of the medal.

It is possible that such researches are in progress but are not yet sufficiently completed to justify publication. If so, all is well, for nothing could be more unfortunate than undue haste in publication.

On the other hand, the thought constantly obtrudes itself that the immediate necessity for the expansion of our chemical industries, the drain upon University staffs for heads of industrial research laboratories, the efforts spent in national scientific organization and the distractions of this distressing period of the world's history have produced an atmosphere uncongenial and unsuited to that quiet growth of ideas and their severe testing in the laboratory which makes for real progress in the science of chemistry.

If these latter thoughts be the correct explanation, the situation is deeply to be regretted, for greatest progress can be realized only through marked advances in both pure and applied chemistry.

CHEMICAL ABSTRACTS AGAIN IN THE SADDLE

During the past year the Editor of *Chemical Abstracts* has been seriously hampered in his work, and the usefulness of that Journal has been markedly curtailed, by the action of the British censors in holding up the shipments of many foreign journals, notably those from Germany. Through the courteous coöperation of the Department of State and especially through the efforts of the Librarian of Congress, all obstacles have been removed and the journals consigned to the American Chemical Society have been duly forwarded as shown in the following letter from Editor Crane:

Dear Dr. Herty:

Because I am sure that you will be interested I am writing to tell you that at last I have succeeded in obtaining a large shipment of German journals on the basis of the special permit obtained last year from the British Government with your help. We have most of the important journals nearly complete to the end of 1916. I have been told that some of these copies are the only ones in this country. We plan to publish abstracts which will be unusually long and detailed in order to make up for the lack of journals in this country in so far as possible.

Thanking you again for your help in this connection, I am
Sincerely yours,

FEBRUARY 12, 1917

E. J. CRANE

That which it is impossible for individuals to accomplish has been done for the American Chemical Society. One more fine illustration of the benefits of organization and coöperation.

REPORT OF AMERICAN INDUSTRIAL COMMISSION TO FRANCE

The American Industrial Commission to France, organized and sent out by the American Manufacturers' Export Association of New York City, left New York at the end of August, 1916, and spent seven weeks inspecting the principal industrial centers of France. The itinerary arranged by the French authorities, represented by Mr. Maurice Damour, Deputy for Bordeaux, and Chief of the French Industrial Commission to the United States of 1915, included all of the important industrial cities of France and covered the entire range of French industrial activity. The investigatory character and large spirit of the French Commission, whose visit to America was being repaid, was strictly adhered to throughout, with gratifying sentimental success as regards the impression created upon the members of the inviting Government, the press, and the French people generally.

The personnel of the Commission was as follows:

W. W. NICHOLS, *Chairman*, Vice President, American Manufacturers' Export Association, New York.

J. G. BUTLER, JR., Vice-President, Brier Hill Steel Company, Youngstown, Ohio.

S. W. FAIRCHILD, President, Drug Section, New York Board of Trade.

A. B. FARQUHAR, Vice-President, Chamber of Commerce of the United States.

G. B. FORD, City Planning Engineer, Member of Geo. B. Post & Sons, New York City.

S. F. HOGGSON, President, Hoggson Brothers, New York City.

F. J. LEMAISTRE, Consulting Chemical Engineer, E. I. du Pont de Nemours & Company, Wilmington, Delaware.

J. R. MACARTHUR, President, MacArthur Bros., New York City.

C. O. MAILLOUX, Consulting Engineer, New York City.

C. G. PRIFFER, Vice-President, Geo. Borgfeldt & Company, New York City.

J. E. SAGUE, Former New York Public Service Commissioner; former Vice-President, American Locomotive Company, New York City.

E. A. WARREN, Vice-President, Universal Winding Company, Boston, Mass.

E. V. DOUGLASS, Secretary, American Manufacturers' Export Association, New York City.

E. GARDEN, French Secretary to the Commission.

The Commission recognized that America must become an important factor in European reconstruction after the war and that whatever tends to throw light on the specific needs of one nation cannot fail to call attention to the similar needs of all.

The following survey of the chemical and allied industries in France was prepared especially for THIS JOURNAL by Mr. Lemaistre. [EDITOR.]

A SURVEY OF THE CHEMICAL AND ALLIED INDUSTRIES IN FRANCE DURING THE WAR

By F. J. LEMAISTRE.

Member of the American Industrial Commission to France

The war has completely changed the normal conditions of the French chemical industry and greatly increased its importance. The following is but a brief survey of the present conditions of this important industry. It is to be regretted that vital statistics are missing in this report. This is due to the government regulations prohibiting factories working on orders for the government issuing statements of any kind. In an analysis of existing conditions, it should not be overlooked that, in many cases, best operating practices have not been selected, due to stress of production at maximum capacity.

From the few plants visited by the Commission, we gathered the impression that the war had convinced many French manufacturers that they were operating on altogether too small a scale, consistent with low cost of production and that, if, after the war, they were to place themselves in a position to compete with German manufacturers, it would be essential to drop certain lines of manufacture and encourage the combination of the others as far as possible.

It has been suggested in numerous instances by those well advised that in coordinating the more important branches of the chemical industries it will be necessary to abandon the old, inefficient plants as well as those plants illogically located both as to railway facilities and distribution of finished products. Such statements were made at many different points during our trip through France by those best qualified to judge. Books have been published expressing this opinion by some of the best advised chemists in France. Such statements as these may be found in the monthly bulletins of the *Société d'Encouragement pour L'Industrie Nationale*.

As regards chemical plant construction, the tendency appears to be to erect permanent buildings which compare very favorably with our best types in America. In many instances, however, insufficient consideration has been given to possible plant expansion, which is in line with the general conservatism of the French people.

France had been a heavy purchaser of chemicals from Germany prior to the war. There is now a general disposition to seek American sources of supply. It is intimated, however, that, if the United States is to compete with Germany in this respect, it will be an essential prerequisite that the American manufacturer study French conditions closely, the French being perfectly candid in their statements that in many instances the German chemical manufacturers were better informed of their probable requirements than they were themselves. Some economists have gone so far as to intimate that, the ultimate success of this trade development with France will depend upon the proper distribution throughout the country of American representatives, conversant with the French language and thoroughly familiar with the chemical trade. Men of wider range of knowledge than those usually assigned to such tasks must be supplied to the American manufacturer.

The old difficulty of the chemical system was referred to, it being exceedingly difficult for the French people to understand why or how could a country as America should be so slow in the adoption of the metric system. The American Association have had an opportunity to take the initiative in this much needed reform in one country. The present time seems opportune, as many mills and factories without any for export have, during the past two years, been forced to educate their employees in the metric system.

The French government, comprising the Secretary

derived by the German manufacturers due to the fullest privileges regarding the use of denatured alcohol in the industries. Recent legislation has been proposed which will undoubtedly place the French chemical manufacturer on a more satisfactory basis than heretofore as compared with their German neighbors. Alcohol manufacture and control has received a very close study during the past two years. Mr. R. P. Duchemin's report entitled "L'Emploi et Le Régime de L'Alcool dans les Industries Chimiques et Pharmaceutiques," appearing in a recent bulletin of the *Société d'Encouragement pour L'Industrie Nationale*, fully discusses all phases of this problem.

It is of interest to note that about 4,000,000 people are employed in the wine industry in France.

TECHNICAL EDUCATION

Considerable attention is being given to the important subject of technical education. The French people recognize that they are extremely backward in this branch of their educational work and that they compare unfavorably with Germany and Switzerland in numbers of trained chemists. On a unit population basis, Switzerland has 300 chemists and Germany 250, while France has only 7.

It has been suggested that chemical courses in American universities should be made known to French educationalists and that interchange of professors and advanced students be encouraged.

According to the statement of a professor of one of the universities in Paris, the present inferiority of the French chemical industry is due to:

- 1—Lack of standard factory methods.
- 2—Insufficient general knowledge.
- 3—Lack of technical education.
- 4—Banking conditions.

In the readjustment period after the war, it is more than possible that the United States may receive a number of men for post-graduate work and study in our colleges having chemical engineering departments. The business men of France, as well as those financially interested in the chemical industries, appreciate more fully than ever that chemists with only a theoretical knowledge are not competent as plant managers. Men holding such positions must also be thoroughly familiar with engineering. It must be admitted, however, that the experience of intensive chemical manufacture in war time has shown that French chemists, when given responsibility, have developed accordingly. It is realized that the former common practice of confining the chemist to mere analytical work must not be reverted to if efficiency is to be maintained.

The more progressive manufacturers appreciate the importance of the development of industrial research laboratories such as have proven so profitable in Germany, as well as in this country.

CHEMICAL LITERATURE

In addition to the standard monthly chemical periodicals, there have recently been issued several journals devoted especially to industrial chemistry, the aim being to publish articles of special interest to chemical engineers confronted with factory troubles. Publications such as these should be encouraged by all the interested parties, and if combined with the

advantages of a large society made up of research and industrial chemists will do much towards the elimination of petty jealousies now existing between the several small groups of chemists distributed throughout the country. The special traditions of each section of France need not be sacrificed by consolidation into one large society. It is apparent that many of the chemists throughout France are not familiar with the best thought of their own country, due, in the main, to the lack of a satisfactory medium of distribution of such information and lack of travel and free intercourse. In our own country, it has been demonstrated that free intercourse among industrial chemists can be had without sacrificing the secret processes of the different industries represented.

It was our observation that very few of the French technical men know of our more important chemical journals. This is a condition which could be readily corrected to our mutual advantage.

Under the respective headings given below, will be found some general information obtained from those interested in the respective industries. On account of the broad scope of the Commission's work, these remarks are merely a brief survey of the more important branches of the chemical industry.

DYES

After the war, France will be in a better position than formerly to manufacture economically many of the chemicals used in large quantities in this industry. The French Commission, appointed to survey this industry, in their report in the July-August issue of the *Bulletin of the Société d'Encouragement pour L'Industrie Nationale*, state that "more coke ovens will be required if this industry is to be placed on a satisfactory commercial basis." It is also stated that "some agreement must be made with other countries for a steady supply of intermediates." The development of this industry, however, brings up for discussion the question of patents and tariffs, and due consideration must be given to the fact that, until the outbreak of the war, Germany had enjoyed an exceptionally favored position as regards French duties. Under such conditions, the French dye industry could not be properly developed. Some consideration has already been given, at the Allies' Economic Conference at Paris, to combining with the British dye industries to work to a common end, with the view of establishing a definite policy of action for the very complicated conditions which must arise after the war. Whereas too much confidence is not placed on plans for future action, it is thought that a tariff plan approved by the Allies will be better than the drifting policy France has followed in the past.

Statements have also been made that, for some period after the war, there will be an opportunity for the sale of considerable quantities of American dyes in France, because it is to be expected that time will elapse before the newly equipped chemical plants will be capable of furnishing more than a part of the requirements of France and her colonies. The problems arising out of the development of a thoroughly coordinated dye industry in a country depleted of

money and men must be classified as among the most difficult of France's commercial problems.

In 1912, France manufactured coke equivalent to 3,925,000 tons of coal and purchased coke equivalent to 2,847,000 tons of coal, representing a total coke consumption in the metallurgical industries equivalent to 6,772,000 tons of coal or a total tar production of 505,250 tons.

It is estimated by one of the foremost industrial chemists in France that by the adoption of the standard German practice they should have obtained a yield of 53,177 tons of benzol or about four to five times the quantity obtained during 1915. It is further estimated that by the adoption of the standard method of washing illuminating gas there would be 24,000 tons of benzol available from the 5,000,000 tons of coal used in the gas industry, which would make a total benzol production for France of about 76,500 tons. On the same basis of calculation, there would also be available 31,000 tons of naphthalene and 3,100 tons of anthracene.

ELECTROCHEMICAL INDUSTRIES

Great activity has been in evidence in these industries which have a popular interest outside of the chemical profession. In the French Alps alone the horse-power development since the war started has increased from 500,000 to 1,500,000 H. P. and plans are under way for further extensions. There are no figures available to determine what percentage of this increase has been for the chemical industries. Many new lines of manufacture have been started, some of which are fairly established. Many, however, will have to be closely investigated, as, under the existing conditions of operation, cost has been sacrificed in the interest of larger production. At one electrochemical plant visited by the Commission, magnesium, sodium and aluminum were being made, as well as sodium hydroxide, compressed oxygen, etc.

ATMOSPHERIC NITRIC ACID

We were informed that extensive developments have been made in the manufacture of nitric acid from the air during the past two years. The government authorities are fully aware of the importance of the permanent development of this industry on a sound economic basis, inasmuch as upon it are dependent the fertilizer trade and the manufacture of dyes and explosives.

Prof. Fleurent, in his book entitled "Les Industries Chimiques en France et en Allemagne," published by the Conservatoire Nationale des Arts et Metiers, 1916, gives a very interesting discussion on the following processes for the manufacture of nitric acid and nitrogen fertilizers from atmospheric nitrogen: Birckeland, Schönherr, Pauling, Serpek, Haber, Cyanamid.

French chemists have given very close study to the Serpek method of manufacture of nitric acid from the air. In this process bauxite is used. If this process can be worked out on a satisfactory basis, it will connect the nitrate industry with the very important aluminum industry.

As regards Cyanamid manufacture, the production in France is small as compared with other countries.

The following figures were collected by the International Institute of Agriculture:

Year	CYANAMID PRODUCTION—METRIC TONS			WORLD
	France	Germany	Canada	
1912	5000	22,000	32,000	105,000
1913	7500	24,000	48,000	155,000

More recent figures indicate that the world production in 1916 was approximately 210,000 metric tons. The bulk of this increase is attributed to Germany owing to the fact that Germany has had to depend on artificial nitrates, which was not the case in France.

PHARMACEUTICAL CHEMICALS

Those interested in this branch of the industry are fully cognizant of the fact that, through a lack of initiative on their part, they have allowed the control of the manufacture of pharmaceutical chemicals to go to Germany.

The existing French law does not permit patenting any particular pharmaceutical composition and it is claimed that the French tariff has encouraged the German manufacturers in the manufacture of these products. A well developed program for the manufacture of pharmaceutical chemicals and synthetic perfumes has been outlined which ought to do much towards placing these industries on a more permanent basis.

The French perfume manufacturers consider that, on account of climatic conditions, they should have no difficulty in maintaining the lead in the manufacture of perfumes. Mr. Justin DuPont estimates that France exports annually perfumes to the value of \$5,000,000 to \$6,000,000. Active development now exists in the manufacture of artificial perfumes.

SULFURIC ACID MANUFACTURE

The demands of the War Department for sulfuric acid have been such as to insure France being entirely independent of any outside source of supply of this commodity for a long time to come. The largest sulfuric acid plants are located in the south of France.

PAPER INDUSTRY

The Commission visited one of the more up-to-date paper mills of central France at which all grades of paper were being made, from the coarse Manila to the finer grades of writing paper. This plant was operating under water power. The principal woods used were spruce, birch and poplar. Part of the plant was devoted to the sulfite process. From information gathered, it appears that France is independent of outside sources of supply of paper.

It is of interest to note that from Algiers, the French shipped to England in 1912, 117,000 tons of Esparto grass, commonly known as "Alfa." This grass grows wild, needs no cultivation and is used by the English in the manufacture of high-grade writing paper.

CEMENT MANUFACTURE

No Portland cement plants were visited, but we were advised that France had manufacturing capacity for her own requirements and that of her visitors. Conferences with several members of the Chambers of Commerce interested in this industry indicated that considerable of the present cement equipment would have to be replaced by equipment of larger capacity.

REFINING OF SUGAR

On account of government regulation, all refineries are enforced to sell sugar at a fixed price. The single refinery visited by the Commission was working on a government order. The by-product, molasses, is used largely for the production of alcohol, and, as in this country, the residues are employed for combining road materials.

France in 1903 had 296 factories with an output of raw sugar of 1,080,000 tons, equivalent to approximately 6,315,300 tons of beets. France stands second to Germany in her development of the beet sugar industry.

Year	RAW SUGAR OUTPUT IN TONS		GERMANY	
	France	Germany	Sugar yield per 100 kg. beets	Annual consumption per head
1840	22,784	19,700	5.9 kg.	2.5 kg.
1850	62,165	53,300	7.3	3.1
1860	126,480	126,520	8.6	4.3
1870	262,136	126,000	8.6	4.7
1890	750,000	133,600	12.5	8.5
1903	1,080,000	192,000	14.4	13.0
1905	1605,000	14.9	14.9
1906	730,000	2400,000	14.7	17.0
1909	807,500	2037,400	16.3	19.5

In 1908, there were approximately 38,000 employees occupied in the beet sugar industry for a period of two months with an average wage of \$0.73 per day. The 520,000 acres under cultivation in France in 1907 was increased in 1910 to 580,000 acres.

In the period 1903 to 1914, the manufacturing tax on beet sugar was reduced by 40 per cent. During this period, the consumption increased 61 per cent. In Germany, during the same period, there was a 33 per cent reduction in taxation, with an increase in consumption of 60 per cent.

The following tabulation indicates the relative importance of the beet sugar industry:

Year	TOTAL WORLD PRODUCTION OF CANE AND BEET SUGAR 1866 TO 1915	
	Total Production in Lbs.	Percentage Represented by Beet Sugar
1866	4,579,000,000	30.7
1878	7,266,000,000	44.0
1887	11,375,000,000	53.8
1893	14,501,000,000	53.0
1899	17,942,000,000	62.6
1901	21,737,000,000	62.5
1911	38,083,000,000	50.4
1913	40,788,000,000	49.3
1915	40,998,000,000	44.9

MANUFACTURE OF BUTTER SUBSTITUTES AND TABLE OILS

At the city of Marseilles there is an extensive production of a number of butter substitutes and table oils, which are sold under various trade names. These are consumed by the poorer classes of the community for table use, replacing the more costly butter and olive oil, and by the hotels for culinary purposes. Copra, palm kernels and peanuts from the Orient are the crude materials used in these refineries. The refining of the oils is carried on under very strict inspection and numerous government investigations have been made to determine the nutritious properties of these products.

We were informed that the permanent success of this industry had been largely due to the careful chemical control enforced by the majority of the plants. At the early stages of the development of this industry, it was not considered that chemists were necessary. Practically all the plants of the Marseilles district were operating to maximum capacity on government orders.

PETROLEUM

This industry in France is on such a small scale that it cannot, of course, compare with the American petroleum industry. Prior to the war, the bulk of the crude petroleum was obtained from Russia. The replacement of this by American crude oil has required considerable change in refining practice. The refining equipment, on the whole, is smaller than that used in this country and is not of recent design. The urgent demands of the Department of War for motor fuels have necessitated a very active study on the part of the engineers and chemists with a view to determining the relative values of gasoline mixtures, which are termed "Essences." It is considered that much valuable information has already been collected. This, of course, will be available in times of peace. Given below are the official receipts of American petroleum at the port of Marseilles during the past five years. Marseilles is the second largest city in France and has a population of over 500,000.

Year.....	1911	1912	1913	1914	1915	Total 1911-15
Tons.....	48,302	21,657	24,700	18,674	33,902	117,235

PORCELAIN

In the Limoges district, several of the porcelain factories have been turned over entirely to the manufacture of chemical-ware for the Department of War. They have overcome the initial difficulties of this new line of manufacture and now make chemical-ware equal to the best English and German grades. The manufacture of porcelain-ware for the laboratory has received very close study. The French manufacturers claim that they will be in a position after the war to meet the strictest specifications for this line of goods.

Remarkable development has also been made in the manufacture of optical instruments. This industry will be on a very permanent basis after the war.

CELLULOSE

France has been a leading nation in this manufacture for years. This special industry is at a standstill at the present time as the government has called upon all these manufacturers to make nitrocellulose.

SODA INDUSTRY

These plants, many of which are located in the south of France, have been taxed to capacity during the past two years. This is also true of the chlorine industry, these heavy chemicals being made on a scale many times greater than ever before. In 1912, France imported 344,348 tons of soda. Of this amount, about 40,000 tons were used in the chemical industries.

SANITATION AND HEALTH

In France, sanitation and health do not receive the same attention as in America. This is especially true in the chemical industry. In more than one instance, operators were kept in poorly equipped rooms, handling toxic chemicals without adequate supervision. Reference is not made here to exigencies which have developed as a result of the war, but to regular operating conditions.

WILMINGTON, DELAWARE

ORIGINAL PAPERS

THE FIXATION OF NITROGEN¹

By JOHN E. BUCHER

The herein described process for the fixation of nitrogen differs primarily from all those now in commercial use in fixing nitrogen in the form of alkali cyanides instead of in the form of oxides of nitrogen, calcium cyanamid, nitriles, or ammonia. It is further characterized by operating at very moderate temperatures such as 900 to 950° C. so that it is not dependent upon cheap electric power and, it can, because of this moderate temperature, be operated in iron retorts. It is of the utmost simplicity, uses iron, which is the cheapest metallic catalyzer, and does not require pure materials such as nitrogen but can use air or producer gas just as well. It requires no special apparatus and can hence be operated at once with what can be found in practically every manufacturing community. It does not require skilled labor to operate it, and it is preëminently a method which can be installed quickly in an emergency for the preparation of cyanides, ammonia and nitric acid.

These statements are based on a very large amount of chemical and engineering work, most of which was done three to five years ago, and which has appeared only in the form of patents from time to time. I have not heretofore published anything regarding any part of this work.

Meanwhile certain circumstances arose which made it necessary to abandon my work on nitrogen fixation and abnormal political and industrial conditions have affected our country as well as the rest of the world. I think that all thoughtful people agree that we are in no position to face any serious crisis which might suddenly arise.

For example, we are now practically in the midst of an alkali cyanide famine which is causing very serious hardships in a number of our industries and our Government officials estimate that we would need 180,000 tons² of nitric acid per year in case of war with any first-class power and that it is of the utmost importance to have some ready means of getting this from atmospheric nitrogen so as not to be dependent on the hazardous expedient of importing it by ocean transportation in the form of sodium nitrate from South America.

The popular idea seems to be that it is necessary to have cheap hydro electric power to provide such quantities of nitric acid together with a costly plant which would require considerable time for its construction.

The data already accumulated in my work show that electric power is not necessary and that the process can be installed in a short time on any scale desired and at comparatively small expense. I had not intended to publish anything on my nitrogen fixation work for a few years more until I could complete

some further important engineering work connected with it. The above considerations, however, led me to the conclusion that I could not in justice delay action any longer, and hence your kind invitation to present this paper was accepted with the hope of completing the work as opportunity offers.

HISTORICAL

The fixation of nitrogen in the form of alkali cyanides is by far the oldest of all such methods and its first period of great commercial activity dates from 1840 to 1847 when it terminated in failure. In January, 1839, there appeared an abstract of the work of Lewis Thompson³ on "Improvement in the Manufacture of Prussian Blue" with the statement that he had been awarded the Gold Isis medal of the Society of Arts in the previous year for this work. After speaking of the wasteful process of producing cyanides from animal matter then in use, he says:

"Reflecting on these circumstances, it occurred to me that the atmosphere might be made to supply, in a very economical manner, the requisite nitrogen, if allowed to act on a mixture of carbon and potash under favorable circumstances. The experiment proved on trial to be correct, and in some measure exceeded my expectation, for the carbonaceous matter employed may be worked over again many times, and is even improved by each operation. I found it necessary to use iron, for a reason which will be apparent in the explanation of this process: when iron is not employed, a much higher temperature is required."

He ground two parts potash, or pearl-ash, two parts coke and one part iron turnings into a coarse powder and heated the mixture in an open crucible in an open fire to a full red heat for about half an hour, stirring the mass occasionally. He obtained an abundant yield of cyanide which he converted into Prussian Blue.

I regard Thompson's remarkable work as the most basic that has ever been done on the fixation of nitrogen by the cyanide process. He discloses clearly the idea of using the nitrogen of the atmosphere and also states with the utmost clearness that iron is "necessary" in the process if it is to be carried out at a temperature short of "much higher" than a "full red heat."

Thompson's article soon led to very active discussions or investigations throughout the scientific world by some of the most noted inventors of the time, such as Berthollet, Berthollet and Mitscherlich, Fownes and Young,⁴ Langbein,⁵ Rickson, Dillworth, and Bunsen and Playfair.⁶

Practically all their conclusions are embodied in the

¹ *Michigan Agricultural Experiment Station Bulletin No. 1* (1914), p. 10. Also *Michigan Agricultural Experiment Station Bulletin No. 1* (1914), p. 10.

² *Berlin, Trans. Roy. Soc.* **21** (1881), 85.

³ *Edinburgh and Manchester Phil. Mag.* **26** (1818), 1.

⁴ *Fownes and Young, Trans. Roy. Soc.* **26** (1818), 1.

⁵ *Langbein, Trans. Roy. Soc.* **26** (1818), 1.

⁶ *Rickson, Trans. Roy. Soc.* **26** (1818), 1. *Bunsen and Playfair, Phil. Mag.* **26** (1818), 1.

¹ Presented before the 9th Annual Meeting of the American Institute of Chemical Engineers, New York, January 10 to 12, 1917.

² *London, Transactions of the American Engineering Society*, **29** (1916), 83.

³ *Edinburgh and Manchester Phil. Mag.* **26** (1818), 1. *Berthollet, Trans. Roy. Soc.* **21** (1881), 85. *Berthollet, Trans. Roy. Soc.* **21** (1881), 85.

that Thompson had not proved the fixation of nitrogen because it might have come from the coke and some of those who did experimental work then prepared charcoal from sugar and heated it with alkali carbonate in a current of nitrogen. They all omitted the iron turnings and hence either obtained no cyanide, or only traces, or else had to heat it to a very high temperature. They finally concluded, however, that nitrogen could actually be fixed in this manner but that the favorable conditions for fixation were not known.

Commercial work began in 1840 and in 1843 Newton¹ took out the first patent for the formation of cyanides from atmospheric nitrogen. Works were finally located at Newcastle-on-Tyne which regularly produced over one ton of yellow prussiate of potash per 24 hours at a cost of 1.86 francs per pound, by drawing air down through retorts filled with charcoal containing potassium carbonate. These processes completely ignored Thompson's recommendation of the uses of iron and consequently had to be operated at a white heat. This caused poor yields, slow action, much loss of alkali, great expense in constantly renewing the refractory clay retorts which were speedily destroyed by the alkali and the process resulted in great loss of money and failure in 1847.

Since this numerous other attempts have been made to get cyanides from atmospheric nitrogen by methods which in the vast majority of cases did not use iron as a catalyzer. In 1881 to 1885 Victor Alder² of Vienna took out a series of patents in Germany and elsewhere. In the first of these he states that alkali carbonates can be converted into cyanides when heated to redness with carbon in nitrogen and that the process is essentially favored by the presence of metals such as finely divided iron, but that the use of iron is not an indispensable condition as the process succeeds completely even without its use. In a second patent he states that the combination takes place copiously only in the presence of gases containing carbon (hydrocarbons, carbon monoxide, or a mixture of the two) in which metals that are able to transmit carbon, such as iron, manganese, chromium, nickel, and cobalt act extraordinarily favorably as will be shown below. These, together with his other statements made in his patents, constitute such a mixture of truth and falsehood that it is not surprising that failure resulted after six years attempt to work the patents in Germany.

Thompson's original disclosure of the necessity of iron was finally so completely ignored or forgotten that Castner,³ who used alkali metals instead of carbonates, stated that iron is "inert" while Acker,⁴ who also used alkali metals, disclaimed iron as a "reactive" metal in the cyanide synthesis.

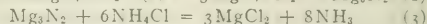
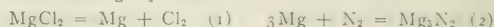
In view of these complete contradictions and the complete failure of the fixation processes depending on the formation of cyanides it is hence not surprising that development took place along the lines of elec-

trical fixation methods such as the arc and Cyanamid processes as soon as the production of large quantities of cheap hydro-electric power was accomplished.

EXPERIMENTAL

I—MAGNESIUM NITRIDE PROCESS

The above hasty study of nitrogen fixation to cyanides did not seem very encouraging and I did not have access to the work of Thompson and Alder at the time. Accordingly some work was done with nitrides with a view to fixing nitrogen according to the following equations:



This process was electrolytic in nature and was designed to affect improvements in the ammonia-soda process. The magnesium chloride would be electrolyzed to magnesium and the resulting metal would be burned in the nitrogen from the towers to fix nitrogen as magnesium nitride. This later would be heated with ammonium chloride obtained from the mother liquors to produce ammonia and regenerate the magnesium chloride for the electrolytic stage. This would greatly modify the ammonia-soda process by fixing its waste nitrogen, recovery of all the waste sodium chloride, elimination of waste liquors containing calcium chloride and the production of chlorine as a new product. It depends, however, on cheap electric power and would depend upon being operated in connection with the ammonia-soda works. As I wished to get a general nitrogen fixation process which was not dependent upon any locality or industry, this work was abandoned.

II—NITROGEN FIXATION WITH ALKALI METALS

The decision was now made to test the chemical principles upon which the fixation of nitrogen to cyanide depended and it was decided to use free alkali metal at first to study the reaction:



An apparatus shown in Fig. 1 was accordingly con-

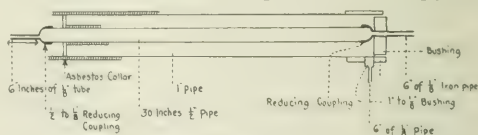


FIG 1

structed of an ordinary 1/2-in. malleable iron pipe about 30 in. long, connected at both ends with a reducing coupling and with 1/8-in. inlet and outlet pipes. This 1/2-in. pipe was then placed inside of a larger outer pipe which had a tee and bushings at one end and a ring of asbestos board at the other. This apparatus gave a means of heating in a combustion furnace while the inner tube was surrounded by an atmosphere of hydrogen or nitrogen to prevent oxides of carbon from diffusing through the walls of the inner tube and forming sodium carbonate with the metallic sodium. Hydrogen diffuses into the inner tube so easily that, with a slow current of nitrogen and a 2-ft.

¹ Bertelsmann, "Die Technologie der Cyanverbindungen," Berlin (1906), p. 85.

² *Ibid.*, pp. 90-91.

³ Castner, U. S. Patent 577,837 (1897).

⁴ Acker, U. S. Patent 1,019,002 (1912).

section red hot, the exit gas at the end of the tube burned and contained about 200 cc. of hydrogen per hour. Carbon monoxide diffuses very much more slowly and was detected with iodine pentoxide.

EXPERIMENT 1—The inner tube was then filled with lampblack containing substantially no ash and the whole heated in a current of hydrogen to a white heat, cooled, opened, and then 14 grams of sodium added at one end and a current of nitrogen passed into the inner tube. Reaction began slowly and continued for three days (25 hours), the current of gas being occasionally reversed to drive sodium vapor first one way and then the other.

The tube was cooled, opened and found to contain perhaps 0.5 gram of unchanged metallic sodium. The tube and contents were washed with water and gave 23.7 grams of sodium cyanide which is 79 per cent of the theory based on the quantity of sodium used.

In another case the inner tube was charged with 80 grams of electrode graphite, powdered to pass through a 100-mesh sieve, and ignited with a current of hydrogen for over one hour. Then it was cooled, 12 grams of metallic sodium were added and then it was heated in a current of nitrogen for 2½ days (about 20 hours) to redness as above and 58 per cent of the theoretical amount of cyanide was obtained.

Quite a number of experiments of this nature were made and while the absorption of nitrogen was sometimes faster than at others, it was always a matter of hours. There is hence no question that cyanide formation is slow under these conditions.

EXPERIMENT 2—I now decided to try my idea that iron should act as a catalyzer notwithstanding the above assertions to the contrary. A ½-in. iron tube was hence heated as before while a current of nitrogen was passing, after being charged with 120 grams finely powdered alcoholized iron, 12 grams of ignited lampblack and after 7 grams of metallic sodium had been pushed into the charge.

When the tube got to a low red heat, absorption of nitrogen began so rapidly that a partial vacuum was formed and the water through which the exit gas bubbles started to rush back towards the hot iron tube and was stopped only by quickly turning on the nitrogen in a torrent. The absorption was practically instantaneous and there was no time to take observations. Only a small quantity of exit gas bubbled through the water and it must have been argon. The whole thing was finished just as soon as the requisite nitrogen could be passed in and 94 per cent of the sodium was converted into cyanide. The absorption was exceedingly sharp and the end of the tube was entirely free from carbon and contained a core of porous iron of a bright silvery luster and so malleable that it flattened out under a pestle.

There were sintered globules of metal showing that the temperature must have risen hundreds of degrees higher inside of the tube than outside owing to the powerful exothermic nature of the reaction. This experiment shows with the utmost sharpness that:

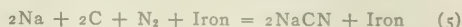
(1) Iron is an exceedingly active catalytic agent in the fixation of nitrogen.

(2) The reaction is powerfully exothermic.

(3) We have a new method for the preparation of argon.

(4) The reaction gives a fine method of separation of nitrogen and the argon group in gas analysis.

We may now write the equation thus:



Suspecting that much of the slow absorption in Experiment 1 was due to the walls of the iron tube, the experiment was repeated by forcing a thin seamless copper tube into the inner ½-in. iron tube. This tube was charged with 4 grams of sodium and some ignited lampblack and heated in a current of nitrogen for 4 hours. No absorption could be noticed and on titration it was found that only 10 cc. of nitrogen had been converted into cyanide. This shows very sharply the catalytic influence of the walls of iron tubes.

III—PURIFICATION OF IRON

The above Experiment 2 and the equation shows that while we are dealing with the fixation of nitrogen with sodium, carbon and iron, we are necessarily removing carbon from the charge and hence purifying the iron. Sodium in the form of solid, liquid or vapor, has frequently been added to iron and so has nitrogen. Sodium and nitrogen have even been added separately or alternately to the same mass of iron. But I have found no disclosure wherein any one even hinted at treating iron with sodium and nitrogen simultaneously so as to remove the carbon in the form of cyanide by virtue of the catalytic action of the iron itself.

This seems to be a novel process which is just as interesting as the nitrogen fixation itself. It depends upon a powerfully reducing action while all large commercial processes depend upon the oxidizing action for the removal of carbon. It cannot attack the iron after the carbon is removed as is the case in oxidation reactions. It will remove not only carbon, but also sulfur, oxygen and phosphorus. It suggests the idea of removing silicon and manganese by the oxidation processes even to the extent of overburning the iron and then removing the remaining oxides, carbon, sulfur and phosphorus with sodium with or without the previous addition of carbon and that a Bessemer converter might be blown with nitrogen and sodium vapor. It also leads one to wonder whether with very cheap sodium it could not be made to apply to iron from ores very rich in phosphorus.

To further test these ideas for solid iron, a number of hacksaw blades were heated to redness in nitrogen and sodium vapor for a number of hours. They came out very soft and silvery in appearance and could not be tempered, thus showing that the carbon had disappeared and that the iron had acted as a catalyzer to purify itself. This removal of carbon, sulfur, and phosphorus must take place substantially instantly at the surface of the iron and if as large amounts practically by the rates of the diffusion of these substances through the hot iron.

The removal of carbon from a piece of steel wire is so complete that when the latter is made the anode in dilute hydrochloric acid, it remains bright and there

is not the slightest sign of carbon as the iron dissolves. If desired the surface of the iron can be purified quickly and the interior will remain in the form of steel. Many interesting topics arise regarding the electrical properties of iron thus purified, corrosion of iron and the coating of the metal with tin, zinc, etc., but their discussion would require a separate paper.

IV. PREPARATION OF METALLIC SODIUM

The general principles of physical chemistry regarding the reversibility of chemical reactions at once led me to consider whether the above reaction for the decarburization of iron might not be reversible and that it might hence be written:



You will at once notice that this is simply the equation for the case-hardening of iron by means of cyanides which has been known for a long time. In fact, it is practically evident that when the iron takes the carbon from sodium cyanide, it must set free the other two elements, sodium and nitrogen, which do not recombine under the conditions at which case-hardening takes place. This hence gives us a new method of getting metallic sodium based simply on the process of case-hardening iron with the additional precaution of keeping away air or gases which would destroy the liberated metallic sodium. With all the practical use of cyanogen compounds in casehardening, it is curious that no record of such a disclosure for preparing sodium could be found.

EXPERIMENT 3—Accordingly some sodium cyanide was mixed with pure iron powder in an iron tube and heated. A considerable layer of metallic sodium was found in the colder part of the tube. Similar experiments with potassium cyanide gave metallic potassium quite readily.

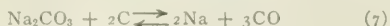
The same thing happens when the cyanide is added to molten iron and this might be of special interest practically because the carbon could be removed from the molten iron by a current of air blown into the converter and cyanide then passed in again as before. The general method of operation would be very similar to that used in making water gas commercially.

I did not follow this up because I had no suitable means for testing the engineering features of such a process and the method of getting sodium by the electrolysis of cyanide with the incident formation of cyanogen, oxamide, oxalic acid and formic acid, which will be described later, seems to offer greater advantages than this new method.

V. NITROGEN FIXATION WITH ALKALI CARBONATES

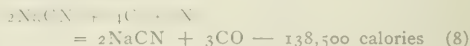
Having now determined that iron, or some similar element, was an exceedingly efficient as well as essential catalytic agent in the fixation of nitrogen, I decided to test the following ideas:

At a given temperature which is quite high, sodium carbonate and carbon give the reaction



which was formerly used for the preparation of sodium. It would hence seem that at moderate temperatures

of, say, from 860 to 980° C., we might get traces of metallic sodium according to the equation. This free sodium should then react practically instantly with the carbon and nitrogen, providing finely divided iron were present as has already been shown. If these ideas are correct, we should get an extraordinarily cheap and efficient method of nitrogen fixation, providing the reaction velocity for the formation of metallic sodium vapor is high. This would mean that as the sodium vapor disappeared to form sodium cyanide, more sodium would immediately be liberated, according to the law of mass action, to re-establish the equilibrium and the process would thereby become continuous, and we could represent it thus:



The following two experiments support these views in the most striking manner:

EXPERIMENT 4—In this experiment a mixture of 10 grams of finely powdered graphite was heated with 5 grams of sodium carbonate from 920 to 940° C. for 50 minutes in a current of nitrogen. A 1/2-in. copper tube was used in order to avoid the catalysis of iron walls. At this temperature there was a very slow but steady evolution of carbon monoxide and some white fumes passed out of the tube with the gas current. These fumes imparted a steady but not very intense yellow color when they were led into a Bunsen flame. Upon cooling, a minute quantity of free metallic sodium was found in the end of the copper tube. This hence gives positive experimental evidence that the formation of metallic sodium from carbonate takes place according to the above equation at temperatures below 940° C.

The contents of the tube were lixiviated and tested for cyanides with iron salts in the usual way. No precipitate of Prussian blue formed even on standing for a few minutes and only a slight greenish blue color showed no more than a trace of cyanide to have been present.

A similar experiment was then made with 30 grams of finely divided iron and 5 grams of sodium carbonate in a slow current of nitrogen for 50 minutes at 920 to 1000° C. In this test the issuing gas did not impart the slightest color to the Bunsen flame, thus showing that no sodium was formed and that the carbonate is so slightly volatile as not to give a flame test under the conditions of the experiment.

EXPERIMENT 5—A mixture of 10 grams of graphite and 10 grams of finely powdered iron with 5 grams of sodium carbonate was now heated in a 1/2-in. iron tube from 920 to 940° C. for 50 minutes in a current of nitrogen, just as in the preceding experiment in which no powdered iron was used. There was a steady flow of gas which burned with the characteristic blue flame of carbon monoxide. The escaping gases showed no fumes nor did they at any time show the slight yellow color.

The product showed a conversion of over 60 per cent sodium carbonate into sodium cyanide and a very heavy precipitate of Prussian blue was obtained.

These two experiments establish the foundation for nitrogen fixation in the sharpest possible manner and they support the above quotation of Lewis Thompson's work in the most striking way. They show that at a red heat we can have no nitrogen fixation with carbon and soda ash alone, but, that when finely divided iron is added, we have an exceedingly efficient method.

These experiments, which cost practically nothing and took only a few hours' time, were made in 1912 and they emphasize the utter inexcusability of those who quoted Thompson's invention and then ignored his positive statement about the necessity of the presence of iron for work at a red heat. They also show that Alder's above-mentioned statement, that the fixation of nitrogen at a red heat succeeds even without the presence of iron, etc., is entirely erroneous and that his claim that "carbonizing" gases, such as carbon monoxide, must be introduced with the nitrogen if cyanides are to be formed abundantly, has not the slightest basis in fact.

It shows at once that, by ignoring the work of Thompson, investigators and manufacturers were forced to work at such exceedingly high temperatures that the results could be only a ruinous destruction of apparatus and commercial failure.

The above facts are in harmony with Dr. Ewan's statement in his carefully prepared article in Thorpe's "Dictionary of Applied Chemistry," Revised Edition, Volume II, 1912, page 196:

"A few temperature measurements which the writer made with a platinum rhodium thermocouple showed that potassium vapor is first evolved from a mixture of potassium carbonate and charcoal at about 1350° and that the formation of cyanide takes place very slowly at this temperature, the potassium cyanide volatilizing for the most part."

These experiments, together with Dr. Ewan's temperature measurement, show why even the methods which used alkali metals *without catalysts* were doomed to failure as well as those using alkali carbonate. It is of no use from the technical point of view to work on any method which involves conditions under which material suitable for apparatus will not stand up. I had this sharply in mind when I determined to get a cyanide fixation process which should be effective at say from 860 to 950° C. so that iron or copper apparatus might be used in carrying out the process. The addition of the iron catalyst solved this problem, which I regard as the most important in my entire work, so completely, that, judging by Dr. Ewan's figure, the temperature of cyanide formation is lowered more than 500° C.

I made hundreds of experiments with powdered carbon in the form of charcoal, coke, lampblack, etc., and with sodium, potassium, caesium, rubidium, and barium compounds in the form of carbonates and hydroxides to test various points under widely varying conditions and to get quantitative data for technical application.

Ultimately a series of tests was made with the powdered materials in horizontal iron tubes of varying sizes which ultimately reached 6 in. in diameter and

10 ft. in length. Time will not permit the description of these experiments and tests. I can say that only the best results were obtained with 2-in. pipes, 10 ft. in length. In some of these cases equal portions of the solution, lixiviated from the cyanized charge, required the same number of cc. of $N/10$ $AgNO_3$ solution, acidified with nitric acid, and of $N/10$ H_2SO_4 (with methyl orange) for titration.

These figures show all the alkali metals to be present as cyanides, and this is what I mean when I speak of cyanide of 100 per cent purity. When such a solution is evaporated to dryness *in vacuo*, it is easy to obtain a residue directly which titrates for over 95 per cent of sodium cyanide.

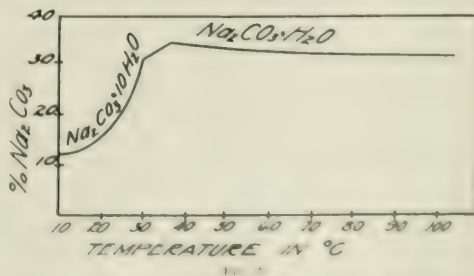
BRIQUETTING

Having thoroughly established the general conditions for efficient nitrogen fixation with substances in powder form, the next thing was to work out engineering methods for handling the materials. The inconvenience of heating powder in a current of nitrogen gas at a red heat, naturally suggests briquetting. A study of the art reveals numerous examples of briquetting, usually done with such substances as tar, pitch, resins, etc., or by use of lumps of charcoal, wood, and like substances to attain the desired porosity.

Desiring to avoid the use of such foreign substances, I first prepared briquettes by heating the mass of sodium carbonate, coke and iron to the melting point of soda ash in the absence of air. The pasty powder upon slight pressure becomes compacted and yields briquettes which are very hard and compact upon cooling. I have found such briquettes to be quite active, and they gave cyanide of 100 per cent purity upon being heated for 10 minutes in a current of nitrogen.

This is a fascinating process since the briquettes would already be at a cyanizing temperature just as they are formed. It would, however, mean the solving of unique engineering problems; hence I did not follow it further at the time.

The experience with the red-hot briquettes led me to conclude that perfectly satisfactory briquettes could be made by adding hot water to the mixed charge of coke, soda ash, and iron, and making use of the solubility curves and transition points of the phases of sodium carbonate as shown approximately in Fig. 2.



The curve in Figure 2 shows that the mass should be mixed with the water at a temperature near the maximum temperature of evaporation of water. We shall

then have a mixture of monohydrate, $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$, coke, and iron moistened with a hot saturated solution of sodium carbonate. These phases cannot change on cooling until the temperature reaches about 35°C ., at which the crystals would take up all the water and we would later have a dry hydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, as far as the water added would permit.

In other words, there is here a range of fully 70°C . through which the mass might cool before the briquetting operation would be interfered with. These predictions were realized in an exceedingly satisfactory manner, and many tons of briquettes were prepared without the slightest trouble. At first an ordinary concrete mixer without steam jacket was used. The hot water and the heat of hydration of the soda ash brought the temperature (work done in the summer) high enough to give fine briquettes, but as the temperature was not much above the transition point, the whole mass had a tendency to set like plaster of Paris if the operations were delayed.

Later a steam-jacketed kneading machine was used with the utmost convenience so that the full length of the monohydrate curve was available before cooling could stop the process. The hot, dough-like mass was briquetted with an ordinary small power-driven meat chopper having a cylindrical worm with a steel disc of $3\frac{1}{2}$ in. diameter and having 37 circular holes of $\frac{1}{8}$ in. diameter. The knife was fixed so that the briquettes were cut off at about 1 in. length. The efficiency of these small machines was surprising, *e. g.*, the 9-gal. steam-jacketed kneading machine gave 7200 lbs. of briquettes per 24 hours with 15 minutes to the charge, and it could just as well have been run at 5 minutes to the charge to give 21,000 lbs. of briquettes per 24 hours. The meat chopper, which was smaller than that often seen in a city market, easily gave 5,000 lbs. of briquettes per 24 hours with inexperienced help, and I have been able to force it to three times this capacity for a short interval. Thus even a few of these machines not much larger than toys would give a very large yearly output. Of course, a large brickmaking machine would give a very large output commercially.

These briquettes should be dried rapidly so as to get them hard and free from dust. Hot waste gases are very satisfactory for such drying. A commercial bake-oven would dry many tons per day or a dryer can be constructed out of brick and iron very quickly. If the briquettes cool before they are sufficiently dry they will harden, and, on further standing, will fall to powder as one might expect when the bulky hydrate, $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, forms to break them up just as freezing water may break a spongy, brittle substance. I have dried briquettes in the hottest part of the Bunsen flame in less than two minutes.

The powder was prepared for this work on a commercial scale by grinding iron scale (magnetite, haematite, etc., will do just as well) to a 100-mesh powder in an iron ball mill with manganoid steel balls; then an equal weight of coke previously ground in a similar way to 100-mesh was added and the grinding continued for

perhaps an hour; then the soda ash was added and the grinding continued for 5 minutes or even less.

The iron or iron scale and coke, being solids, must be mixed with the utmost thoroughness, but the soda ash becomes mobile by addition of water in briquetting as well as by fusing at 860°C . in the furnace so that no great care is necessary in mixing it with the other two constituents. Briquettes thus prepared with iron scale gave as high as 28 per cent of NaCN in the heated charge. Thus it is shown that we may start with iron oxides instead of metallic iron. In the first run we may thus produce finely divided iron which is in very fine condition for subsequent runs.

I will hereafter, for convenience, speak of the surface of carburized iron which is in close contact with the ground carbon as the "catalytic solution surface." For cyanide formation it is only necessary to have nitrogen, sodium carbonate, and such a catalytic solution surface in contact simultaneously. It is, hence, evident that sodium carbonate in too large quantity will flood the solution surface so that the nitrogen cannot get at it readily. This will smother the reaction so as to make it sluggish, and it is, thus evident that there must be a percentage of soda ash which will give maximum commercial efficiency.

The three following experiments were made to give a rough quantitative idea of this factor: They were made with 50 lbs. of alcoholized iron and with 50 lbs. of pulverized coke ground for 5 hours in the ball mill and the mixture was then briquetted with three different proportions of soda ash.

EXPERIMENT 6—In this case the iron-coke-soda ash was briquetted in the ratio respectively of 2 : 2 : 1 so as to give a 20 per cent soda ash briquette. Then 150 grams of these briquettes were heated in a 1-in. iron pipe in a current of nitrogen at a temperature from 600 to 1000°C . The reaction took place briskly and the issuing gas burned finely. The briquettes were cooled, lixiviated and titrated in the manner described above. They were found to contain 13.7 per cent of actual NaCN corresponding to 85 per cent of the total alkali metal in the solution. For brevity, I shall speak of such cases as 85 per cent purity.

EXPERIMENT 7—Here the same materials were briquetted to make a 1 : 1 : 1 iron-coke-soda ash ratio and 150 grams were heated as before in the 1-in. horizontal iron tube at a temperature from 600 to 1030°C . for 30 minutes. The gas evolution was considerably slower than in Experiment 6. The resulting briquettes contained 20 per cent of actual NaCN of 95 per cent purity.

EXPERIMENT 8—In this case the iron-coke-soda ash mixture was made into 1 : 1 : 2 briquettes which contained 50 per cent of soda ash, and 150 grams were heated in the same horizontal iron pipe in the nitrogen current for one hour at 600 to 1090°C . The combustible gas evolved sluggishly during the entire time, and the mass finally contained 14 per cent of actual cyanide of 80 per cent purity.

These three experiments show that the 20 per cent soda ash briquettes were quite reactive, the 33 per cent ones intermediate, and the 50 per cent one rather

sluggish so that they had to be heated longer and to a higher temperature in order to get the poorer result. These experiments rather indicate that with either larger or continuous acting furnaces it should be easy to get cyanized briquettes to contain at least 30 to 35 per cent of actual NaCN and this prediction was later verified. The experiments also clearly show the loss of alkali compounds by volatilization during the run.

If the briquettes do not completely fill a horizontal pipe, or, if they sag somewhat, as inevitably they must as soon as they become plastic when soda ash melts, then the nitrogen will tend to pass through the upper channel rather than through the briquettes. This is further aggravated by the counter-current of carbon monoxide which is formed in the reaction.

This factor is not very serious in a $\frac{1}{2}$ -in. pipe or even a 1-in. pipe, but it must become more serious with larger diameters. The following two experiments give conclusive data on this point.

EXPERIMENT 9—Twenty-five pounds of the same 2 : 2 : 1 briquettes such as were used in the 1-in. pipe in Experiment 6 were heated in a horizontal 6-ft. piece of 6-in. iron pipe and the temperature kept from 1000 to 1080° C. for 1 hour and 20 minutes while a current of nitrogen was passing.

Upon cooling it was found that the plastic charge had sagged $\frac{1}{2}$ in. in the upper part of the tube to produce a crescent-shaped channel as shown in Fig. 3.

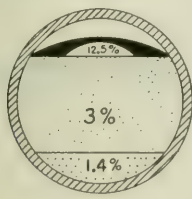


FIG. 3

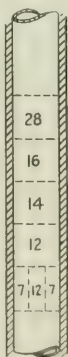


FIG. 4

The entire charge averaged only 3.5 per cent of actual NaCN of very low purity as against 13.7 per cent cyanide of 85 per cent purity under the far milder and shorter treatment of the same sample of briquettes in the 1-in. horizontal pipe in Experiment 6. A vertical section at about the middle of the charge was also tested and it showed 12.5 per cent cyanide in a narrow top layer, then 3 per cent in the broad intermediate layer, while the bottom layer showed only 1.4 per cent NaCN. This is also shown diagrammatically in Fig. 3.

EXPERIMENT 10—The result in the preceding experiment showed that increasing the size of a horizontal pipe to 6 inches, when the current of nitrogen passed into the end, completely ruined the process commercially. If this theory is correct, then this damage could be avoided entirely by placing the pipe vertically.

This was done with the same 6-ft. pipe of 6 in. diameter, and as I had no more of the 2 : 2 : 1 briquettes on hand, we used the more sluggish 1 : 1 : 1 briquettes as a 50-lb. charge.

The pipe was heated from 1000 to 1090° C. for only 1 hour and 10 minutes with a rapid current of nitrogen passing. This gave a massive column of yellow flame which at its maximum arose to a height of 4 to 5 ft. above the mouth of the vertical 6-in. shaft.

On cooling, the top of the charge was found to contain 24 per cent of actual NaCN while the bottom contained 20 per cent, giving an average for the entire charge of 22 per cent, and showing that over 10 lbs. of cyanide must have been produced in this run.

These two spectacular runs on a semi-commercial scale show at a glance that my process can be absolutely ruined by simply placing the retort horizontally in the furnace instead of vertically.

The same thing was also shown with longer and larger pipes in which the charges were on a scale of hundreds of pounds of briquettes in each run.

EXPERIMENT 11—This run was made in the same vertical pipe of 6 in. diameter as had been used in the preceding Experiment 10. It was made to test the volatility of the alkali compounds quantitatively: The charge happened to be 55 lbs. of briquettes consisting of 22 lbs. of iron scale, 24 lbs. coke and 9 lbs. of soda ash. The heating continued for 2 hours at 1000 to 1100° C.

Upon cooling, the top layer of briquettes was found to contain 28 per cent of actual NaCN of 87 per cent purity. Passing down, the other sections showed, respectively, 16, 14, 12 and 10 per cent of actual NaCN and the purity of the four sections varied from 90 to 93 per cent.

The lower section contained a central cone of moderately firm briquettes whose content was 12 per cent of NaCN of 100 per cent purity. This cone was surrounded by an annular section which had fallen to powder because its content of 7 per cent sodium cyanide was no longer enough to hold the particles of iron and carbon together.

These results are shown diagrammatically in Fig. 4, and they show exactly the general results we should expect in an experiment of this sort where we have heat passing in through the walls of the tube and a rapid gas current sweeping through the hot briquettes exposing a large surface for the evaporation of alkali compounds. The endothermic reactions in this case intensify the effect.

This experiment at once suggests two methods of solution, both of which I have carried out successfully in practice. The first would be to make the briquettes so active that they could be cyanized at lower temperatures, thus reducing the loss by volatility very greatly and by making other suitable changes. The other solution would be a continuously operating furnace, and here great volatility would be a most valuable asset.

ACTIVITY OF BRIQUETTES

The two following experiments were made with 25 grams of briquettes heated in each case in a current

of nitrogen in a $1\frac{1}{2}$ -in. iron tube which was laid horizontally into the heat zone of the furnace.

EXPERIMENT 12—In this case 2 : 2 : 1 iron-coke-soda ash briquettes were used. They were heated from 710 to 920° C. in 13 minutes. There was an exceedingly rapid evolution of carbon monoxide which died down to almost nothing in 6 minutes before a temperature of 900° was reached. The product contained 15.2 per cent of actual NaCN of 92 per cent purity. We may, hence, conclude that 2 : 2 : 1 briquettes should give over 15 per cent cyanide of over 90 per cent purity in 10 minutes at temperatures below 920° C.

EXPERIMENT 13—In this case the alkali was washed out of the briquettes and soda ash then added directly to the moist filter cake of iron and coke so as to make 1 : 1 : 1 iron-coke-soda ash briquettes.

These briquettes did not give the rush of carbon monoxide which was noted in the preceding experiment, but there was a steady evolution of gas during most of the 28 minutes while the tube was being heated from 620 to 920° C. There was still some action when the heating was stopped.

The resulting briquettes contained 30 per cent of actual NaCN and the purity was 87 per cent. This very satisfactory experiment shows that we can get over 30 per cent cyanide of 87 per cent purity in a batch furnace below 920° C. in less than 30 min. heating. We may, hence, conclude that an efficient nitrogen fixation takes place below 920° C.

In another experiment briquettes from the same lot of 2 : 2 : 1 iron-coke-soda ash briquettes used in Experiment 12 were heated for 10 minutes from 560 to 820° C. and gave 11.5 per cent of actual NaCN of 61 per cent purity. This shows that even below 820° C. we get considerable quantities in a few minutes. The process can, hence, certainly be carried out at very reasonable temperatures.

This reaction could easily be carried out in copper tubes which do not oxidize easily. It also shows that at mines the cyanide could be lixiviated and the moist filter cake could be treated with soda ash in the kneading machine, briquetted, and used over again.

CONTINUOUS FURNACES

The second way of overcoming the loss of alkali noted under Experiment 11 is to have the charge moving continuously, preferably by gravity; this would keep the final concentration of alkali in the briquettes just the same as at the beginning, because, whatever distilled from the heat zone would necessarily have to return to it and, hence, would be of advantage in insuring contact rather than a disadvantage.

This type of process would have great advantages in many other ways, some of which will be pointed out. The process would act very much like a blast-furnace but it would differ in yielding a plastic product instead of molten products.

The first experiment was carried out with an 8-in. iron pipe, 8 ft. long, placed vertically in a furnace and connected by means of a tee with a worm conveyor immediately below the furnace. Everything worked well for a while until the hot plastic briquettes

got into the conveyor and hardened so that it could not be turned. This was rather what had been expected; therefore, the experiment was modified by using a tube 14 ft. long so that the worm conveyor could be placed about 4 ft. below the bottom of the furnace. Fig. 5 shows the principle of the arrange-

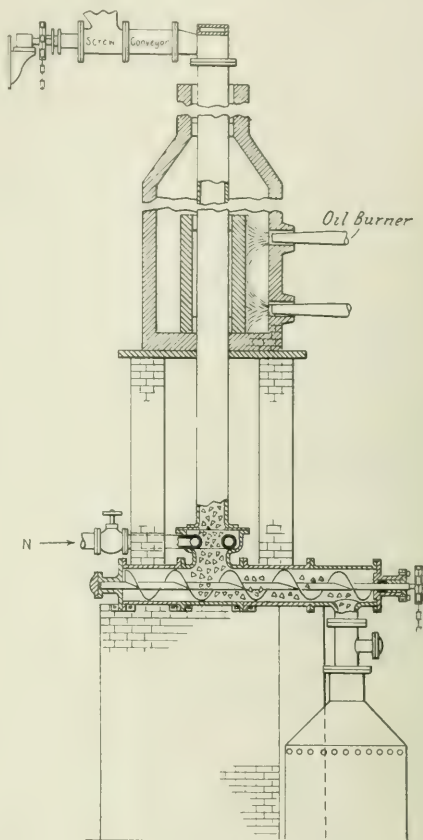


FIG. 5

ment. Here the descending, incandescent, plastic briquettes would cool by the ascending current of nitrogen, and by the air outside. The cooling was made more thorough still by using a current of water and a piece of cloth wrapped around the pipe below the heat zone. In this way the briquettes became cooled and hardened so that they passed through the conveyor in about the same physical condition as that in which they entered the furnace.

The hardened briquettes, however, stick in the pipe so that hammering may be necessary to move them, and at times when the pipe was rough it gave much trouble. This can be helped in various ways, such as making the entire pipe conical, or by making only that part below the heat zone conical, by making the briquettes larger, by feeding briquettes poor in alkali in the annular ring next to the wall of the pipe, or

even, pieces of coal or coke might be fed into the outer annular space while the core of the charge contained the briquettes richer in alkali, or, the cooling zone might be a larger pipe than that used for the heat zone as shown in Fig. 6. A complete solution would no doubt be obtained by making the cooling zone so wide that the hot cyanized briquettes would have to cool below the solidifying point of the sodium cyanide before they could come in contact with the iron walls.

The idea is well shown in Fig. 7 where the hot plastic

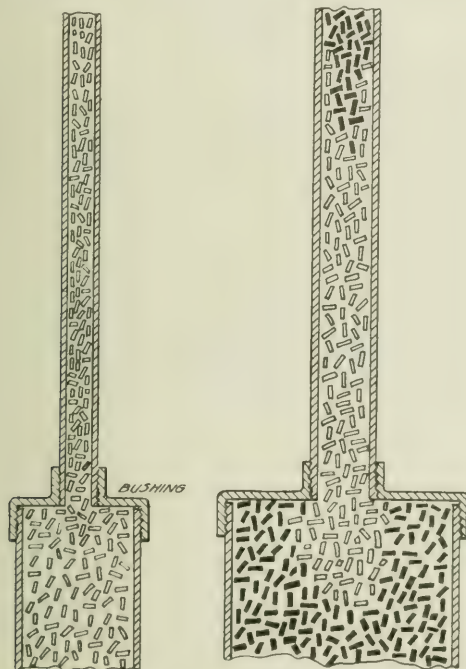


Fig. 6

Fig. 7

briquettes are shown not shaded while the cooler hardened briquettes are shaded. I have never had the hot plastic briquettes stick in a furnace operated according to my directions; the sticking always took place after they had hardened. Also, solid briquettes never stick in a properly operated furnace.

This very simple principle shown diagrammatically in Fig. 7 can, hence, scarcely fail to remove this difficulty absolutely. There is a slight tendency to stick at the top of the heat zone where the briquettes are just softening, but I have also been able to obviate this with the utmost ease by observing certain conditions.

In some of the work I made tests in a vertical iron pipe 22 ft. long and 8 in. in diameter. This required 300 lbs. of briquettes to charge it and then, in some tests, 3,000 lbs. were fed in a 24-hr. run.

The furnace was constructed on an improved principle as compared with that shown in Fig. 2. The furnace consisted essentially of a double chimney

with a thin partition separating the two compartments. An oil burner flame was directed vertically down one flue and the flame then led around baffles into the other flue which contained the 22-ft. pipe. The flame then passed up around the pipe and by controlling the draft at the top an effective furnace was obtained.

I further led a number of air jets into the main flue in such a way that the air oozed through long, narrow slits into the burning gases. In this way a reducing combustion could be maintained in the heat zone and the entire length of pipe in the furnace could be heated to a perfectly uniform temperature when desired. The whole furnace was within a derrick-like structure high enough so that burned-out pipes could be hoisted out mechanically without cooling them, and new ones inserted. Considering that these were simply first crude attempts, the furnaces worked surprisingly well. I believe that they are practical and that a gas producer would do the work far more easily, but, unfortunately, I did not have one—hence, the oil burner furnaces.

AN ELECTRIC FURNACE

When the price of yellow prussiate of soda and red prussiate of potash began to rise and ultimately reach values of \$7.00 and \$28.00, respectively, for each pound of nitrogen they contained, I decided to construct two types of electric furnaces which depended on the principles I had in mind for years in case of emergency either at the mines or for these chemicals. It was self-evident that they would work and that they could be installed in a few hours where any sort of commercial current is available. They depend simply upon using iron as a resistor and then keeping away oxygen so that they cannot burn out.

The first one was merely a piece of 1½-in. galvanized iron pipe such as is used on buildings as a water conductor. Two strips of copper were clamped about the ends for leads and the whole tube set vertically in a chimney of brick which were piled on the floor to give an opening 9 inches square. The space between the galvanized pipe and the brick were filled with magnesia asbestos and the furnace was complete. It was filled with briquettes and the currents of nitrogen and electricity were turned on. The zinc burned off like a flash and in a very few minutes there was a steady uniform heat in the briquettes and a fine flame of carbon monoxide. The transformer gave only 350 amperes and I had no means of reducing the voltage which was probably not over 100 volts. Result: Resistor briquettes contained over 99 per cent NaCN.

Wishing to carry out this exceedingly satisfactory experiment quickly on a larger scale, and being unable to get a suitable transformer, I purchased a small 1 kilowatt welding machine for the purpose. These machines are rated at 100 volts but the second are connected and easily can be set for much less voltage. In cases that are tight and crowded make for satisfactory service.

The furnace was now made from a piece of red brick

Y-connection and I was thus enabled to get 18 H. P. in the furnace instead of 12 by a single phase.

A slow current of nitrogen carrying some gasoline vapor, was passed into the annular space to prevent oxidation of the thin white-hot wire. This worked finely and gave over 30 per cent of NaCN in the briquettes used. The wire, even with this imperfect construction, lasted 9 hours, while it probably would not have lasted 9 minutes if air had been admitted.

On a large scale this furnace would be very simple since we would use only a single phase to each furnace and also use the furnaces in series and we would soon have to use say 1-in. iron rods for the resistors even with fairly high voltages such as 250 to 500. This entirely practicable type of furnace would probably be less desirable than that described already where the pipe itself is the resistor, but, in small scale work, it can be connected at once to any city current without expense of loss of time in waiting to have special low-voltage transformers made.

The resistance of iron increases probably 5 or 6-fold in heating from the room temperature to the cyanizing temperature, and varies with carbonization, etc. I have not been able to make strictly accurate observations, but in all of my work I found that the following formula gave me sufficiently accurate results so that the field rheostat regulation gave me entire control over the current.

$$\text{Amperes} = \frac{500 \text{ VW}}{L^2}$$

where V is the voltage used, W the total weight of iron in lbs. and L the total length of the conductor. I found it to hold for 1/16-in. wire, and for rods 1/2 in. in diameter as well as for pipes from 1 to 4 in. in diameter.

These electric furnaces are not what I should intend to install if I were asked to put up a large plant but they are what I would put up for an emergency plant (to which I will again refer) because I have personally worked through every phase of these processes and nothing whatever is left to chance or guess work. The time factor would in such a case be more important than the greater economy and speed which I feel can almost certainly be obtained by internal electrical heating where the briquettes themselves are the resistor.

While we are speaking of the application of electrical heating with solid catalytic solution surfaces, it may also be well to mention the experiment with molten iron.

Fig. 10 shows the apparatus and is almost self-explanatory. It represents a cylindrical furnace with basic lining and a perforated bottom like a Bessemer converter. It contains molten iron into which coke or graphite fragments are deeply pressed. The graphite column acts as electric resistor to produce the heat and, while in the bath, it serves both to retard the gas bubbles so as to insure sufficient contact and to keep the iron saturated with dissolved carbon.

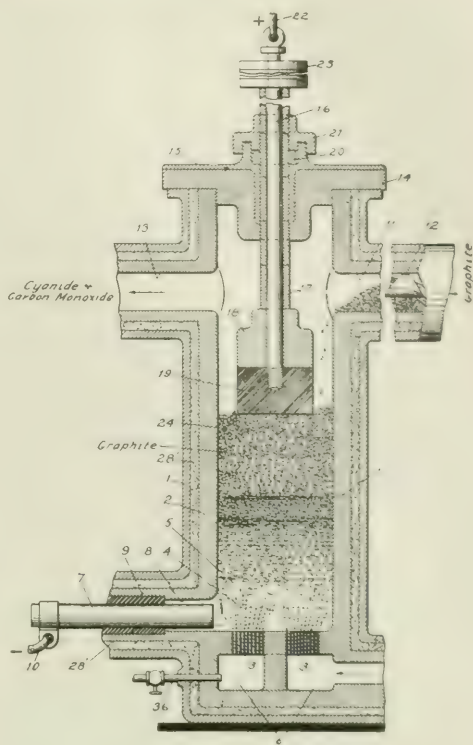


FIG. 10

Sodium vapor and nitrogen are blown into the bottom of the furnace and cyanide distils out at the top with the argon. The linings I used in the short time of the run stood better than I had expected. If the lining will stand sufficiently in actual work then I feel that ash in the carbon will be the other serious factor since the method of getting ashless carbon mentioned hereafter will not apply. However, there are other methods of solution.

RATE OF HEAT PENETRATION

In considering the technical application of these inventions, the rate of heat penetration into the briquettes becomes very important. The following experiment enables us to form some idea of the magnitude of this factor.

EXPERIMENT 14—In this run a 4-in. vertical pipe of iron was used with a pyrometer inserted in the center of the 8-lb. charge of the 2 : 2 : 1 iron-coke-soda ash briquettes through a 1/2-in. iron tube. The whole was placed in a cold furnace and a powerful oil flame used in the heating. By the time the outer pyrometer read 1050° C. the inner one in the charge read only 150° C. After 40 minutes more the outer one reached 1080° C. while the inner one registered only 880° C. In another 20 minutes the inside temperature read 1010° C. while the outer remained constant at 1080° C.

The heat, hence, flows in slowly and the rise is influenced by many factors of which the heat absorption of 138,500 calories is one. The result was 17 per cent of NaCN of 99 per cent purity in the briquettes.

This experiment gives the valuable data which enables us to say that it would take quite a while to heat a 6 or 8-in. column of briquettes to a uniform temperature. It also seems to confirm the very probable idea that the charge will conduct much better after it is partially heated than when it is cold. The importance of both these observations will be shown later.

INTERNAL ELECTRICAL HEATING

Experiment 14 shows that this factor would seriously retard rapid working in cyanide formation with large masses where the heat had to penetrate in from the outside. It would be a question of hours in large tubes. If we could use the charge directly as a resistor and thus generate the heat within the briquettes themselves, the heating would be reduced from hours to minutes with proportional saving of radiation losses and increase of output. Experiments along this line are very hopeful and wonderfully interesting, and I think no similar thing has ever arisen in electrical furnace work. To discuss adequately the very important results already obtained would require more time than is available for this entire paper, and I am not yet at liberty to disclose the most important of them.

I am, hence, compelled to dismiss this with the following general statements: The briquettes contain an insulator, soda ash, which makes them practically non-conductors at the room temperature but the conductivity increases very rapidly until at cyanizing temperatures it may easily increase 3,000-fold. It is, hence, only necessary to heat the charge to start the current or to put the briquettes into a hot furnace. I have heated a charge in a glass tube with the current in a few seconds so that the entire run was finished in less than 1 minute with abundant yield of cyanide and I have also heated charges of many lbs. in a few minutes. This suggests wonderful possibilities and shows that here is an entirely different proposition from that discussed in the case of the electric furnace shown in Fig. 8.

AIR INSTEAD OF NITROGEN

Having now shown how to fix nitrogen with simple apparatus with pure nitrogen, I desired to get away from the use of pure nitrogen so that my process would not be tied up to ammonia-soda or similar works, where nitrogen is a waste product. Also I did not wish to be compelled to put up a liquid air or other plant in order to get nitrogen. I suspected from the fact that carbon monoxide is formed in large quantity in the process, that a little more would do no harm under the right conditions. This suggested at once the use of producer gas in place of pure nitrogen or even the use of air directly providing it passed through hot coke before it reached the catalytic solution surface.

A number of runs were, hence, made in horizontal iron pipes of 1 in. diameter as shown in Fig. 11.

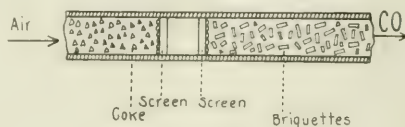


FIG. 11

Several inches of layers of coke were held in position in the tube with iron screens and then another screen kept the briquettes away from the porous absorbing surface of the coke. The pipe was heated to the cyanizing temperature and a current of air then passed in. Of course, this gave an extra fine carbon monoxide flame. When the process was over the air was shut off before the tube was cooled.

Similar runs were made in the apparatus by using pure nitrogen and the results were just the same as when air was used. In other cases the producer gas was made in a separate furnace and then passed into the cyanizing tube.

There was no apparent difference in any of these results. It is, hence, evident that the process is independent of pure nitrogen and that air, producer gas, flue gas, or even the gases from the combustion chamber of the furnace could be drawn through the cyanizing tube just as well. To make the test still more striking on a commercial scale, two pipes of iron 8 ft. long were put side by side vertically in a furnace as shown diagrammatically in Fig. 12.

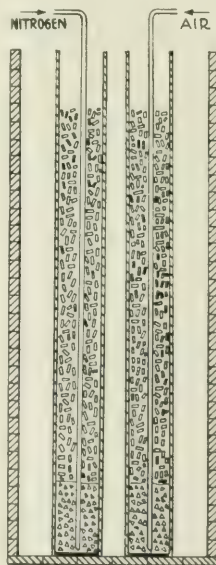


FIG. 12

One pipe was 6 in. in diameter and as I had no other of this size, the other was taken of 4 in. diameter. The

pipes were closed with caps at the bottom and then iron pipes of $\frac{1}{2}$ in. diameter were thrust to the bottom of the larger pipes and about a foot layer of coke was dropped into each one. Then 72 lbs. of briquettes were poured into the larger pipe and an equally deep layer was placed in the 4-in. pipe.

The whole apparatus was now heated red hot for a considerable time and pure nitrogen passed into one and air into the other. The result was 19 per cent of NaCN in the pipe which had the air and 18 per cent in that through which the pure nitrogen passed. These results are practically identical, thus showing that air can be used and that the process can now be operated anywhere. You can now see how easily producer gas could replace the nitrogen in working the electric furnace shown above in Fig. 8.

PRODUCTION OF NITROGEN

Although I do not need nitrogen in my fixation process with carbonates, it is, nevertheless, very convenient to have it for tests and when working with the alkali metals themselves. The passing of air over heated copper has many great advantages, particularly in the fact that the reagent is solid. Notwithstanding this, there seems to be much prejudice against it commercially and it was condemned as impractical or impossible just as many of the other basic things I have described to-night.

As no one cited any physical or chemical principle against it which seemed reasonable, it was in order either to show that it could be done or else why it could not be done.

Accordingly a 2-in. iron pipe 40 in. long was filled with the turnings which result as a waste product when the copper rolls used in the textile industry are turned down in a lathe. These turnings can be gathered in quantity and at a price below that of copper ingots. The copper used may contain considerable zinc and still be entirely suitable for the work. Four lbs. were tamped into the iron pipe to give a 28-in. column.

These pipes were heated in a combustion furnace to a low red heat and they easily gave 200 liters of nitrogen before they were exhausted. Then they were reduced with hydrogen and were again ready. I never used gasometers, but simply passed the air blast furnished by a small glass suction pump over the hot copper and then used the gas directly in the runs.

The arrangement is shown in Fig. 12 and shows how easily one can get the current of nitrogen automatically at constant pressure in any quantity varying from a few bubbles to 2 liters per minute. The tubes were run for months and were just as good as when they were first made.

It was then desired to construct a large commercial unit and in order to test how much sagging, analogous to that shown by the briquettes in Fig. 6, would take place, the horizontal pipe was, hence, purposely taken $\frac{1}{2}$ in. in diameter by 16 ft. long and charged with the

copper turnings. It gave 300 liters of nitrogen per minute at first but in a few days was completely useless. Examination showed that the copper had sagged 4 in. and was, moreover, covered with iron scale from the pipe so that the air did not get in contact at all. In another case, about a 6-in. tube was placed vertically but the plastic copper soon compacted by its own weight so as to shut off the gas current.

These factors having been determined to be large, it was evident that they must be avoided. This was very easily done and the first furnace constructed did so well that I should simply duplicate it if more nitrogen were needed.

I used a vertical pipe 10 in. in diameter and 6 ft. long, which was heated in a furnace having two vertical flues, one for the burner flame and the other for the tube containing the copper. The supports for the copper were made from two ordinary 1-in. iron crosses with side openings which were connected by a threaded 6-in. piece of iron rod through the side openings. Then 4-in. iron nipples were turned into the 8 remaining openings so as to make the 8-armed support which would just slide down into the 10-in. pipe.

One was dropped in and the copper tamped down just level with the top of the cross with a stick. Then another support was dropped down so that it rested on top of the lower cross and copper was tamped in as before. This was continued until the top was reached and the pipe contained 280 lbs. of copper turnings. Every section of copper was thus supported firmly and independently. It could not sag from the sides because the tube was vertical. It could not compact itself because each section had to sustain only its own weight and whatever sag there was in a section could simply open a horizontal section which would do no harm.

This furnace was run hard for 6 weeks in the tests and I could not detect the slightest deterioration. It gave 16,000 liters of nitrogen in 2 to 3 hours before requiring reduction and then it was reduced by cautiously adding a number of liters of wood alcohol at the top. This served not only for reduction but also as a measure of the capacity of the furnace. I never heated it above 450° C. In actual practice one would reduce the copper with the carbon monoxide from the cyanizing furnace and on a large scale perhaps it might not be necessary to apply external heat since the reactions in the copper turnings are exothermic. The reductions should, hence, not be too energetic as otherwise it might heat the copper too high. I do not know how others construct their furnaces but this one is eminently satisfactory.

The expense of copper need hardly be mentioned because the cyanide produced would now pay for the copper every 40 minutes and even in normal times in less than half a day. If anyone is doing electrolytic work and has waste hydrogen, this will also give nitrogen with the nitrous oxide since it is only necessary to burn the hydrogen and air in regulated streams in a $\frac{1}{2}$ sec. or so. apparatus. It seems simply of

iron tubes which may be lined with fire-brick inside in the combustion space.

This is about the same as the above scheme with copper, only the copper is left out and the hydrogen and air act simultaneously. The steam formed condenses out and leaves the nitrogen which may contain a slight excess of hydrogen if desired and the heat generated can be used for evaporation purposes.

A still simpler device follows from my method of changing cyanide into urea as shown below. In fact, it will be seen that the nitrogen there becomes a waste product in nitrogen fixation and it may accumulate twice as fast as it is being fixed.

DISTILLATION OF CYANIDE

Having now shown methods of obtaining alkali cyanides, it is naturally in order to consider methods of getting the cyanide from the briquettes. One would wish to avoid lixiviation if possible and, hence, the following work on distillation. As we would destroy the catalytic solution surface by heating the iron-carbon mixture above the eutectic point (about 1120° C.) because of the iron melting to globules, it seemed worth while to try the distillation in either a current of nitrogen or in a vacuum. Both seem to work.

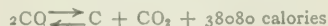
For example: Some cyanized briquettes were placed in a copper tube, heated to 1000° C. and at about 2 mm. pressure. The cyanide collected in a pool which solidified to a clear mass which could not be told from glass by appearance. There was no cyanide whatever left in the iron-coke mixture and only the merest trace of alkali.

In another case the specimen of distilled cyanide was titrated and found to be 99.9 per cent NaCN. I have also distilled both sodium and potassium cyanides *in vacuo* while a melting point tube filled with sodium chloride was in the mixture. The sodium chloride did not melt; hence the cyanide must have distilled below this melting point (792 or 820° C.).

$K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ were also heated *in vacuo*. This gave a fine distillate of KCN while iron-carbon in very finely divided form remained. This would be slightly wasteful but would work finely since the iron, carbon and nitrogen obtained in decomposition would go back into the cyanizing process again.

ASHLESS CARBON

The great promise of the above method of distilling cyanides would soon come to grief by having the ash from the coke accumulate with each repetition until it would stop the process. If we could get this carbon from carbon monoxide, it would be ideal. This suggests the following equation:



The equilibrium for this equation gives almost pure carbon monoxide at 1050° C. while at 500° C. it is almost reversed so that carbon monoxide must be unstable at low temperatures and if we could find a suitable catalyzer we should be able to get carbon from it.

I first passed pure carbon monoxide over ground coke but could notice no change. No carbon dioxide could be detected with the Hempel burette and only a trace of precipitate was obtained with lime-water. Evidently the catalysis was negligible.

The experiment was repeated as before in a combustion tube of hard glass which had a layer of finely divided iron in the bottom. A very striking change took place at once. The surface of the iron blackened at once and the issuing gas contained over 40 per cent of carbon dioxide in spite of the rapid current and the very slight contact. The catalysis must, hence, be exceedingly efficient and in a few hours the bulk of the whole charge had so increased from the deposited carbon that the entire section of the tube became filled so that the gas could no longer pass through.

The wonderful importance of this when applied to the iron-coke-soda ash can be seen at once. It gives us ashless carbon, in the form of very finely divided lampblack, together with 38,080 calories of heat developed within the charge itself. In addition, since the coke does not appreciably catalyze the reaction, the deposited carbon must, hence, be in very close contact with the iron.

We thus have this automatic process to do away with the ash in the carbon, with grinding the carbon, with mixing the carbon and iron and it provides internal heat in the briquettes themselves. It is, hence, equivalent to that much internal electric heating.

I will show how this will apply later under the theory of the continuous furnace. Suspecting that Mond¹ might have done such work in connection with his metal carbonyl compounds, I looked up the literature and found that he had done so. He found that with 15 parts of nickel, he could deposit 85 parts of carbon.

I also noticed that I could not obtain over about 43 to 45 per cent of carbon dioxide in the experiments and this suggests that there must be an equilibrium which should not be here if the process were one of pure catalysis since the catalyst should simply hasten the velocity of transformation but should not completely change its course.

A search of the literature revealed considerable work along this line from the point of view of the phase rule. Findlay² discusses the work of Baur and Glaessner, Boudouard and Hahn.

Fig. 13 shows a diagram embodying part of their important work on the equilibrium relation of carbon dioxide, carbon monoxide, iron and carbon at varying temperatures, while the dotted line in the curve shows what the relation should be if no catalyzer were present or if the catalyzer exerted no foreign function.

It is evident at a glance that as soon as the concentration of CO_2 reaches a certain value, it will begin to oxidize the iron to FeO , thus destroying the catalyzer and completely changing the action.

The curve *ABC* of Fig. 13 marks the concentrations

¹ Jour. Am. Chem. Soc., 57 (1890), 749.

² Findlay, "The Phase Rule, 3d Impression," page 306.

of CO and CO₂ which correspond to each temperature as long as any metallic iron is present. The maximum value we can get for the formation of CO₂ is hence about 42 per cent at the temperature of 680° C.

On the other hand, nickel does not form oxides as readily as iron and it will, hence, transform CO almost quantitatively into CO₂. This can be shown beautifully as a lecture experiment by placing finely divided nickel in a glass tube heated to perhaps 300 to 400° C. When pure CO is passed into the tube it is so completely transformed that the CO flame goes out and the exit gas contains 98 per cent of CO₂.

These phase rule studies are of great importance in the study of blast-furnace reactions, case-hardening, etc., and I will further apply them under the question of the oxidation of iron pipes.

OXIDATION OF IRON PIPES

In conducting the above process by external heating, the question of oxidation of iron pipes must be seriously considered, but, from some thousands of experiments I feel sure that this will not be of the slightest trouble when operations are based upon scientific principles. If we use electrical heating, the oxidation is absolutely avoided in the furnace shown above in Fig. 8, which was designed and built for this very purpose.

My experience leads me to believe that it can be entirely avoided in fuel-heated furnaces. For example, the temperature-concentration diagram in Fig. 13

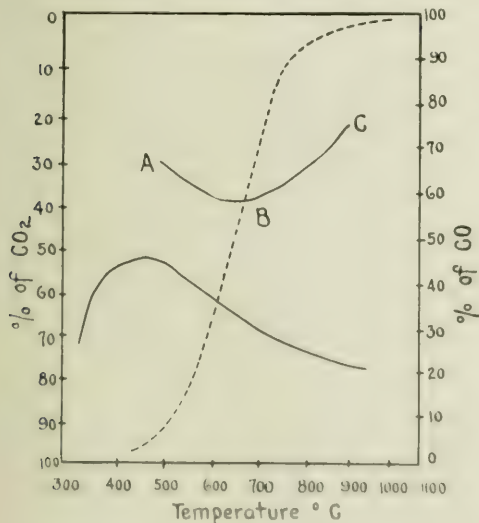


FIG. 13

shows that iron oxide cannot exist in the field above the curve ABC and, hence, it is impossible even to oxidize the iron pipe until the heating flame contains the corresponding value of CO₂.

For instance, if the iron pipe is heated to 950° C.

then we could have 25 per cent of CO₂ present and still have oxidation impossible; that is, we could burn carbon according to the equation,



without any possibility of oxidizing the tube and then the remaining 203,010 calories could be obtained by admitting enough air in the preheating zone to burn the 3CO where oxidation would no longer take place because of the lower temperature. We might also combine the principle of the regenerative oven here if we desired.

These figures would be modified somewhat by considering the diluting influence of nitrogen, but I have only time to state general principles without giving details. It is very likely indeed that much more heat may be liberated in the heat zone because of the protective influence of a layer of oxide on the surface of the tube, but I always prefer to calculate on the most unfavorable case.

Also, we might consider admitting hydrogen with the producer gas as by having a steam-blown producer. The hydrogen present would then steadily diffuse through the red-hot iron walls as explained above under Fig. 1. The outward diffusing hydrogen, aided by the outward diffusing carbon and carbon monoxide, would meet the ingoing layer of oxide and would drive it back under the right conditions.

Also copper tubes would absolutely avoid this oxidation and they would easily stand the temperature. I have, in fact, used copper tubes largely at 950 to 1000° in another line of work with the greatest success. I could notice no damage to the tube either inside or outside. The expense of the copper would not be prohibitive and it could be cut down by using it only in the actual heat zone, and by using it as a sheathing for iron tubes; perhaps iron plated with copper would do. I have also tried nickel sheathing with results which would warrant a longer test.

There is no doubt that the trouble from the oxidation of iron tubes has been grossly exaggerated, and, personally, I feel convinced that there is nothing to it.

THEORY OF BATCH FURNACE

The theory of the batch furnace is also the theory of the process in its simplest form. We merely grind together intimately, iron, coke and soda ash, moisten and briquette the material. The dry briquettes are then heated in a vertical pipe, to over 950° C., in a current of nitrogen or producer gas until carbon monoxide no longer escapes. This is exceedingly simple and is all that there is to the process.

The theory is that the iron, by dissolving the carbon, gives a solid solution in which the carbon may move freely and it becomes active. This gives us our "catalytic solution surface."

It is hence only necessary to produce the extremely active catalytic solution surface, to maintain it unimpaired during the process, and to give the nitrogen and allow metal to compound free access to the hot face during the run.

ENRICHING PRODUCER GAS

You will note from Equation 8 that nitrogen gas is absorbed in the process and carbon monoxide is formed in large volume. The gas is enriched in a two-fold way and I have noted 75 per cent of carbon monoxide in the exit gas from the batch furnaces.

Bunsen and Playfair absorbed all their nitrogen; hence it is probable that under the right conditions producer gas can be enriched so that it will be substantially pure carbon monoxide.

DESTRUCTIVE EFFECT OF CARBON MONOXIDE

You will notice that in using producer gas, I always shut off the gas current before the briquettes began to cool. This is a vital point. For example, briquettes containing 19 per cent of sodium cyanide were heated red hot in a current of producer gas and cooled slowly

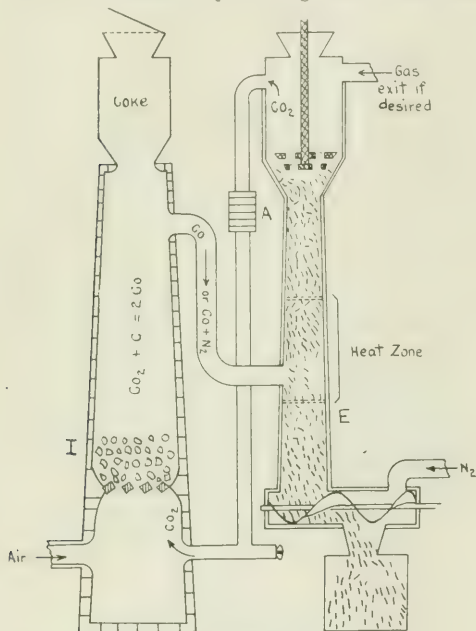


FIG. 14

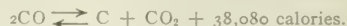
while the current continued. When cold, they contained only 3 per cent of cyanide of sodium. This shows that we have almost complete destruction of cyanide when the briquettes cool in a producer gas current and that we avoid all trouble in the above batch furnace, Fig. 8, by merely stopping the current before the charge cools, or, by dumping the hot briquettes so that the gas current can not pass through while they are cooling.

This destruction may well be due to carbon dioxide formed by the catalysis of the iron in causing the formation of ashless carbon by the equation $2CO \rightleftharpoons C + CO_2$. If this be the true explanation, the iron acts both as a destructive and constructive catalyzer in the process.

If this be so, then at 500 to 600° C., cyanide should be destroyed rapidly (see the temperature concentration diagram, Fig. 13) while, at, say, 950 to 1000° C., the CO_2 has almost disappeared and the speed of the cyanide formation has increased so that no harm is done. This is very important in the continuous furnace shown in Fig. 14.

THEORY OF THE CONTINUOUS FURNACE

It would take a separate paper to deal with the general features of such a furnace as that shown in Fig. 5. The briquettes passing in the top become preheated, by utilizing the waste heat from the gases of the reaction zone, and then collect all the cyanide fumes which are liable to distil in clouds from the batch furnace. When they get red hot they will, by catalysis of their iron content, produce the reaction



This gives finely divided ash-free carbon which is necessarily in intimate mixture with the finely divided iron. It also gives out heat in the briquettes themselves and therefore has the same exceedingly important effect as internal electric heating. Unfortunately the equilibrium relations of curve ABC in Fig. 13 must be applied, but, even if we take the maximum value at 680° C. this would contribute over 20,000 calories towards the 138,500 calories needed in the heat zone for the reaction



This is an exceedingly great advantage. Then in the cyanizing zone the same reaction takes place as in a batch furnace, but the intense volatilization from the porous briquettes carries the alkali upwards to be recondensed on the cooler briquettes above with corresponding heat changes. This distillation gives fine circulation of alkali to the solution surface and is carried back by the descending briquette column.

Below the cyanizing zone, the nitrogen cools the briquettes and itself becomes preheated so as to carry the waste heat back into the heat zone. The plastic briquettes now harden again and are removed by the conveyor. When producer gas washed with caustic alkali to remove CO_2 is used instead of nitrogen we have in some ways a very different problem.

For example, in a run in a 14 ft. 6-in. pipe which should have yielded at least 20 per cent of NaCN in the briquettes, I got only 5 per cent of cyanide when feeding at the rate of 2000 lbs. per day. When the feeding was reduced to 1000 lbs. per day the yield dropped to 1 per cent of NaCN in the briquettes. In view of the facts already disclosed it is evident that the producer gas destroyed $\frac{3}{4}$ of the cyanide formed with the 2,000-lb. feed, and when this was made slower the producer gas had a longer time to act and $\frac{19}{20}$ of the cyanide was destroyed.

This looked bad for the continuous process with the producer gas. The difficulty was overcome, however, by simply passing the producer gas into the briquette

column at the base of the heat zone. In this case the cyanized briquettes as they cool are entirely away from the current of producer gas (there must be no leak in the lower fitting of the furnace pipe, otherwise some of the producer gas would be forced downward with the briquettes and thus do harm).

This arrangement is shown diagrammatically in Fig. 14 and is arranged so that we may use either nitrogen or producer gas and it shows the principle of transferring carbon from one part of a closed system to another with oxides of carbon so as to separate from ash; incidentally such a simple modification in the furnace gives 25 per cent NaCN in the briquettes.

Even poor briquettes will give good results in these continuous furnaces. Some of the advantages can, however, be attained in batch furnaces by running the waste gases and fumes from the top of one into the bottom of the next furnace.

LIMITING FACTS

Suppose we consider, for example, a vertical 6-in. iron pipe, 6 ft. in length charged with briquettes of the usual size. Thus the speed of operation would be limited by the activity of the briquettes, by the rate at which nitrogen could be passed in, and by the rate at which heat could penetrate through the charge to the center of the core. Results already mentioned show that the briquettes are active enough to be cyanized in 1 or 2 minutes. The requisite nitrogen could be passed through them in 10 minutes. The heating could be done in 2 hrs. without undue excess of temperature outside.

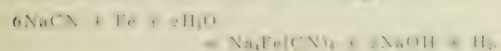
These data show why heat conduction is the slow factor and why internal heating by electricity or by the ashless carbon method are so interesting. Also the slow conduction determines the furnace design. It means above all else a long heat zone, just as long as possible, so that it will not be necessary to force an excessive amount of heat through a short heat zone with all the ruinous effects that follow.

I should use the full length commercial pipes of 20 to 24-ft. length unless the plastic briquettes compacted too much. In that case I should try slanting the pipes and if this did not work I would cut the pipe so as to bring the preheating zone in at an angle which should be sure to relieve the pressure.

SODIUM FERROCYANIDE

Having now shown how to fix nitrogen in the briquettes, it is in order to show how compounds can be recovered from them. If we add hot water to the cyanized briquettes to make a slurry paste and then steam them in an agitator you will see at once that we have an electrolyte of sodium cyanide and immovable carbon-iron elements in contact with it.

We might hence expect to get as a result of electrical action, or otherwise, the following reaction:



This reaction takes place with great ease, hydrogen being given off in large quantity. After agitating for several hours, the hot mass is filtered and the black powder turned back into the process again.

The hot filtrate deposits an exceptionally fine quality of sodium ferrocyanide on cooling, and upon concentrating the filtrate the rest deposits out from the strong solution of caustic soda which is formed. The caustic soda is either turned right back into the process or used otherwise. The method is exceedingly effective.

LIXIVIATION FOR CYANIDES

From this behavior of the briquettes with hot water, we see that it will be necessary to observe certain precautions in lixiviating to get sodium cyanide. On the other hand, the solubility curve in Fig. 15 shows that at temperatures below 35° C. the mass will take up water of crystallization to form $\text{NaCN} \cdot 2\text{H}_2\text{O}$ which will "set" the mass just like plaster of Paris.

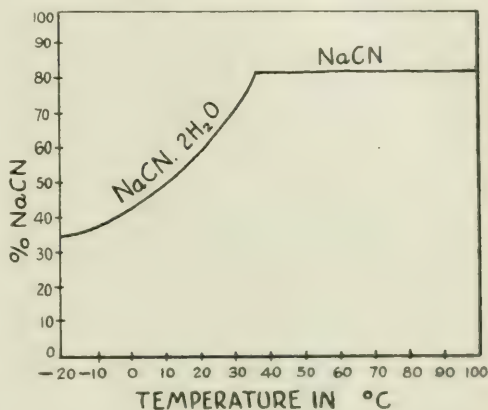


Fig. 15

To avoid both dilemmas we should lixiviate at a temperature slightly above 35° C., the transition point of the cyanide. This should be done quickly because the ferrocyanide reaction is going on slowly even at this temperature.

The solution can be concentrated *in vacuo* if desired. The cyanide is pure enough for many purposes. Or, it can be distilled as concentrated glass. If large quantities added lime to it to causticize any soda ash present as this would prevent the hydrolytic dissociation to form hydrocyanic acid,



for which some authors frequently recommend, intentionally.

Also we may add sodium chloride to remove the carbonate and reduce it to sodium cyanide thus:

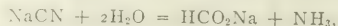


For these discussions, my water for heating is distilled

chloride and sodium cyanide which is so much sought in the jewelry trade.

AMMONIA AND SODIUM FORMATE

If we boil sodium cyanide solution to get ammonia and sodium formate,



we can only get to the boiling point of the solution. the action is slow and hydrocyanic acid is likely to form according to the already mentioned hydrolytic dissociation.

If, however, we add caustic soda (or prepare it with lime in the lixiviated solution), we get these effects: the caustic soda prevents hydrolytic dissociation to form hydrocyanic acid, it raises the boiling-point of the solution and it salts out the sodium formate from the solution by making it many times less soluble than in pure water.

The operation is carried out with a return condenser and the ammonia after passing through a caustic soda dryer is chemically pure and anhydrous and can be compressed at once into cylinders, if desired. The sodium formate can be turned back into the cyanizing process or it can be converted into sodium oxalate at once by merely heating *in vacuo*; from these we can easily obtain formic and oxalic acids.

UREA, AMMONIA AND NITROGEN

If we can arrange a flanged cast-iron pot, 3 in. in diameter by 12 in. deep, with a cover, inlet and

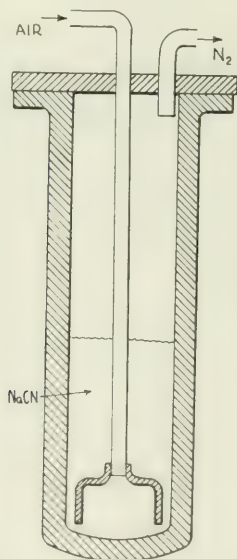
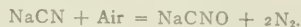


FIG. 16

exit pipes, and a 2-in. reducing coupling as shown in Fig. 16, we have a serviceable laboratory unit to convert

cyanide into urea. The cyanide is kept just above its melting point and a current of air is passed through the molten cyanide. It burns to sodium cyanate according to the approximate equation,



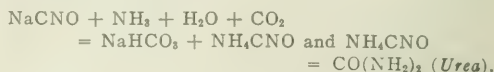
The nitrogen thus formed is turned into the cyanizing furnaces and this gives us 4 atoms of nitrogen for each 2 atoms fixed. The process hence takes its own nitrogen from the air to such an extent that theoretically one-half would have to be thrown away as a waste product in spite of the process being one for the fixation of nitrogen.

One-half of the cyanate is now heated with water which converts it into ammonia long before the boiling point is reached according to the equation,

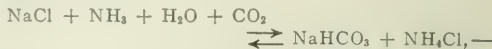


The sodium bicarbonate is thrown back into the process and the ammonia saved or else converted into urea as follows.

The other half of the NaCNO is added to water and the ammonia then passed in. Then CO₂ from the cyanizing furnaces is also passed into the liquid. The change is represented by,



You will notice that this is exactly similar to the ammonia-soda process,



the radical —CNO taking the place of the chlorine atom of sodium chloride.

The urea reaction takes place much better than the ammonia-soda one because the NH₄CNO is passed into urea and hence practically does away with reversibility while the NH₄Cl in the ammonia-soda process causes a loss of 30 or 40 per cent because of this factor.

The bicarbonate is returned to the process. We thus have a very inexpensive way of getting urea which has over 46 per cent of nitrogen and which is about three times as rich in nitrogen as sodium nitrate. It is about twice as rich in nitrogen as ammonium sulfate and would not introduce sulfuric acid into our soils, many of which are already too acid.

The urea was tested in water culture in the botanical laboratory of this university and found to give results equal to that of the nitrogen from potassium nitrate.

The urea may also be combined with nitric acid produced from ammonia so as to form urea nitrate (CO(NH₂)₂.HNO₃, which is still very rich in nitrogen but less soluble than urea.

METALLIC SODIUM

Sodium cyanide melts at a much lower temperature than salt and requires much less voltage for electrol-

ysis. My experiments indicate that it can be easily electrolyzed [$2\text{NaCN} = 2\text{Na} + (\text{CN})_2$] to sodium and cyanogen. This should give us a very cheap way of getting sodium from sodium carbonate with the incidental fixation of nitrogen.

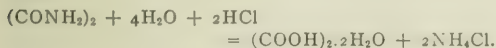
OXAMID, OXALIC AND FORMIC ACIDS

The cyanogen obtained from above was not supposed to be readily convertible into oxamid but I find it converts with the utmost ease under the right conditions. The gas is rapidly absorbed in hydrochloric acid (44 per cent) and then changes to oxamid thus: $(\text{CN})_2 + 2\text{H}_2\text{O} = \text{CO}(\text{NH}_2)_2$, which being practically insoluble separates out as a pure white powder.

Here we have the remarkable case of the hydrochloric acid acting as a catalyzer to concentrate itself even to the point of becoming gaseous, while at the same time precipitating out the resultant compound.

Curiously enough, the reaction practically stops when the hydrochloric acid is slightly dilute (14 per cent). The oxamid has nearly 32 per cent of nitrogen and is nearly insoluble in water and it should be especially of value as a fertilizer and should partially approximate the effect of the nitrogen in dried blood rather than that from the more soluble sodium nitrate. This has apparently already been verified by Dr. Hartwell of the Rhode Island Agricultural Experiment Station.

We get chemically pure oxalic acid from the oxamid by merely heating it for a minute or so with the concentrated hydrochloric acid to add more water, thus:



The acid crystallizes out free from all mineral salts.

The acid upon heating with glycerin transforms at once into formic acid according to the equation,
 $(\text{COOH})_2 = \text{HCO}_2\text{H} + \text{CO}_2$.

CAUSES OF FAILURE

A few of the large number of reasons for the absolute failure to achieve commercial results worthy of consideration by the methods described in this paper may be given:

(1) The omission of iron (which, by the way, is probably the only technically suitable catalyzer where alkali carbonates are used), absolutely ruins the process.

(2) Failure to mix the constituent properly is nearly equally ruinous and has no doubt contributed largely to failure.

(3) Heating a briquette a little too high will melt the iron at the eutectic point into globules, thus destroying the extended catalytic solution surface and thereby completely ruining the process.

(4) It is also above shown that simply putting a large vertical retort in the furnace horizontally will

completely ruin the process whenever the charge is plastic.

Alder preferred to mix his powdered materials with water and then with pieces of charcoal from "size of pea to size of fist." You can see at once that here the charcoal would absorb the molten cyanide just as a sponge absorbs water, thereby preventing the alkali from contacting freely with the catalytic solution surface even when he had one present by using iron. To show how serious this is, I prepared an active iron-coke-soda ash mixture according to my specifications which yielded cyanide of 98 per cent purity. A portion was then mixed with water and charcoal and it now yielded cyanide of only 14 per cent purity. This shows conclusively that Alder's preferred directions will ruin even an initially active mixture. You can now see why I was careful to have the screens spaced in Fig. 11 to keep the coke and briquettes apart.

(5) The above work shows that cooling a cyanized charge containing iron in producer gas ruins the process.

(6) Evidently oxygen would be worse and you can form your own inference about cooling the descending charge in nitrogen containing 2.5 per cent of oxygen.

(7) The quantitative measurement of heat penetration also shows that the heat zone should be long so as to allow time for the heat to penetrate to the center of the charge without having to force the process and thereby causing no end of needless trouble.

EMERGENCY PROCESS

I have carefully distinguished between what I have actually demonstrated with units which were of commercial size and those other things which have not been worked out as far.

In view of the conditions now existing, I wish to call attention to this topic so definitely that the issue will be so sharply defined that anyone interested can test the matter for himself by direct experiment within a few hours. This is a perfectly fair way of finding the truth or falsity of the statements and criticisms I have felt compelled to make.

If one wishes an operative process at once, it is only necessary to construct the furnace shown in Fig. 8. Construct a platform about 6 feet by 8 feet with 6 feet of free space underneath out of 4×6 timbers and 2-in. planks, cutting a hole through which the iron pipe may pass. Put on four small piles of brick to support the metal drum which should be, say, 30 in. in diameter by 6 feet in height and fill it with magnesia asbestos after inserting the drilled pipe and fastening with locknuts. Put on the reducing coupling, stuffing box and iron support as shown in Fig. 8 and drop in the brick support *Si* and turn on the gas, removing pipe.

This completes the furnace and with the help of several workmen, I would find it not too hard to build the whole thing in a few hours. The same can now added and

the copper leads attached. With sufficient current the first run will be finished and drawn within 2 hours and then runs can be made every hour; this can be kept up indefinitely if the drum be air-tight.

This furnace can be in operation in less than 24 hours, giving its output steadily and will easily yield 150 lbs. of sodium cyanide per 24 hours or over 200 lbs. of sodium ferrocyanide in the same time. An ordinary meat chopper will easily supply briquettes enough to run 8 such furnaces.

With over \$2.00 per lb. now asked for sodium cyanide, and with sodium ferrocyanide at over \$1.25 per lb. and potassium ferrocyanide at over \$7.00 per lb. within the past 10 months and great anxiety in both the mining and jewelry industries it seems that the above furnace which costs less than \$100.00 and can be put up and operating in less than a day might have been tried.

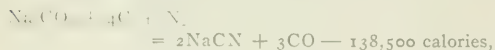
It would, at a stroke, either have shown how to relieve the situation immediately or else have shown that what I have been telling you to-night is worthless.

If no high amperage is available, the ordinary lighting current of 120 or 220 volts with iron rods analogous to the construction above indicated in Fig. 9 would work just as well. If electricity were not available then an oil burner would answer just as well as any burning-out of pipes would not need to be considered at such prices. I am not here advocating any particular furnace, hence there is no cause for discussion about its merit or lack of merit. It simply shows a means of getting away from endless discussion by doing something to get chemicals which are sorely needed.

These units could be enlarged and put in series to take practically any current and I have data for the design of a plant capable of producing the ammonia for 180,000 tons of nitric acid per year along these lines and it would be something which could be done quickly in case of need.

COST OF PROCESS

I do not have time to go into the question of cost of production this evening but I have estimated it very carefully from what I have actually tested with commercial units as well as from theory. I will hence say that the equation,

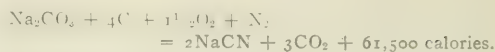


would theoretically require about 35,000 H. P. to produce 180,000 tons of nitric acid, allowing 85 per cent efficiency in oxidizing the ammonia.

But the three molecules of CO in the above equations would give on burning,



equivalent to about 50,000 H. P. to help make up the unavoidable heat losses. Combining these two equations we have



The total process is hence really an exothermic one and, in any case, it does not require electric power. Owing to its great simplicity and to the inexpensive materials, the cost is exceptionally favorable for the fixation of nitrogen and the production of cyanides, ammonia, urea and the other substances above mentioned.

COMPARISONS

We are now in a position to compare the above process with three of the commercial methods now in successful operation. The arc process which has been developed on such a large scale in Norway yields nitric acid and nitrates but it requires a very high temperature and is hence absolutely dependent not only on electric power, but, I think all agree that it can succeed only where the power is very cheap because the requirement of current is very large. It is further handicapped by yielding very dilute products which must be worked over.

The Cyanamid process requires calcium carbide which can be made practically only at the high temperatures of the electric arc. It is therefore also absolutely dependent upon electric power but it can make use of more expensive power than the arc process.

It has hence a correspondingly wider choice of locations. It is also handicapped by using nitrogen itself rather than producer gas.

My process differs from the above processes by operating at temperatures which may be below 950° C. and it is therefore independent of electric power. This means that it can be operated at any locality suitable for manufacturing purposes. I can use producer gas just as well as nitrogen and the process is therefore independent of pure atmospheric nitrogen. It is so exceedingly simple that it can be installed immediately with apparatus obtainable in the open market and because of the remarkable transformations of the cyanogen it opens the way for the cheap production of organic substances such as urea, oxamid, etc., as well as new commercial methods for oxalic and formic acids and many other substances I have in mind.

The Haber process fixes nitrogen by combining it with hydrogen and requires these substances in the pure state. It requires costly machinery, and its development required the highest type of engineering skill. These highly specialized things, however, mean that it will also require especially competent people to run it.

On the other hand, the process I have described to you this evening represents the other extreme. It makes use of the crudest things such as coke, producer gas and water. These are handled by the simplest possible mechanical operations and the catalyzer, iron, is not bothered even by the gross assortment of elements in the ash of the coke, and any sort of labor, when properly directed, can handle it.

REMARKS

It is not worth while to make a summary of the work I have described, because the whole presentation has been condensed so as practically to be a summary. Almost everything mentioned can be done in a variety of ways which I did not have time to mention and even the most important things could not be much more than mentioned.

I hope that the evidence presented to-night has cleared away some of the erroneous statements which have hindered progress in this field which has been handled in an exceptionally unfortunate way. I also hope that the statements under "Emergency Process" will, if sudden need arise, lead to instant action instead of interminable discussion and counter-propositions. The way to test the matter is to set up the apparatus as is sharply set forth. A roof can be put over it after it is in operation and blueprints, plans and improvements can await their turn.

None of the things mentioned in the above work were discovered by chance. All were predicted by a carefully considered application of the very simple but fundamental principles of physics, chemistry and mathematics, which every undergraduate in chemistry is taught. They were then verified by experiments which were chosen to give decisive answers to questions and to establish quantitative data.

Only a comparatively short time could be given to the work because of the heavy pressure of other duties, and it would certainly have been impossible to carry it out if it were not true that pure science is the only foundation for industrial work.

I have been connected with universities and technical schools for 28 years as student and teacher. I have always used every effort to further the view that all industries must be based directly on work in pure science and that the only way to succeed is to become thoroughly master of these fundamental principles and then look at things from every point of view in order to solve whatever problems may be encountered.

There seems to be a constantly increasing pressure both from within as well as from without the university, which is inimical to this ideal and many cures, which are at variance with it, are advocated, in the rush to get results quickly by a short cut to knowledge.

If it had been more generally realized that hard work and careful, self-sacrificing preparation are very likely ultimately to lead to quick, certain, solution of difficulties rather than perhaps to years of misguided effort and enormous expenditures of money, with, like as not, ultimate failure, things would not have drifted to their present condition.

If these illustrations have some influence in the direction I believe that it will be more important to the country than even a successful nitrogen fixation process.

THOMAS UNIVERSITY
PROVIDENCE, R. I.

THE VOLATILIZATION OF POTASH FROM CEMENT MATERIALS¹

By E. ANDERSON AND R. J. NESTELL

Received January 25, 1917

In the course of an extended series of investigations upon the subject of potash volatilization from silicate mixtures, the following report was prepared, covering that portion of the laboratory work which was incident to the study of volatilization of potash from cement making materials.

The work reviewed in this report forms one link in a chain of investigations covering various possibilities of volatilizing potash from silicates during the process of manufacturing Portland cement, with subsequent collection of the volatilized potash from the furnace gases by means of electrical precipitation. The process of electrical precipitation can be applied in two ways: should the total dust and fume issuing from the furnace contain a large percentage of potash, the total suspended material can be collected in a single electrical precipitator; should, on the other hand, the potash content be low, a fractionation of the suspended material may be resorted to, as for example by utilizing a two-stage fractional precipitation apparatus.

OBJECT—It has long been known that the raw material used in cement making contains potassium salts which are partly volatilized in the burning, and from experiments in field and laboratory, some data bearing on this volatilization have been obtained and published. Very little exact information, and particularly such directly applicable to the potash volatilization from actual cement materials has, however, been available, and the following series of experiments were undertaken for the purpose of obtaining such information regarding the factors which influence the liberation of potash in actual cement burning.

SCOPE OF THE INVESTIGATION—The rate of volatilization of a potash salt from cement mix in the highly heated zone of a cement kiln, is dependent upon a number of factors. As predominating factors affecting the possible recovery in the furnace gases beyond the furnace, there may be mentioned: (1) the temperature prevailing in the kiln; (2) volume of gas passing; (3) the intimacy of contact between the furnace gases and the cement mix; (4) the vapor pressure of the potash salt or salts formed; (5) the possibility of dissociation under certain furnace conditions (oxidizing, neutral or reducing atmosphere — directly temperature); (6) the degree of saturation of the gas in contact with cement materials; (7) the partial diffusion both of the salt vapors and of the liberated gas of the cement mix to the surface of contact with the gas stream, and of the saturated gas to the surface of the furnace gas space beyond.

Furthermore, since the cement burning, being a material process, from a matter of time and may be a factor concerning largely of climate and abundance of labor, the results in connection of the volatilized salt

¹ Report on the investigation conducted by the Western Engineering Company.

must also depend upon the stage reached in this change, as well as on the temperature at that point. Since an investigation of the dependence of the rate of volatilization upon the factors mentioned was too extensive to be undertaken with the time and resources at our command, the more empirical method was chosen of simply establishing conditions as nearly as possible identical with kiln practice, and determining the rate directly under those conditions.

In order that the data obtained should be as comprehensive and conclusive as possible, experiments were made on ten different cement materials from different parts of the United States and from Japan. The following are the names and locations of the cement mills from which the samples investigated were obtained:

MILLS	LOCATION	MILLS	LOCATION
Alpha	Cementon, N. Y.	Utah	Salt Lake City, Utah
Atlas	Northampton, Pa.	Pacific	Cement, Cal.
Dexter	Nazareth, Pa.	Santa Cruz	Davenport, Cal.
Security	Hagerstown, Md.	Riverside	Crestmore, Cal.
Olympic	Bellingham, Wash.	Asano	Moji, Japan

DESCRIPTION OF APPARATUS AND EXPERIMENTS

Since the information desired was primarily in regard to cement burning, it would have been very desirable to duplicate exactly the conditions found in a rotary kiln. This would, however, have entailed both elaborate apparatus and large amounts of material, so the scheme finally adopted was simply to heat small

should be in contact with gases similar, as nearly as possible, to those in a cement kiln. For this reason the heating was done in a gas-fired furnace of a modified Fletcher type. This furnace (Fig. 1) was constructed especially for these experiments from Johns-Manville high temperature cement No. 32, fire clay being impracticable on account of its lower melting point. Although this high temperature cement is rather slow in setting, and has a tendency to crack on heating, it served the purpose very well, and withstood temperatures as high as 1500° C.

The furnace was heated by means of a blast Méker burner, and manometers on the gas and air connections made it possible to control the temperature very accurately and to duplicate any previous run. One of the air intakes of the burner was connected with an SO₂ container, so that this gas could be mixed with the incoming air when desired. Here also a manometer served to indicate the relative amounts of gas admitted, but the absolute SO₂ content of the furnace gas was determined by analyses. The temperature was measured with a LeChatelier pyrometer and platinum-rhodium couple.

In making a run, the material was placed in a shallow platinum dish, supported in the center of the furnace so that the flame and gases passed directly over it. A platinum shield around the dish served to equalize the temperature and prevent local overheating. The end of the pyrometer-couple was inserted directly in the material heated. Under these conditions it was possible to maintain temperatures constant to within 10° C. anywhere from 800 to 1400° C. The sketch gives an outline of the furnace and set up.

In the first experiments it was attempted to stir the charge regularly during each run. This, however, gave very non-uniform results, due to the impossibility of providing, by intermittent hand-stirring, a surface exposure or renewal consistent throughout the period of a test or of a series of experimental runs. Since the volatilization is dependent upon the factors of temperature and rapidity of removal of the vaporized potash by the moving gas stream, and the rate of diffusion of the gaseous potash salt from the interior of the charge into the gas stream above, the scheme finally adopted was to discontinue the stirring and to use a small amount of sample, about 1 g., which was placed as a thin layer in the dish in as nearly the same manner as possible, each time. In this way, and without stirring, good check runs could be secured, and uniform results obtained.

All the experiments were made on material previously calcined at about 900° C. which, however, still contained small amounts of CO₂. At high temperatures and long exposures this lost, in addition to the CO₂, also the K₂O and Na₂O, while when heated in an atmosphere of SO₂, much of this latter gas was absorbed, so it was necessary to determine the change in weight of the charge for each run, in order that the K₂O analyses could be correctly interpreted.

OUTLINE OF INVESTIGATION

The scheme of the experiments was, first, to investigate rather thoroughly two of the ten cement

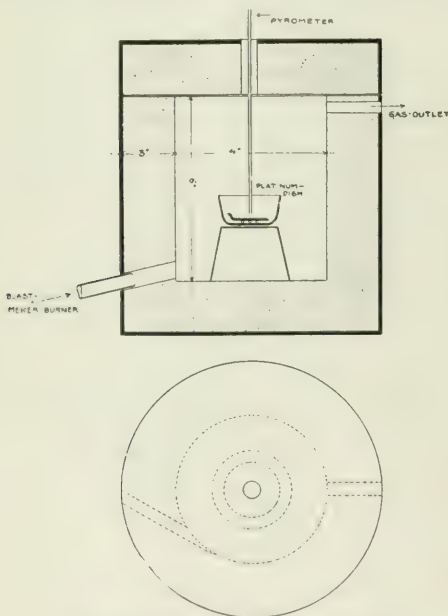


FIG. 1—GAS FURNACE FOR POTASH VOLATILIZATION

amounts of the material in a furnace where the temperature, and, to a certain extent also, the nature of the gases in contact with the material, could be controlled. Analyses of the material for K₂O before and after heating then showed the extent of the volatilization.

It was desirable also that the material, when heated,

mixes, and then to run a series of shorter tests on the entire ten.

Thus tests were made on either the Security or Alpha material to determine:

- (1) The rate of volatilization at different temperatures.
- (2) The effect of SO_2 in furnace gases on the volatilization-rate.
- (3) The time factor of volatilization at 1200°C .
- (4) The time factor of volatilization at 1400°C .
- (5) The effect of reducing gases on the volatilization rate.
- (6) The volatilization from unground clinker.
- (7) The effect of addition of gypsum to raw mix.
- (8) The effect of addition of calcium oxide to raw mix.
- (9) The effect of addition of calcium chloride to raw mix.
- (10) The effect of addition of sodium chloride to raw mix.
- (11) The volatilization of sodium.

Having in this manner investigated the behavior of two of the cement mixes, the volatilization rate at different temperatures was determined also for the remaining eight.

In addition to the regular raw material, so called "treater dust" was also tested, since this is used as part of the feed in certain cement mills. The tests on this included determination of the rate of potash volatilization as well as the effect on this rate of the addition of chlorides.

Supplementing these laboratory experiments, data regarding actual kiln operation have been added.

PROCEDURE

The procedure in these volatilization tests was, as has already been indicated, first to calcine the material at about 900°C ., after which its K_2O content was determined. Then small amounts, usually between one and two grams, were heated in the furnace under the required conditions, after which the K_2O remaining in the heated material was again determined as well as the loss in weight. From this was calculated the per cent of the original potash which had been volatilized. Duplicate runs were made in most cases so that errors in analyses and temperature control were minimized.

DESCRIPTION AND DISCUSSION OF EXPERIMENTAL DATA

CEMENT MATERIALS—Table I and Fig. II show the volatilization of potash from the Security cement material, in one hour at 1100° , 1150° , 1200° , 1250° ,

had been added to these gases. These results are very concordant, and show conclusively that the presence of SO_2 in the gases in contact with the material retards the volatilization of the potassium compounds.

In the case of the Alpha material (Table I and Fig. III), the retardation due to the SO_2 is just as positive and regular as with the Security cement material. The 15-min. treatment of the "Security" shows this retarding effect at 1400° , and while the retardation is less here than at lower temperatures, it is just as positive.

Regarding the explanation of this retardation with SO_2 , tests made on pure K_2SO_4 and K_2CO_3 show that the carbonate is much more easily volatilized than the sulfate. The carbonate lost 65 per cent of its weight in half an hour at 1300°C ., while the sulfate lost only 1 per cent in the same time and at the same temperature. These tests also proved that the carbonate is changed to sulfate when treated in an atmosphere of SO_2 and air, and that in such an atmosphere, much less of the carbonate is volatilized than in the ordinary SO_2 -free furnace gases. It is, therefore, probable that, in the presence of SO_2 , the potassium in the cement material combines to form the sulfate, and remains as such in the clinker.

At temperatures below 1350°C ., the lime in the material also combines with the SO_2 to form sulfates and sulfites. Thus at 1100°C . the charge gained 19 per cent in weight in one hour, when SO_2 was present. Of this 19 per cent increase, one-half was sulfur. At temperatures above 1350°C ., the sulfur combined with the lime is again driven off.

The fact that so much of the lime combines with the SO_2 would also account, in part, for the retardation of the potash volatilization. A certain amount of lime, over that theoretically necessary to combine with the silica present in the mix, seems to be indispensable for a fair liberation of the alkali salts, and the formation of any appreciable amounts of calcium sulfate would easily reduce this excess below its optimum value.

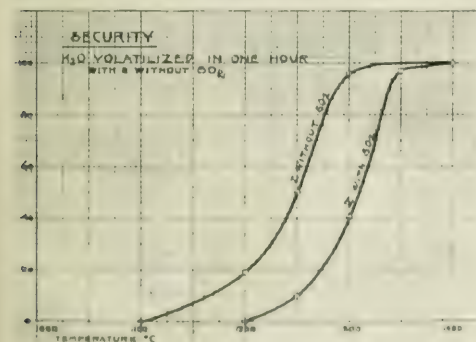


FIG. II

and 1400°C . when the furnace gases were free of sulfurous acid. Table I and Fig. II also include data for a series of tests at 1100° , 1150° , and

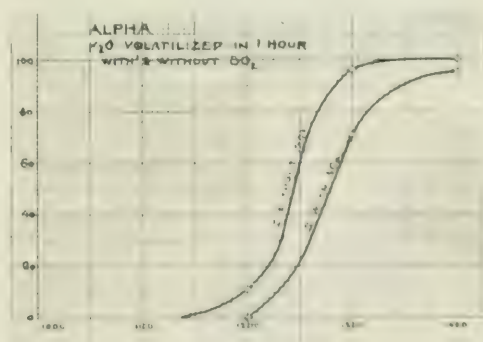


FIG. III

1200 and 1400°C . when the furnace gases were free of sulfurous acid. Table I and Fig. II also include data for a series of tests at 1100° , 1150° , and

TABLE I—VOLATILIZATION OF POTASH FROM SECURITY CEMENT—TEMPERATURE VARIED

KIND OF CEMENT USED	Period of Treatment	Temp. C.	Per cent K ₂ O before Heating	IN AN ATMOSPHERE FREE FROM SO ₂		FROM SO ₂ HEATING		IN AN ATMOSPHERE CONTAINING 0.2 PER CENT SO ₂	
				Change in Wt. Per cent	Per cent K ₂ O AFTER HEATING	Per cent K ₂ O AFTER HEATING	Per cent K ₂ O AFTER HEATING	Change in Wt. Per cent	Per cent K ₂ O AFTER HEATING
"Security"	1 hr.	1100	1.47	—2.5	1.53	1.46	1.49	1.45	1
	1 hr.	1200	1.47	—2.5	1.18	1.27	1.22	1.19	19
	1 hr.	1250	1.47	—4.5	0.78	0.78	0.74	50	96
	1 hr.	1300	1.47	—4.5	0.051	0.068	0.06	96	96
	1 hr.	1350	1.47	—4.5	0.00	0.03	0.015	99	99
	1 hr.	1400	1.47	—4.5	Trace	Trace	Trace	100	100
"Alpha" (Raw Mix)	1 hr.	1200	0.91	—2.0	0.83	0.81	0.81	11	11
	1 hr.	1300	0.91	—2.0	0.044	0.043	0.043	96	96
	1 hr.	1400	0.91	—6.0	Trace	Trace	Trace	100	100
"Security" + 5% CaSO ₄	15 min.	1400	1.47	—2.5	Trace	Trace	Trace	100	100
	15 min.	1400	1.40	—2.3	0.50	0.48	0.49	66	66

In general, Curves I and II (Fig. II) show that the presence of 0.2 per cent SO₂ in the furnace gases necessitates an increase in temperature of 50°, to maintain any given volatilization. The retardation, however, decreases with rise in temperature, due to the breaking up of the calcium sulfate formed.

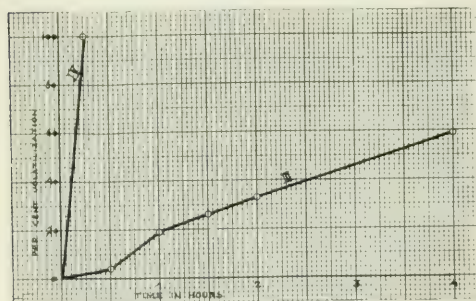
The relation between the volatilization rate and temperature will be discussed in connection with the experiments on the other cement materials.

Table II and Fig. IV show the rate of volatilization of potash from the Security raw material at 1200° C.

TABLE II—VOLATILIZATION AT 1200° C., IN VARYING TIMES, IN SO₂-FREE ATMOSPHERE

Time Hr.	Per cent K ₂ O before Heating	Change in Wt. Per cent	PER CENT K ₂ O AFTER HEATING	Per cent Total K ₂ O Volatilized
			Apparent	Corrected
1/2	1.47	2.5 loss	1.45	1.41
1	1.47	2 loss	1.22	1.19
1 1/2	1.47	2 loss	1.11	1.08
2	1.47	4.5 loss	1.03	0.99
4	1.47	6.4 loss	0.64	0.60

Evidently a 100 per cent expulsion at this temperature would require several hours. Curve IV (Fig. IV)

FIG. IV—PER CENT K₂O VOLATILIZED AT 120 AND 1400° C.

with its single point showing the rate of volatilization at 1400° C., was drawn only to emphasize the enormous increase in the volatilization velocity, as the temperature is increased.

The two preceding tests were made on finely ground material where the volatilization would necessarily be greater than from partially or wholly clinkered cement. Table III and Fig. V show what can be ex-

TABLE III—VOLATILIZATION OF POTASH FROM UNGROUND CLINKER—TEMPERATURE 1400° C.

Time Hr.	Per cent K ₂ O before Heating	PER CENT K ₂ O AFTER HEATING	Per cent Total K ₂ O Volatilized
		Apparent	Corrected
1/4	0.82	0.21	0.21
1/2	0.82	0.15	0.15
1	0.82	0.14	0.14

pected in such a case. In these tests, a large piece of clinker was broken in four parts, making approxi-

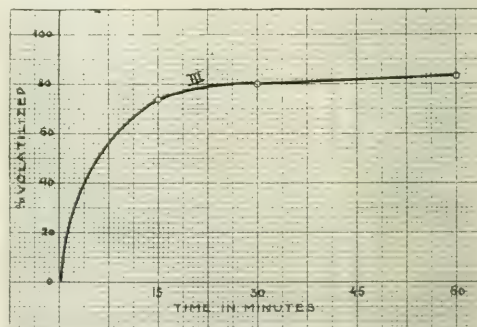
mately half-inch cubes. Of these one was analyzed, and the other three heated at 1400° C. for 1/4, 1/2 and 1 hour, respectively. From the results it is evident that the greater part of the potash remaining in the clinker can be driven off, with sufficiently high and continued heating.

That the addition of chlorides to a potash-bearing mineral facilitates the volatilization, is, of course, universally recognized and Table IV shows the effect

TABLE IV—VOLATILIZATION AT 1200° C. IN 1 HOUR WITH AND WITHOUT THE ADDITION OF CaO OR NaCl TO MATERIAL

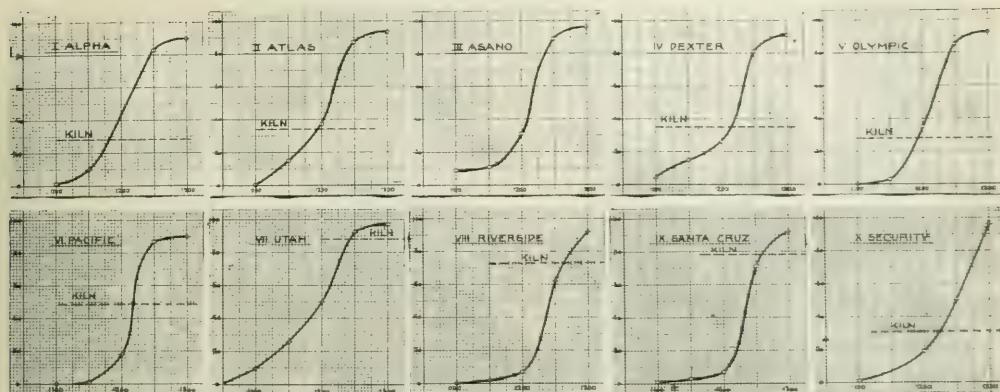
ADDITION TO MATERIAL	Per cent K ₂ O before Heating	Change in Wt. Per cent	PER CENT K ₂ O AFTER HEATING		Cor. Total K ₂ O Volatilized	Per cent Total K ₂ O Volatilized
			Duplicates	Av.		
16% CaO	1.23	—2.1	0.95	0.90	0.92	0.90
5% NaCl	1.40	—9.0	0.57	0.49	0.53	0.48

of 5 per cent NaCl on the Security raw material. Here the volatilization was increased from 19 to 66 per cent. The addition of 16 per cent lime was also tried—as the table shows. As was to be expected, the increase in volatilization caused by this was very

FIG. V—PER CENT K₂O VOLATILIZED AT 1400° C. FROM UNGROUND CLINKER

small, ordinary cement mixes, of course, having an ample excess of calcium oxide for the silica present. In this connection it might be of interest to note that with ordinary feldspar the potash does not begin to volatilize appreciably until over 50 per cent CaCO₃ has been added.

Quite often in cement burning insufficient air is admitted to the kiln, giving a reducing atmosphere. The assumption has been made that such reducing gases retard the volatilization of potash from the material being burned, and to test this, samples of the Security raw mix were heated in as powerfully reducing an atmosphere as was possible to obtain by maintaining the temperature in the furnace on a minimum amount of air. Table V shows the comparison between the

FIG. VI. PER CENT K_2O VOLATILIZED FROM CEMENT MATERIALS IN ONE HOUR

volatilization in such an atmosphere, and in ordinary furnace gas, and the results indicate that the assumption is unfounded, the reducing atmosphere being, if anything, more favorable, at least for the lower temperatures.

TABLE V. VOLATILIZATION OF POTASH IN OXIDIZING AND REDUCING ATMOSPHERE "SECURITY" CALCINED RAW MIX

Temperature	Time	PER CENT K_2O VOLATILIZED
		Oxidizing Reducing
1200° C.	1 hour	19 34
1250° C.	1 hour	80 66
1300° C.	1 hour	96 91

The claim has also been made that the sodium is less readily volatilized than the potassium. In the case of cement, however, the difference does not seem to be very great, for with the Security raw material, 95 per cent of the soda was driven off in one hour at 1300° C. with a parallel volatilization of 96 per cent of the potash (see Table VI).

TABLE VI. VOLATILIZATION OF SODIUM "SECURITY" RAW MIX, HEATED ONE HOUR

Temp. ° C.	Per cent Na_2O in Calined Material	Loss in Weight Per cent	PER CENT Na_2O AFTER HEATING	Per cent Total Na_2O Volatilized
1300	0.65	4.5	0.04 0.04	94

The object of the experiments just discussed was, as has already been pointed out, to throw as much light as possible on the behavior of any one cement material. In the following experiments the aim has been to apply what seemed to be the most important test, that of the volatilization at different temperatures, to a number of different cement materials.

Fig. VI shows the volatilization of potash in one hour at 1100, 1150, 1250 and 1300° C. from ten cement materials obtained from different localities.

The similarity of these curves makes it evident that the potash volatilization from any cement material follows the same general law, and that, of course, but natural, considering the similarity of the material. Thus it can be seen that in an ordinary cement until the potash does not begin to be driven off until a temperature of 1100° C. has been reached. The only exceptions found were in cement material from Utah and from Japan. The rate of volatilization increases rapidly with the temperature, the change being par-

ticularly rapid about 1250° C. and at 1300° C. practically all of the potash is driven off in one hour under the conditions of these experiments.

This remarkable uniformity of behavior of these different cement materials, obtained from such widely separated sources, is strikingly brought out by the volatilization curves; the additional data for these appear in Table VII. In order to show this more clearly, these curves have all been plotted superimposed (Fig. VII); the still greater similarity between certain individual ones has been indicated by plotting

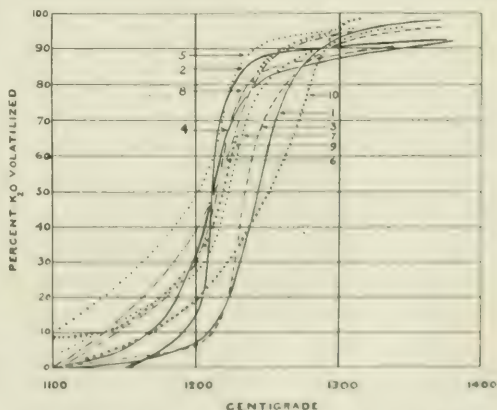


FIG. VII. POTASH VOLATILIZED FROM CEMENT RAW MIX IN ONE HOUR

together in four groups, shown in Figs. VIII A, B, C, D. The last two, however, are similar only in curvature, being separated by about 10° in temperature. It is significant that this arrangement groups together the cement material of the Far East, Japan, the South west, the Northwest, and mostly Utah with Maryland. The reason for this is probably to be found in the mineralogical nature of the resulting cement of cement material.

To give more idea of the variation between the curves in these matter, the curves are shown in Fig.

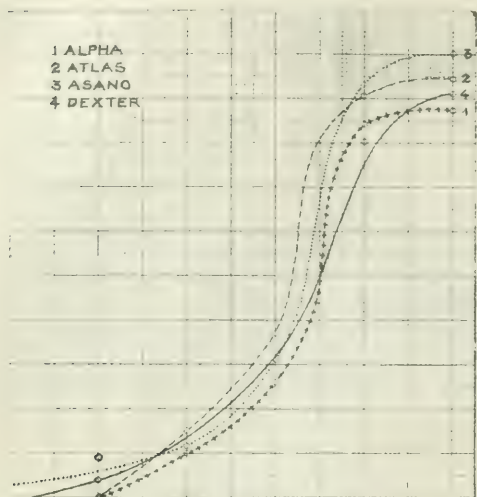


FIG. VIII-1

kiln, this latter has been calculated from the K_2O content of the clinker, where this was known, and these values given in a separate column headed "Per cent K_2O Volatilized in Kiln." On the charts this has been indicated by a dotted horizontal line.

TABLE VII. ADDITIONAL DATA FOR VOLATILIZATION CURVES

CEMENT MATERIAL	Per cent K_2O in Calced Material	Temp. $^{\circ}C$	Loss in Weight Per cent	PER CENT K_2O AFTER HEATING APPARENT		Volatilized in Clunker	Volatilized in Kiln
				Duplicates	Av. Corrected		
Alpha	1.00	1100	1.8	1.08	1.06	0	
		1150	1.3	0.88	0.95	0.91	10
		1200		0.88	0.95	0.91	10
		1250	2.5	0.18	0.16	0.17	83
		1300	2.5	0.13	0.12	0.128	88
Atlas	1.01	1100	1.8	1.29	1.26	0	
		1150	1.8	1.05	1.05	1.03	15
		1200	1.6	0.77		0.77	76
		1250	3.0	0.18	0.15	0.165	87
		1300	4.1	0.07	0.10	0.085	93
Asano	0.90	1100	1.8	0.83		0.83	82
		1150	1.8	0.82	0.81	0.81	80
		1200	1.8	0.70	0.55	0.625	61
		1250	2.5	0.11	0.09	0.10	80
		1300	2.7	0.04		0.04	96
Dexter	1.33	1100	1.4	1.30		1.30	128
		1150	0.5	1.14		1.14	113
		1200	1.2	0.99		0.99	98
		1250	3.0	0.26		0.26	81
		1300	5.0	0.13		0.13	91
Olympic	0.61	1100	1.8	0.65		0.65	64
		1150	1.8	0.59	0.60	0.59	58
		1200	1.8	0.40	0.43	0.41	40
		1250	3.2	0.11	0.08	0.095	88
		1300	2.7	0.06		0.06	92
Pacific	0.88	1100	1.0	0.96		0.90	89
		1150	1.0	0.85	0.85	0.65	84
		1200	1.8	0.68	0.74	0.71	70
		1250	2.3	0.10	0.12	0.11	87
		1300	3.5	0.09		0.09	90
Totah	0.44	1100	1.5	1.32		1.30	10
		1150	1.8	1.08	1.10	1.09	107
		1200	2.0	0.8	0.73	0.74	73
		1250	2.7	0.11	0.12	0.11	91
		1300	3.5	0.08	0.09	0.085	94
Riveride	0.80	1100	1.0	0.81		0.82	0
		1150	1.0	0.78	0.80	0.79	78
		1200	1.5	0.74	0.78	0.76	75
		1250	2.5	0.28	0.34	0.31	30
		1300	2.5	0.08	0.05	0.065	96
Santa Cruz	1.24	1100	1.8	1.30		1.28	0
		1150	2.0	1.22	1.21	1.21	120
		1200	2.0	1.21	1.17	1.19	116
		1250	3.5	0.30	0.40	0.35	34
		1300	4.0	0.12	0.10	0.11	10

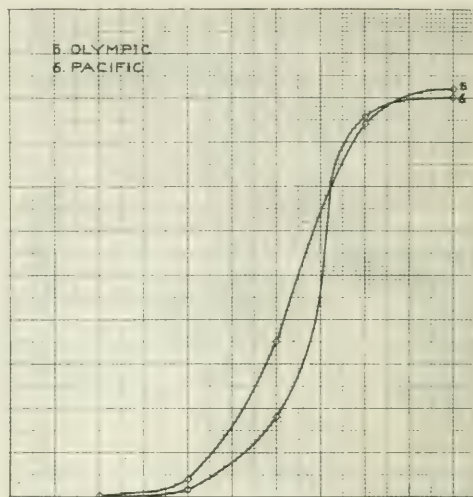


FIG. VIII-2

Since the volume of gases through a kiln is roughly constant the potash volatilization in the kiln necessarily depends on two factors, *viz.*, the time and temperature of burning, and the specific nature of the potassium compounds in the material. Consequently the kiln-volatilization is subject to variation; not only with different materials, but also in the case of any one material the volatilization will vary with different methods of burning. It is seen, however, that in all cases, the kiln-volatilization is equivalent to one hour's heating in the furnace used at from 1160 to 1260 $^{\circ}C$.

TREATER DUST

As has been mentioned, treater dust, or material collected in dust precipitating equipment is also used in certain cement mills as raw material for cement. As a matter of fact, the heavy portion of any dust so collected is essentially partly calcined raw material, to which have been added varying amounts of alkali salts, usually sulfates. The object of this secondary burning, aside from saving that much raw material, is to obtain a "treater dust" comparatively rich in potash, by burning a very low-grade potash material.

TABLE VIII

Riveride Treater Dust Material	K ₂ O in Riverside	Calced Temp	Loss in Wt Per cent	PER CENT K_2O AFTER HEATING APPARENT			Per cent K_2O in Clunker	Per cent K_2O Volatilized in Kiln
				Duplicates	Av.	Corrected		
	1.36	1200	2	3.74	3.78	3.76	3.68	16
	1.36	1300	2	0.13	0.10	0.11	0.09	98
100 NaCl	3.97	1300	18	0.78	0.96	0.85	0.81	81
100 CaCl	3.97	1300	26	0.17	0.13	0.15	0.11	97

It has been found, however, that the volatilization of potash in the kiln from such dust is much less satisfactory than from the regular raw material. Thus

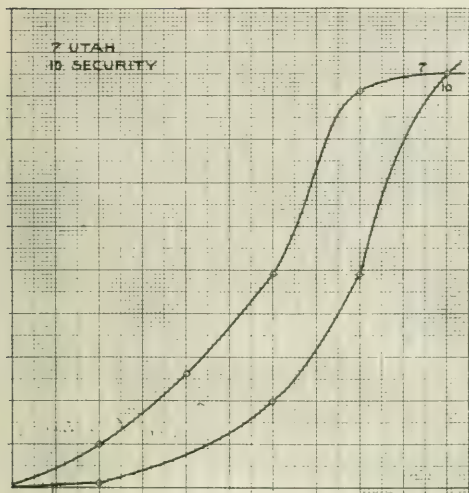
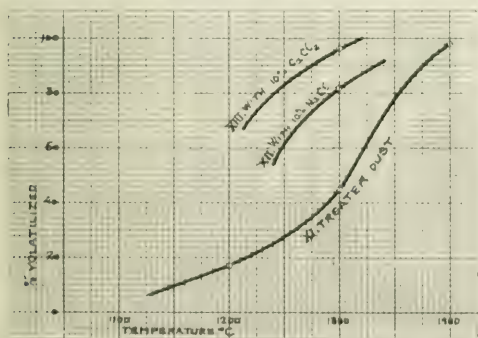


FIG. VIII

at the Riverside plant, the volatilization from the regular "raw mix" is 73 per cent, while the treater dust, burned in the secondary kiln, gives a volatilization of only 16 per cent. It is probable that this low liberation from the dust is largely due to the presence of sulfates in the dust, of lower vapor pressure than the oxide, the product apparently volatilized from the original raw mix.

That here also all of the potash can be driven off, is shown by Table VIII and Fig. IX. These results

FIG. IX. PER CENT K₂O VOLATILIZED FROM RIVERSIDE TREATER DUST AT 1050 DEGREES

were obtained in the same manner as those previously recorded. Higher temperature or longer heating than with the regular cement material, was however necessary, for at 1400° C. only one half of the potash had been expelled, but at 1450° C. the volatilization was practically complete.

The addition of chloride increased the amount of the volatilization in this case, as when potassium material, practically dissolving the salt, at 1400° C.

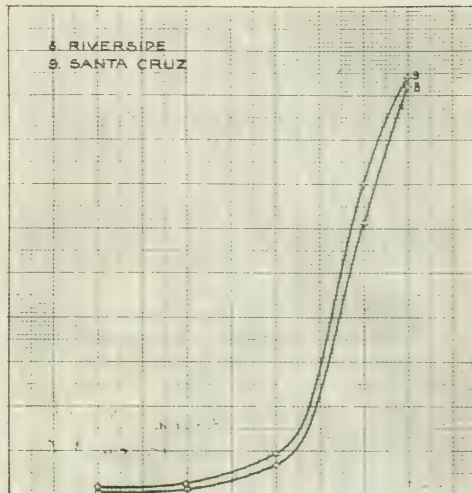


FIG. VIIIb

Calcium chloride seems more effective than the corresponding sodium salt, and this also appears to have been the experience of others who have investigated these reactions.

It is interesting to note that even here, with a material containing over 4 per cent K₂O, and much SO₃, the kiln volatilization is equivalent to one hour's furnace treatment at about 1200° C.

VOLATILIZATION IN KILNS

Regarding the volatilization of potash in actual kiln operation, Table IX gives some data obtained

TABLE IX. EXPERIMENTS ON THE LIBERATION OF POTASH IN COMMERCIAL KILNS

Date Dec. 1915	FURNACING CONDITIONS	SOCIETY PLANT & LIME CO.		RIVERSIDE KILN		Percent of Total K ₂ O Volatilized
		Normal Charge	Hot Charge	Normal Charge	Hot Charge	
9	Normal Burning	1.05	0.67	1.25	0.10	11.0
10	Hard Burning Mix. Kiln Hotter	1.01	0.73	1.20	0.10	11.0
11	Normal Mix. Kiln Hot	0.93	0.83	1.20	0.10	11.0
12	Kiln Very Hot. A broken piece burned	0.84	0.63	1.20	0.10	11.0

(1) Net per cent K₂O calculated on the original mix, and as weight in kiln.

from the Society plant. The more the plant is supplied with material and operates at low normal kiln temperature. Thus, while with normal burning 11 per cent of the potash was volatilized, this was increased to 13 per cent by raising the temperature of the kiln.

Tests made in another cement plant have not been sufficient to show that heating at a higher temperature increases the potash volatilization. In this case only the raw mix was used, as the product was formed in the kiln, and the temperature was not high enough to cause the potash to volatilize. The raw mix was the same as that used in the Society plant, and the results were very much the same. The potash was volatilized at about 11 per cent, and the results were the same. The

following proved to be the K_2O content of the two samples:

Soft burned clinker . . .	$K_2O = 0.50\%$
Hard burned clinker . . .	$K_2O = 0.17\%$

Then a large sample of normal clinker was separated in three sizes, labeled "coarse," "medium" and "fine," the approximate average diameters of each size being 1 in., $\frac{3}{8}$ in. and $\frac{1}{8}$ in., respectively.

The potash content of these samples was:

Coarse clinker . . .	$K_2O = 0.377\%$
Medium clinker . . .	$K_2O = 0.278\%$
Fine clinker	$K_2O = 0.240\%$

So the conclusions arrived at from the laboratory experiments, that time and temperature of heating were the important factors in potash volatilization, are well substantiated by results obtained in practice. And to the above two main factors in the volatilization can then also be added the size of the product, since the smaller the clinker, the more completely will the potash be driven off.

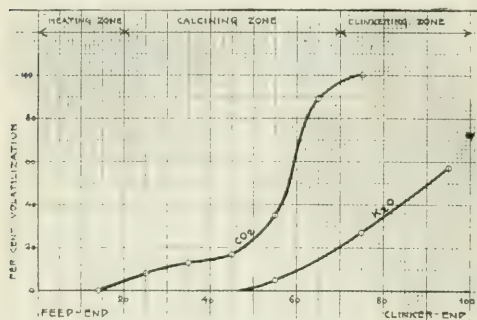


FIG. X. CALCINATION AND POTASH VOLATILIZATION IN CEMENT KILN

Table X and Fig. X show the volatilization and heating zones in a rotary cement kiln. These data

TABLE X. KILN LOSSES OF CO_2 AND K_2O
RIVERSIDE PORTLAND CEMENT CO.

Distance from Feed End	Per cent CO_2	Per cent in Wt. Loss	Per cent Apparent	Per cent Corrected	Per cent Lost CO_2	Per cent Lost K_2O
0	32.0	0	0.460	0.460	0.0	0.0
5	32.0	0	0.460	0.460	0.0	0.0
15	32.0	0	0.460	0.460	0.0	0.0
25	30.0	2	0.460	0.460	8.1	0.0
35	29.0	3	0.460	0.460	12.2	0.0
45	28.0	4	0.460	0.460	15.9	0.0
55	23.0	9	0.480	0.437	34.6	5.0
65	7.0	28	0.490	0.333	88.6	27.6
75	0.0	32	0.490	0.333	100.0	27.6
85	0.0	32	0.490	0.333	100.0	27.6
95	0.0	32	0.490	0.333	100.0	27.6
100	0.0	32	0.490	0.333	100.0	27.6

were the results of analyses of samples taken every five feet in a 100-foot kiln which had been shut down for a re-lining without first "running out" the feed. Although samples were taken every five feet, only the 10-foot samples for CO_2 and the 30-foot samples for K_2O have been included in the table.

It is seen that in a cement kiln there is first a heating zone, then a calcining zone, and finally the clinkering zone. Evidently very little of the potash is driven off before the material begins to clinker. This was, of course, to be expected from the experimental data given.

It might be added here, that in no case of the experimental heating was a permanent clinker produced

in one hour below $1350^\circ C$. At $1300^\circ C$. there always resulted a seemingly normal black and hard clinker, which, on cooling, rapidly disintegrated into a fine grayish powder.

GENERAL DISCUSSION

Although the preceding experiments and data show little that was new or unlooked for, they do, however, indicate some of the factors governing the volatilization of potash from the average cement material.

Evidently the nature of the potassium-bearing compound varies, and the potash is driven off more easily in some cases than in others, but the data and curves here shown indicate that practically all of this compound can be driven off at from 1200 to $1300^\circ C$. from any material, if time enough be allowed. They show also that the volatilization rate increases very rapidly with the temperature, so that at $1400^\circ C$. the time needed to drive off practically all of the potash is very short indeed.

Time and temperature, therefore, can be said to be the determining factors, while the tests on actual kilns which were reported on, show that the size of the clinker is also important.

In order to increase the volatilization otherwise than by longer and harder burning, it has been shown that chlorides can be added advantageously. The addition of sulfates, as gypsum, or, what amounts to the same thing, the introduction of SO_2 in the furnace gases, through the burning of sulfur-carrying fuel, instead of improving the volatilization, has been shown to be decidedly detrimental.

Unfortunately there is very little information available on potash volatilization in actual kiln practice. The data obtained, however, agree well with the experimental results of this investigation, in that they show that time and temperature are the determining factors. In addition, these data indicate the importance of producing small size clinker, so as to expose a relatively larger surface to the heating effect in the kiln.

Burning at high temperature, then, in kilns so constructed as to keep the material in the hot zone and in contact with the highly heated moving gas stream as long as possible, would seem to be the logical means of obtaining the maximum potash volatilization from a potash-bearing cement material.

SUMMARY

The following conclusions seem fully warranted by the experimental data presented:

I—The potash in any cement material can all be volatilized.

II—The determining factors in this reaction are temperature and length of time exposure of the cement material to temperature and gas volume prevailing.

III—The lower limit of temperature for potash volatilization is $1100^\circ C$., and the rate of volatilization increases rapidly with the temperature.

IV—The presence of chlorides, particularly calcium chloride, increases the velocity of the volatilization, while sulfates decrease this rate.

V—Because of the formation of sulfates, SO_2 in the furnace gases retards the volatilization.

VI—Sodium is driven off nearly as easily as is the potassium.

VII—In the kiln, besides the factors of time and temperature, the size of the clinker also affects the volatilization-rate. The smaller the clinker, the better the volatilization of potash from it.

VIII—Although the potash in any cement mix can be driven off, the rate of expulsion at any given temperature varies for different materials, and is probably dependent on the mineralogical character of the potash-bearing component of the cement material.

WESTERN PRECIPITATION COMPANY LABORATORIES
LOS ANGELES, CALIFORNIA

THE EFFECT OF TEMPERATURE AND DURATION OF REACTION ON THE FORMATION OF LIGHT OILS IN COAL CARBONIZATION AT ATMOSPHERIC PRESSURE

By M. C. WHITAKER AND W. R. CROWELL

Received December 11, 1916

The object of the present investigation was to study in a qualitative way the effect of temperature and duration of the reaction on the formation of the light oils obtained in coal carbonization at atmospheric pressure. By light oils here we mean those distilling from the tar at temperatures below 210°C : the individual members of the light oil family which will receive particular consideration are those of interest from an industrial standpoint—viz., the phenols or tar acids, benzene, toluene and xylene.

To study the effect of duration of reaction, the so-called "recirculation" process of coal carbonization was employed, and the effects thus obtained were compared with those obtained in another series of experiments in which the coal was distilled in a manner similar to that employed in current practice.

HISTORICAL REVIEW

EFFECT OF TEMPERATURE ON LIGHT OIL FORMATION

The work of Lewes¹ and Börnstein² on low temperature oils and the work of Jones and Wheeler³ and Pictet and Bouvier⁴ on low temperature vacuum tar oils indicate that the low temperature oils are characterized by a low specific gravity, high liquid paraffin content, comparatively high tar acid content and low aromatic content. In tars produced below 500°C . the liquid paraffins consist of those of the hexane, heptane, octane and possibly of the higher series, while there are also present considerable quantities of olefines and the naphthenes. Phenol, itself, occurs in small quantities, but its higher homologues, such as the cresols, occur in greater quantities than in ordinary coal tar. Coals rich in oxygen (10 to 11 per cent) and hydrogen (above 5 per cent) and which, therefore, have large percentage of resinous bodies, on being carbonized at low temperatures, yield tar, rich in phenol and cresol.

¹ *J. Gas Lighting*, **101**, 885. The carbonization of coal. Lecture IV, *J. Roy. Soc. Arts*, **60**, 516.

² *Z. anorg. Chem.*, **17** (1901), 363; **18**, 30; *J. chem.*, **49** (1906), 67; *648* etc.; *J. Chem. Ind.*, **26** (1906), 513, 583; *Chem. Rev.*, **1904**, 57.

³ *J. Chem. Soc.*, **108** (1911), 140-51, 556-57.

⁴ *Compt. rend.*, **107** (1911), 59-61.

The work of L. T. Wright,¹ Watson Smith,² Börnstein and others shows that the tendency of increasing the temperature of carbonization is to cause a falling off in the actual and percentage yields of the light oils, a decrease in the actual yield of heavy oil, but an increase in the percentage yield of heavy oil. The specific gravities of both fractions tend to increase and the yield of tar acids tends to decrease with increased temperature. At very high temperatures benzol falls off and the light oils are lacking in the phenols which are carried to the creosote oil.

THE EFFECT OF TEMPERATURE ON THE FORMATION OF THE INDIVIDUAL AROMATICS—A special study of the effect of temperature on the formation of the individual aromatics benzene, toluene and xylene in coal carbonization was suggested by the work of Rittman, Egloff and Twomey in the cracking of petroleum oils at atmospheric pressure.

Starting with cymene, they found it possible to produce by "cracking" all the other hydrocarbons of the series, such as xylene, toluene, benzene, naphthalene and anthracene.³ From xylene alone they obtained toluene, benzene, naphthalene and anthracene, but no cymene. Toluene yielded benzene, naphthalene and anthracene, but no cymene or xylene. Benzene went to diphenyl, naphthalene and anthracene, but not to any of its higher homologues. From naphthalene, anthracene is readily obtainable but none of the monocyclic hydrocarbons, benzene, toluene, xylene, and cymene are produced. Anthracene yielded no naphthalene but went entirely to tarry matter, carbon and gas. On the foregoing evidence the authors claimed that they were justified in stating that the course of the cracking reaction in the aromatic series might be indicated as follows:

Higher benzene homologues \rightarrow lower benzene homologue \rightarrow benzene \rightarrow (diphenyl) \rightarrow naphthalene \rightarrow anthracene \rightarrow carbon and gas.

In further work along these same lines, Egloff and Twomey⁴ cracked a Pennsylvania gas oil at atmospheric pressure and besides verifying the course of reactions of the aromatics as just described, they also discovered valuable relations existing between temperature and rate of formation of the individual aromatics. The salient features of their results may be seen from a study of Fig. 1, taken from their report. These curves show that:

1—All of the aromatics, benzene, toluene, and xylene, begin to form in appreciable quantities at about 500°C .

2—The points of maximum aromatic formation are definite: that for benzene is at 580°C . and those for toluene and xylene are at 700°C .

3—In the zone of maximum aromatic formation (550-850 $^{\circ}\text{C}$.) there is a higher percentage yield of benzene than of toluene and a higher percentage yield of toluene than of xylene, thus offering further evidence that the course of the reaction is as previously indicated: the lighter aromatics first are

¹ *J. Gas Lighting*, **101**, 885.

² *J. Gas Lighting*, **101**, 885.

³ *J. Gas Lighting*, **101**, 885.

⁴ *J. Gas Lighting*, **101**, 885.

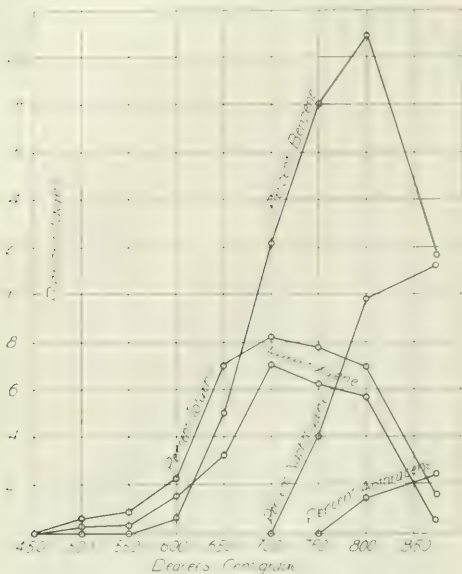


FIG. 1—ANALYSIS OF CRACKED PETROLEUM OIL ON THE BASIS OF RECOVERED OIL (Ejloff & Twomey)

mesitylene, pseudocumene, etc. \rightarrow xylene \rightarrow toluene \rightarrow benzene.

The authors suggested that a study of the temperature effect on the distillation of coal would undoubtedly give results similar to those obtained by them in oil cracking.

We have seen that, starting with an oil consisting almost entirely of paraffin hydrocarbons, it is possible to produce by cracking the various aromatics in the manner described. But what of the reactions taking place in the steps intermediary between the paraffin and the aromatic stages? A general survey of the work of many investigators in the field of thermal hydrocarbon decomposition furnished us with the following general conclusions:

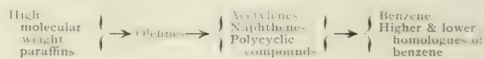
1—When a paraffin of high molecular weight is decomposed by heat, the products of the first stages of decomposition consist of paraffins of lower molecular weight and of olefines. The point of rupture of the carbon chain depends upon conditions of temperature and pressure.

2—Among the most important products resulting from a decomposition of the olefines just mentioned are acetylenes and other unsaturated compounds, alicyclic compounds or naphthenes, and probably various polycyclic compounds, etc.

3—Benzene and its higher and lower homologues are formed largely at the expense of the products of olefine decomposition¹ mentioned in (2).

By furnishing these links connecting the points of high molecular weight paraffin decomposition with

those of aromatic formation, the general course of the cracking reactions might be represented as follows:



A striking evidence that the important aromatics may be obtained by the thermal decomposition of mixtures of gaseous paraffin hydrocarbons is presented in the recent work of Zanetti on the cracking of the propane-butane fraction from natural gas condensate.¹ At temperatures from 700 to 900°, he was able to collect about 30 cc. of tar which yielded both toluene and benzene, and at 200° C. naphthalene began to come over and crystallize in the condenser.

THE RECIRCULATION PRINCIPLE

In the recirculation process, coal is carbonized in a closed retort in an atmosphere of the permanent gases generated during the heating, while at the same time these gases are continuously recirculated through the retort and the rest of the system. In following out this scheme, first the tars are swept out of the furnace and immediately condensed and then the remaining incondensable or permanent gases are passed by means of a fan through the retort again in order to repeat the same cycle of operations. The main object of this procedure is to sweep out of the carbonizing chamber all the distillation products before they are further decomposed by the action of continued heating. The mechanical details of the apparatus used as well as a more detailed account of the experimental procedure are described in later paragraphs.

In the process of coal distillation described as representing most closely that of standard practice, the coal was carbonized in the same retort under the same conditions as above, except that all of the products evolved were expelled from the furnace under their own pressure instead of through the medium of recirculated gases.

THE GENERAL EFFECT OF RECIRCULATION—According to the literature, the presence of an excess of an inert gas, such as carbon monoxide, hydrogen, etc., has two important effects on carbonization: the first is a dilution effect, which causes a decrease in the partial pressures of the constituent gases, and the second is an increase in volume effect which tends to cut down the time of heating. Of less importance is the absorption effect such as hydrogenation, etc.² It is obvious that the chief effect of recirculation is also to cut down the time of heating and this effect in combination with the others just mentioned tends to favor those reactions occurring at the earlier stages of hydrocarbon decomposition. We would expect, therefore, that recirculation would tend to increase the yield of the paraffins more than that of the unsaturated bodies, and that it would tend to increase the yield of unsaturated bodies more than that of the aromatics.

¹ H. L. H. in "The Decomposition of Hydrocarbons and the Influence of Hydrogen in Carbureted Water Gas Manufacture," pp. 1-35. Abstract of thesis in *THIS JOURNAL*, 8 (1916), 593.

THIS JOURNAL, 8 (1916), 6-1.

² Leslie, Thesis, p. 39.

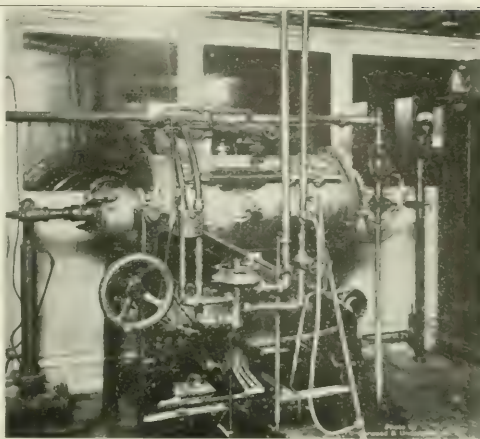
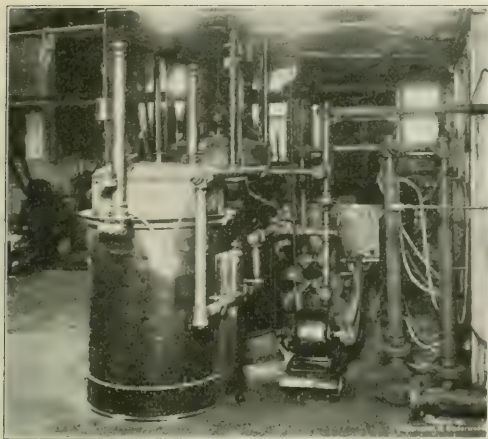


FIG. 2. GENERAL VIEW OF THE CARBONIZING SYSTEM (PHOTOGRAPH TAKEN IN TWO SECTIONS).

INDUSTRIAL PROCESSES OF RECIRCULATION—Numerous patents have been taken out for distilling coal on a commercial scale by the recirculation process,¹ but there seems to be little reliable information or scientific data published showing actual results obtained.

A number of articles have appeared, no doubt backed by the promoters of the Del Monte process which is being operated in England. The following is a quotation concerning the character of the Del Monte tars:²

"The liquid condensate is neither the heavy tars produced by high temperature methods nor the light tars which have hitherto resulted from various low temperature processes. It is a true petroleum of the paraffin series, its chemical formula, C_nH_{2n+2} , being identical with the petroleum produced by the Pennsylvania oil wells. It is amenable to cracking and yields by this treatment a very high percentage of motor spirit. On refining, all the petroleum products are obtained."

Carbonizing temperatures as low as 500° F. and yields of crude oil varying from 85 gal. per ton for coal to 135 gal. per ton for shales and bitumens are claimed.

FACTORS TO BE CONSIDERED IN ANY COAL CARBONIZA-
TION PROCESS

In the experimental investigation of any process of coal carbonization it is assumed that the following factors should be taken into consideration:

1. *Temperature* at which carbonizing reactions take place.
2. *Pressure* in the carbonizing vessel.
3. *Concentration* of the various constituents involved in the carbonizing reactions.
4. *Duration* of the reactions taking place in the system during carbonization.

[illegible]

5—Size and character of the surfaces in contact with the constituents undergoing decomposition, or the *catalytic effect*.

6—Nature of the coal.

It is evident that Factors (2), (5) and (6) may be kept constant in their effect throughout any series of experiments. It is also evident that the nature of the carbonization process makes impracticable any attempt at control of the concentration factor.

Experimental evidence indicates that the bulk of the volatile matter of coal under the proper conditions may be liberated at quite low temperatures—say at temperatures below 500°C . With sufficient surface exposure of the coal it would seem probable that at most of the carbonizing temperatures the important reactions take place after the tars and gases have been freed from the coal. For this reason it would seem more important to know the temperature of the atmosphere of the retort than that of the coal itself, therefore the best location of the pyrods would seem to be at each end of the coal charge as shown in Fig. 3. The chief error in the measurement of the temperature of the atmosphere of the retort is due to the tendency of the metal pyrods to absorb radiant energy more readily than the gases. Heat is transferred to the gases largely through conduction and convection. Therefore the main cause of error is due to a large extent to heating the pyrods by radiation, which is situated at the bottom of the retort. The error can be corrected after the manner of the method of

gases through the zone of heating should be under control, and that the dimensions of the heating zone and size of the coal charge should be the same for all runs. The rotation of the retort would tend to increase the amount of surface exposure of the coal as well as to insure a more uniform heating of the coal charge and also stimulate the conduction and convection of heat to the gases.

COAL USED IN TESTS

A selected grade of Pennsylvania bituminous coal especially suited for gas making was crushed and screened; all the particles passing through a 4-mesh screen were rejected. The size of the particles of coal taken varied from about $\frac{1}{4}$ to 1 in. in diameter. These were carefully sampled and stored away in covered barrels. The percentage analysis of this coal was as follows:

	Moisture	Volatile Matter	Fixed Carbon	Ash
Proximate.....	0.9	34.1	59.2	5.8
	Carbon	Hydrogen	Nitrogen	
Ultimate (Dry Basis).....	80.2	5.7	1.6	

EXPERIMENTAL APPARATUS AND PROCEDURE

A general plan of the carbonizing system may be seen in Figs. 2 and 3. During recirculation runs

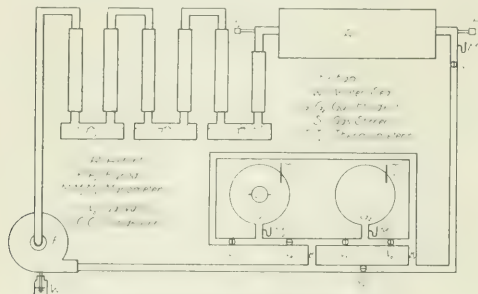


FIG. 3—PLAN OF CARBONIZING SYSTEM

the procedure was as follows: Coal was carbonized in the retort *R*. The volatile products passed to the condensers *C*₁, *C*₂ and *C*₃, where most of the water and part of the tar were deposited. The remaining volatile products then passed to the fan *F*, where most of the light tars were deposited in the water-sealed bottle *W*. The remaining volatile products consisting of incompressible gases were then passed by the fan to the by-pass *B*₁, where a part went to the gas holder *G*₁ and the remainder were sent into the retort again in order to sweep out the freshly generated tars and gases and repeat the same cycle of operations.

Since it is assumed here that the aromatics are the products of secondary and higher hydrocarbon decomposition, it seemed evident that the only mode of experimental procedure that would give consistent results would be that in which the temperature of the retort was maintained constant at all stages of the runs. To accomplish this purpose, the coal charge was thrust into the retort while it was heated to full temperature. All air was displaced by an inert gas, such as carbon dioxide, and this was quickly displaced by gas from a previous run.

In the runs in which recirculation was not employed, the procedure was similar to that just described except that the fan was not in operation and the return connection to the retort was cut off. The products of carbonization, therefore, passed under their own pressure from the retort through condensers and fan to a gas holder depositing the condensable products on the way.

In both circulating and non-circulating runs the heating was continued until the rate of gas evolution was about 0.1 cu. ft. per hour. This made the length of the runs from 1 to 3 hours.

The pressure at the retort was 0.8 in. of water in all runs.

In all runs the charges consisted of 5 lbs. of coal; and, except in the cases of the 500° non-circulating and the 700° circulating runs, at least two runs were made. In the case of these two, single runs were made. In the case of the 800° and 900° non-circulating runs, five runs were made in order to secure enough tar for light oil fractionation.

THE FURNACE—Fig. 4 shows a cross section of the furnace used. The furnace is a type of so-called "heating machine" put out by the American Gas Furnace Co. and was modified in construction to meet the needs of the present experiments. The retort is of the revolving type and the speed of rotation was about 1 r. p. m. In Fig. 4 the basket of coal is shown in position and the general course of the gases and tars may be followed. The coal basket consisted of two concentric cylindrical rolls of 4-mesh heavy wire screen wired at each end to annular rings of the same material. The furnace was heated by two sets of gas burners consisting of 5 burners to a set. The temperature of the retort was automatically controlled by a special temperature regulator so that the variation in temperature was not greater than 20° F. Parts of this regulator may be seen at the extreme right and just below the body of the furnace in Fig. 2. A detailed description of the operation of the regulator is contained in a bulletin published by the American Gas Furnace Co.

CONDENSERS, FAN AND GAS HOLDERS, ETC.—The condensers consisted of six 2-ft. lengths of 1½ in.-pipe provided with water jacket of 2-in. pipe. The base of the condensers consisted of 3-in. heavy cast iron piping. In these latter were placed thin sheet iron tar pans for catching the condensed tar.

The fan was a Sturtevant Monogram type, and rotated at a speed of 2000 r. p. m. Besides acting as a gas circulator it also served as a tar extractor. The rapidly revolving blades tended to beat out the particles of tar which were not deposited in the condensers.

The gas holders were of standard type, each 10 cu. ft. in capacity, and were calibrated by calculating their volumes from their linear dimensions. On one of the holders was mounted a motor-driven stirrer.

All pipe connections were 1½ in. standard wrought iron.

MEASUREMENT OF TEMPERATURE AND RATE OF GAS CIRCULATION—The temperatures at each end of the coal charge were measured by the base metal pyrods *P*₁

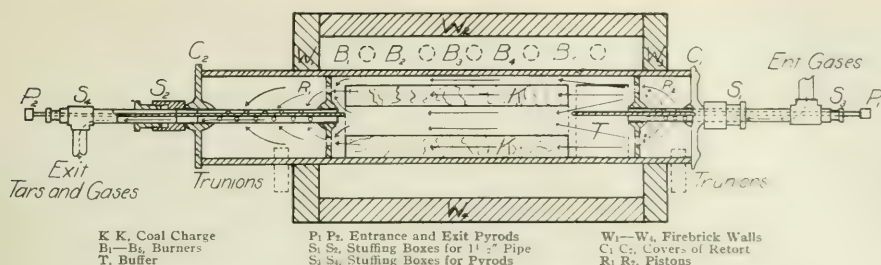


FIG. 4—CROSS SECTION OF FURNACE USED FOR COAL CARBONIZATION

and P_2 shown in Fig. 4. These pyrods were calibrated against a standard platinum-platinum-iridium junction.

The rate of circulation of the gases was determined by passing the gases obtained from various runs from one tank to the other through the whole carbonizing system under the same conditions as were maintained during the runs. The rate of circulation was found to be from 4 to 5 cu. ft. per minute.

YIELDS OF THE PRODUCTS OBTAINED—Because of the small size of the charges of coal treated (5 lbs.), it is evident that the actual yields of the products obtained by the experimental processes used cannot be compared with those which would be obtained if these processes were operated on an industrial scale. It was not proposed to study actual yields in themselves, but rather to compare the yields obtained in the two processes studied and to examine into the character of the important reactions involved in coal carbonization.

ANALYSIS OF THE TAR—The crude tar as recovered from the condensers and fan contained considerable amounts of water. As much as possible of this water was removed by gravity and the remainder by distillation. Distillation of the crude tar was conducted in an iron cylindrical still of about 500 cc. capacity. The crude oil was separated from the tar, and the light oil distilling below 210°C . was separated from the dry crude oil by distilling in a Jena flask provided with a Glinzky tube. The tar acids were removed from the light oil by treatment with 10 per cent caustic soda solution. The tar bases were removed by treating the residue from the caustic soda treatment with warm sulfuric acid of 1.15 specific gravity.

The light neutral oil was dried and fractionated in a flask provided with a Glinzky tube. The distillation cuts chosen were as follows:

0 to 95°C .	95 to 135°C .	135 to 180°C .	185 to 210°C .
Benzene Cut	Toluene Cut	Xylene Cut	Solvent Naphtha Cut

The unsaturated bodies were removed from each fraction by treatment with sulfuric acid (1.84 sp. gr.) in an ice bath. The aromatics were removed by treating the fractions after separation of the unsaturated bodies with fuming sulfuric acid in an ice bath. The residue from this treatment represented the amount of paraffin present. The amounts of benzene, toluene, and xylene were calculated from the amounts of the aromatics in the benzene, toluene, and xylene cuts, and also from the specific gravities of each cut, using

constants representing the average values for the gravities of the aromatics and non-aromatics present.¹ The results obtained by the two methods checked very closely.

In all cases where the volume of oil was great enough, the specific gravity was determined by means of a Mohr-Westphal balance. For determining the specific gravity of very small volumes of oil, the use of a modification of the Drushell type of pycnometer² was found to be most satisfactory. All specific gravity determinations were made at 15°C .

EXPERIMENTAL RESULTS

THE TOTAL, LIGHT, AND HEAVY OIL YIELDS Table I shows the specific gravities and actual yields of total, light, and heavy oil. These are plotted in Figs. 5, 6

TABLE I—YIELDS OF TOTAL, LIGHT, AND HEAVY OILS—BASIS ONE SHORT TON OF COAL

Temp $^\circ\text{C}$.	CONDITIONS	TOTAL OIL		LIGHT OIL (0 to 210°C Cut)		HEAVY OIL (210° to Pitch)	
		Liters	Sp. Gr.	Liters	Sp. Gr.	Liters	Sp. Gr.
400	Circ.	84.4	0.945	22.0	0.866	62.4	0.978
500	Non-circ.	84.4	0.946	26.0	0.867	58.4	0.990
600	Circ.	51.6	0.981	16.2	0.914	35.4	0.989
	Non-circ.	33.6	0.971	11.3	0.920	22.3	1.000
700	Circ.	33.3	0.997	9.7	0.952	23.6	1.020
	Non-circ.	26.0	1.007	7.3	0.943	18.7	1.030
800	Circ.	29.3	1.006	7.5	0.954	21.8	1.034
	Non-circ.	10.4	1.016	2.4	0.950	8.0	1.035
900	Circ.	19.4	1.050	3.3	0.960	16.1	1.041
	Non-circ.	2.4	...	0.00	...	2.4	...

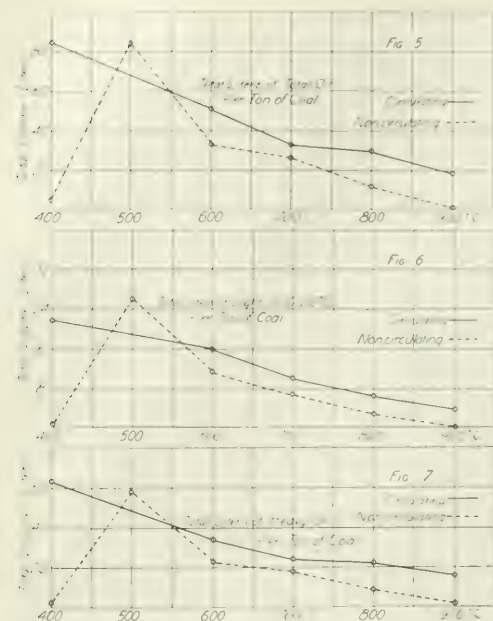
and 7, which shows that the general effect of increasing temperature is to cut down very materially the yields of total, light, and heavy oil. However, it is evident that while the *percentage* yield of light oil diminishes, the *percentage* yield of heavy oil increases. An inspection of Table I shows that the specific gravities in all cases tend to increase with rising temperature.

In the run at 900°C . without circulation it was impossible to obtain any light oil. Although 25 lbs. of coal were carbonized, besides 25 g. of water, only about 6 cc. of a mixture consisting mostly of naphthalene and anthracene were obtained.

The question may arise as to the reason for the yields of all the oils being so low at 900°C . in the case of no circulation. The values plotted here represent the amounts of oil that it was possible to recover in the condensing system. These yields were low in the case of no circulation because the vapor pressure of the tar was not great enough to cause much of it out of the retort. At a temperature a large part of it remained behind and formed a sticky residue with the non-composed base and oils.

¹ Burrows, *Trans. Inst. Chem. Eng.* **13** (1915), No. 1, p. 68.

² Burrows, *ibid.*, 1916, No. 2, p. 101.



It will be seen that the general effect of recirculation at all temperatures, except possibly 500° C., is to increase the yields of total, light, and heavy oils. In the majority of cases the gravities of the oils produced in recirculation runs are lower than those produced in non-circulating runs at corresponding temperatures.

THE LIGHT OIL (0-210° C.)—Table II shows results of tests on the light oil cut to 210° C.

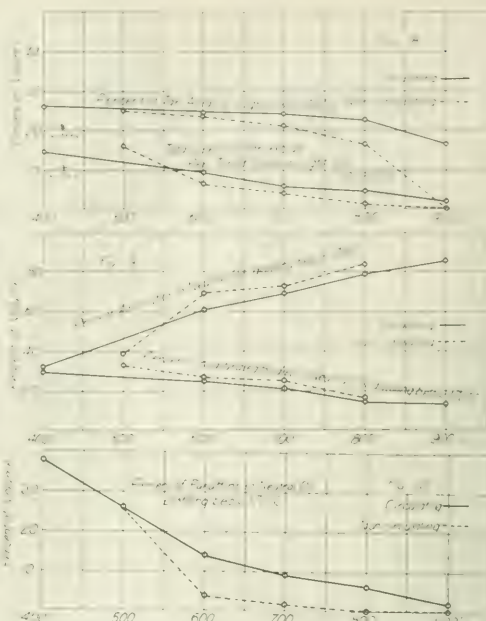
TABLE II.—TESTS ON LIGHT OIL (0-210° C.)

Temp. ° C.	CONDITIONS	Neutral Light Oil Sp. Gr.	Tar Acids of Light Oil Per cent. Volume	Lighters per Short Ton of Coal	Tar Bases Per cent. Volume
400	Circ.	0.816	26.3	5.8	0.9
500	Non-circ.	0.830	28.0	6.5	1.4
600	Circ.	0.892	24.2	3.9	1.9
	Non-circ.	0.901	24.0	2.7	1.7
700	Circ.	0.920	24.0	2.3	3.3
	Non-circ.	0.930	21.0	1.5	2.3
800	Circ.	0.922	22.8	1.7	2.6
	Non-circ.	0.932	17.0	0.4	3.3
900	Circ.	0.927	17.1	0.6	3.4
	Non-circ.		0.0	0.0	0.0

The actual and percentage yields of tar acids are plotted in Fig. 8, which shows that increase of temperature tends to decrease both the actual and the percentage yields of tar acids very materially, and that recirculation increases both the actual and the percentage yields of tar acids. This effect is most noticeable at temperatures above 600° C.

The tendency of recirculation to produce oils of low specific gravity is shown in the case of the neutral light oil (Table II) better than in the case of the light oil before the removal of tar acids and bases (Table I). The specific gravities in the latter case hold up in the circulating runs probably because of the high tar acid content.

TESTS ON NEUTRAL LIGHT OIL DISTILLING BELOW 170° C.—Table III shows the results of the tests on the



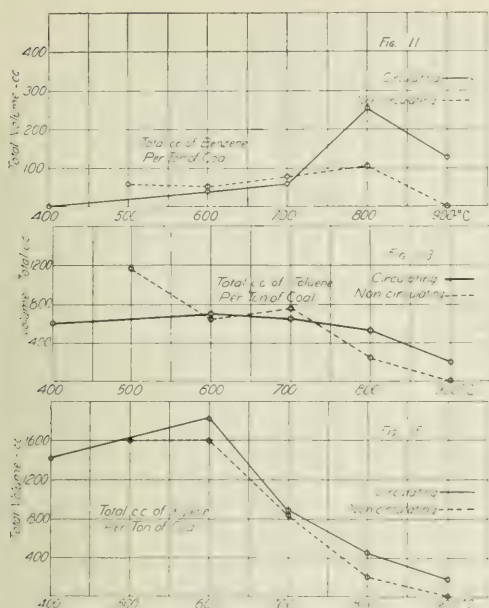
neutral oil distilling below 170° C. All percentages are expressed on the basis of the volumes of the 170° cuts. The percentage volumes of aromatics and unsaturated bodies are plotted in Fig. 9. The percentage volumes of paraffins are plotted in Fig. 10.

TABLE III.—TESTS ON NEUTRAL LIGHT OIL DISTILLING BELOW 170° C.

Temp. ° C.	CONDITIONS	PER CENT VOLUME Unsaturated	Aromatics	Paraffins
400	Circ.	29.4	32.6	38.0
500	Non-circ.	34.2	39.6	26.2
600	Circ.	25.0	61.0	14.0
	Non-circ.	26.8	69.5	3.7
700	Circ.	21.0	69.5	9.3
	Non-circ.	28.3	73.5	1.2
800	Circ.	14.7	79.0	6.3
	Non-circ.	16.8	83.8	0.0
900	Circ.	13.7	84.5	1.8
	Non-circ.	0.0	0.0	0.0

Fig. 9 shows that the effect of rise in temperature is to increase the percentage of aromatics and decrease the percentage of unsaturated bodies, contained in the neutral oil boiling below 170° C. Recirculation decreases the percentage yield of both, especially of the aromatics. Still more marked is the fall of the percentage yield of paraffins with increased temperature, and their conservation by recirculation, as shown in Fig. 10.

The fact that the aromatics increase so materially with rise in temperature while both paraffins and unsaturated bodies fall off seems to indicate that the aromatics are formed at the expense of the other two. Further evidence of this action is shown in the tendency of recirculation. The fact that recirculation tends to increase the percentage yield of paraffins and cut down the percentage yield of aromatics and unsaturated bodies indicates that the first named is a product of earlier decomposition than that of the other two.



THE BENZENE, TOLUENE AND XYLENE FRACTIONS

Table IV shows the total volumes and specific gravities of the benzene (0-95°), toluene (95-125°) and solvent naphtha (125-170°) cuts before the removal of

TABLE IV. VOLUMES AND SPECIFIC GRAVITIES OF BENZENE, TOLUENE AND XYLENE CUTS (BASIS ONE SHORT TON OF COAL)

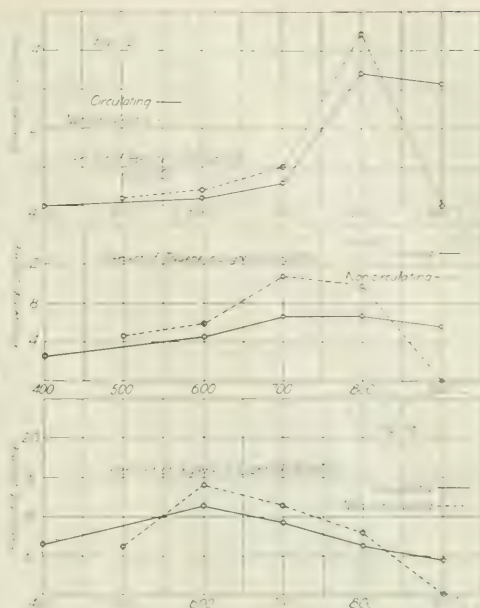
Temp. ° C.	CONDITIONS	BENZENE CUT		TOLUENE CUT		NAPHTHA CUT	
		Cc.	Sp. Gr.	Cc.	Sp. Gr.	Cc.	Sp. Gr.
400	Circ.	976	0.720	2480	0.764	7080	0.806
500	Non-circ.	928	0.730	3212	0.782	8120	0.813
600	Circ.	328	0.740	1048	0.825	3260	0.859
700	Non-circ.	176	0.750	880	0.839	3056	0.870
800	Circ.	124	0.800	768	0.850	2040	0.883
900	Non-circ.	88	0.850	800	0.865	1932	0.905
1000	Circ.	512	0.807	620	0.847	1288	0.899
1100	Non-circ.	124	0.857	236	0.868	576	0.903
1200	Circ.	176	0.825	332	0.845	784	0.905
1300	Non-circ.	0	0	0	0	0	0

the aromatics. Table V shows the actual and percentage yields of benzene, toluene and xylene contained in these cuts. Actual yields are on the basis of total volumes per short ton of coal.

TABLE V. ACTUAL AND PERCENTAGE YIELDS OF BENZENE, TOLUENE AND XYLENE (BASIS ONE SHORT TON OF COAL)

Temp. ° C.	CONDITIONS	ACTUAL YIELDS			PER CENT VOLUME OF		
		Benzene	Toluene	Xylene	Benzene	Toluene	Xylene
400	Circ.	0	89.7	141.7	0.0	2.5	6.4
500	Non-circ.	5.6	118.8	139.5	0.2	4.6	6.1
600	Circ.	10	90.1	130.8	0.7	4.1	5.7
700	Non-circ.	18	68.0	130.7	0.4	3.9	5.1
800	Circ.	60	60.2	88.0	0.6	6.7	9.1
900	Non-circ.	7	64	84.6	1.0	10.3	11.4
1000	Circ.	13.6	11.7	13.3	3.4	6.8	6.0
1100	Non-circ.	10.1	5.2	19.1	1.1	2.7	5.0
1200	Circ.	10.1	18.8	18.1	3.1	5.7	4.5
1300	Non-circ.	0	0	0	0.0	0.0	0.0

The actual and percentage yield of benzene are plotted in Fig. 11 and 12. It will be seen that benzene begins to form between 600 and 700° C., rises to a maximum at 800°, and in the case of the non-circulating runs, drops off to zero at 900°. The effect of recirculation in the case of all temperatures except 900° is to decrease the percentage yield of benzene



but in the zone of maximum formation (700-900°) the actual yields are favored by recirculation. It will be noted that at 900°, while the yield without circulation is zero, the yield with circulation is greater than the maximum obtained in the former case. Since analysis of the gases indicated that the amount of "gas benzol" was greater in the circulating runs than in the non-circulating runs at temperatures above 700°, it cannot be said that the increased yields in the former case are due to the scrubbing action of the fan.

The actual and percentage yields of toluene are plotted in Figs. 13 and 14, which show that toluene forms at 400° and in the case of the non-circulating runs tends to approach a maximum at 700°, and drops off to zero at 900°. The tendency of recirculation is to decrease the percentage yields at all temperatures and to increase the actual yields at temperatures above 700°. Toluene seems to begin to form at an earlier temperature than benzene, and there is a fairly appreciable yield of the former at 400°.

Figs. 15 and 16 show that xylene forms at 500°, and that it has a greater yield than toluene at that temperature, thus indicating that it is formed first. The maximum percentage yield of xylene is at 600°. The yield then drops off in the case of benzene and toluene. Recirculation seems to favor both the actual and the percentage yield of xylene at temperatures above 700°.

Table IV shows that the actual yields of benzene, toluene and xylene are in the same relative proportions as the percentage yields of aromatics in coal. At some temperatures a part of the benzene present in these fractions might be in the form of circulating gases at temperatures

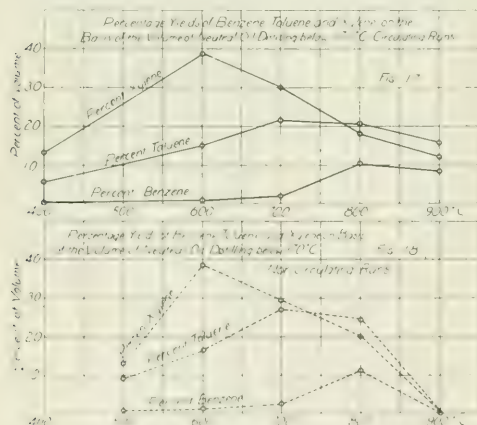
at the lower temperatures. The boiling points observed indicated that in the benzene fraction there were present paraffins of the hexane and heptane series, and possibly some naphthenes boiling in the eighties and nineties. The toluene fraction probably contained, besides some benzene and toluene, naphthenes ranging in boiling points from 100 to 125° C. The solvent naphtha fraction besides the xylenes ranging in boiling points from about 136° to 150° C., probably also contained also other homologues of benzene such as ethyl benzene, mesitylene, pseudo cumene, etc., as well as naphthenes ranging in boiling points from 130 to 150° and from 168 to 170°.

PERCENTAGE YIELDS OF BENZENE, TOLUENE AND XYLENE (BASIS OF VOLUMES OF NEUTRAL OIL DISTILLING BELOW 170° C.).—Table VI shows the percentages of benzene, toluene and xylene on the basis of neutral oil distilling below 170° C. By having these values plotted together on the same scale the course of the reactions of the three aromatics may be followed and the character of benzene, toluene and xylene formation in the case of coal compared to that obtained in the case of petroleum oil and shown in Fig. 1.

TABLE VI—PERCENTAGE YIELDS OF BENZENE, TOLUENE AND XYLENE ON THE BASIS OF THE NEUTRAL OIL CUT TO 170° C.

Temp., ° C.	CONDITION	Benzene	Toluene	Xylene
400	Circ.	0.0	5.6	13.4
500	Non-circ.	0.5	9.7	13.0
600	Circ.	0.9	15.1	39.0
	Non-circ.	1.2	16.5	38.8
700	Circ.	2.1	22.2	30.0
	Non-circ.	2.5	27.2	29.7
800	Circ.	10.6	21.2	18.7
	Non-circ.	11.2	24.4	20.5
900	Circ.	8.7	16.0	12.6
	Non-circ.	0.0	0.0	0.0

Fig. 17 shows the percentages for the circulating runs and Fig. 18 shows the percentages for non-



circulating runs. A comparison of these curves with those contained in Fig. 1 showing the results of Egloff and Twomey on the cracking of petroleum oil brings out the following facts:

1—The points of maximum formation of toluene and benzene are the same, viz., 700 and 800° C., respectively.

2—The point of maximum formation of xylene in the case of the coal runs occurs at 600° C., while it

occurs at 700° in the case of the oil runs. It was learned recently that experiments on other oils have given points of maximum xylene formation at temperatures between 600 and 700° C.

3—The order of magnitude of the percentages of benzene, toluene and xylene at 400° and low temperatures in the coal runs is opposite to that in the oil runs. We would expect this when we have conditions such that we get larger yields at very low temperatures where the speed of the reactions is low. The fact that xylene has a higher percentage yield than toluene at 400° and that toluene has a higher percentage yield than benzene might indicate that xylene forms before toluene and that toluene forms before benzene.

4—It will be noted that at temperatures higher than 700°, the point of maximum formation of toluene, the xylene falls below toluene in the coal runs in the same way as in the oil runs.

5—The benzene curve in the coal runs is different from that of the oil runs in that the percentage yields at no point rise above those of toluene. Hence this curve does not indicate that benzene is formed at the expense of toluene and xylene at any stage of the carbonization. We would expect this in the case of coal since it must be remembered that most of the benzene is in the gas. If this were added to that recovered in the tar, no doubt the relations in the case of coal would be the same as those shown in Fig. 1.

6—Taking everything into consideration, it is probable that the course of the reactions of the individual aromatics is the same in the case of coal as in the case of the oil.

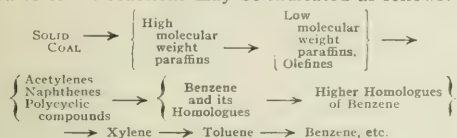
SUMMARY AND CONCLUSIONS

I—The results of the present investigation confirm those of other investigations in regard to the effect of temperature on the formation of the total, light and heavy oil, and of the tar acids in the light oil. Low temperatures favor the formation of the total, light and heavy oil and tar acids. Increasing temperature causes a falling off in the percentage yields of light oil and tar acids and an increase in the percentage yields of heavy oil. The low temperature oils are characterized by high content of paraffins and unsaturated bodies and low content of aromatics. Increased temperature causes the percentage yields of paraffins to decrease and that of the aromatics to increase. In the zones of maximum aromatic formation the percentages of unsaturated bodies fall off decidedly.

II—In the case of the coal used, the relations between temperature and the rate of formation of benzene, toluene and xylene seem to be quite definite. Xylene and toluene seem to form between 400 and 900° C., and benzene between 500 and 900° C. The point of maximum formation of benzene is 800° C. That of toluene is 700° C., and that of xylene is 600° C.

III—The results stated in II agree closely with those obtained in the cracking of petroleum oils and seem to indicate that the course of the reactions in the formation of benzene, toluene and xylene from higher benzene homologues is the same in the case of coal carbonization as in the case of oil cracking. This

leads us to suppose that a large portion of the primary products of the decomposition of coal are high molecular weight paraffins. These decompose into olefines which in turn form the decomposition products for the formation of benzene and its homologues. The course of the reactions may be indicated as follows:



IV—Diminishing the duration of the carbonization reactions by recirculation tends to increase the actual yields of total, light and heavy oils as well as the yields of the total benzene, toluene and xylene fractions.

V—Recirculation tends to increase the percentage yields of the paraffins and to decrease the percentage yields of aromatics and unsaturated bodies thus offering further evidence that the aromatics are formed at the expense of the other two.

VI—Although the *percentage* yields of the individual aromatics, benzene, toluene and xylene, are favored by increasing the duration of the carbonizing reactions by non-circulation, in the zones of maximum aromatic formation—usually between 700 and 900° C.—the *actual* yields are favored by recirculation.

VII—Recirculation tends to increase both the *actual* and the *percentage* yields of tar acids in the light oil. This would tend to confirm the conclusions of other investigators that the tar acids are products of the primary decomposition of coal.

VIII—The results as a whole emphasize the necessity of temperature control in coal carbonization if the yields of the important aromatics are to be considered. Under the conditions usually maintained in standard practice, it is evident that for actual efficient combined yields of benzene, toluene and xylene, the carbonizing temperatures should not greatly exceed 800° C., nor should they lie much lower than 700° C. The fact that such good yields of the aromatics are obtained at the gas and coke works where very high temperatures are employed is, no doubt, due to the protection offered by the cooler central core of coal which does not reach the cracking temperatures, and to the cooling effect on the hotter gases due to dilution with the cooler gases emerging from the center of the charge.

IX—By the use of any device whereby the duration of the carbonizing reactions is shortened, it seems possible both to increase the yields of the paraffin oils at the lower temperatures and the yields of the aromatics at the higher temperatures. It is also possible to operate at higher carbonizing temperatures.

X—The similarity of the coal carbonizing reactions to those undergone during oil cracking suggests the possibilities of carbonization at low temperatures and a treatment of the low temperature tar by the cracking processes used on the petroleum oils. In this way the valuable tar acids could be conserved by removing them before the cracking treatment, and

more efficient yields of the aromatics (or possibly of the lower boiling paraffins) could be obtained. However, until the oil cracking processes prove more fully their industrial worth, this phase of by-product recovery will not be entitled to serious consideration.

The authors wish to express their thanks to Professor Floyd J. Metzger, Mr. R. J. Moore and Mr. John R. Suydam for their help and suggestions. They desire also to thank Dr. Gustav Egloff for his interest and valuable help in the study of the hydrocarbon oils.

DEPARTMENT OF CHEMICAL ENGINEERING
COLUMBIA UNIVERSITY, NEW YORK CITY

INFLAMMABILITY OF CARBONACEOUS DUSTS

By H. H. BROWN
Received November 13, 1916

The fact that coal dust is explosive is very generally known to-day. The large loss of life that often accompanies a mine disaster has forcibly called attention to this. As early as 1844, Faraday recognized that coal dust was an important factor in explosions in mines. But only within the last thirty years has it been fully recognized that coal dust alone was explosive without the presence of gas. To-day nearly every large country has its experiment station to study causes and means of prevention of mine explosions.

It must not be concluded, however, that coal dust is the only dust that will explode, as experiments have clearly shown that many other carbonaceous dusts are at least as easily ignited and as capable of propagating an explosion as is coal dust. While most of the dust explosions reported in surface plants occur in mills and elevators handling wheat, oats and corn, and their products, it appears that no mill handling carbonaceous material is immune from the possibility of an explosion. The list of known explosions in other kinds of mills includes those handling dextrine, sugar, starch, malt, wood, linseed meal, cottonseed meal, paper, cork, fertilizer, sulfur, cocoa, and spice dusts.

That flour dust will explode was clearly demonstrated in 1878 by a tremendous explosion in the Washburn Flour Mills in Minneapolis. An investigation was made by Professors Peek and Peckham¹ in connection with which they tested the explosibility of a variety of dusts by blowing them as a cloud into a closed box containing a small flame. They concluded that practically all finely divided, highly carbonaceous material would explode under the conditions tried. More recently R. V. Wheeler,² chief chemist for the *Explosion in Mines* Committee, England, carried out some systematic tests for the purpose of discriminating between harmless and dangerous dusts, and to determine the temperatures at which inflammation of the dangerous dusts takes place readily. As a result of these tests he divided the dusts into three classes:

I.—Dusts which ignite and propagate flame readily, the source of heat supplied for ignition being comparatively small, for example, a lighted match.

¹ *Mines and Minerals*, 29 (1888), 35.

² Report of the International Conference on the Prevention of Explosions of Carbonaceous Dusts, 1910 (London), pp. 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100.

II—Dusts which are readily ignited but which, for the propagation of flame, require a source of heat of large size and high temperature, such as an electric arc, or of long duration, such as the flame of a Bunsen burner.

III—Dusts which do not appear to be capable of propagating flame under any conditions likely to obtain in a factory, because (a) they do not readily form a cloud in air, or (b) they are contaminated with a large quantity of incombustible matter, or (c) the material of which they are composed does not burn rapidly enough.

Certain dusts of interest in the present investigation were classified by Wheeler as follows:

	Sugar	Grain (flour mill)
	Starch	Maize
CLASS I	Rice meal and sugar refuse	Grain (grain storage)
	Wood flour	Rape seed
	Malt	Corn flour
	Out husk	Flour (flour mill)
CLASS II	Rice milling	Grist milling
	Castor oil meal	Horn meal
	Old grinding (bran)	Mustard
CLASS III	Spice milling	Sack cleaning
	Cottonseed	Rape seed (Russia)
	Cottonseed and soya bean	Grain cleaning

The Minneapolis explosion aroused milling men to the danger of existing conditions and caused many to take precautions immediately to guard against repetition of similar occurrences. The impression was not lasting and although a large number of grain dust explosions occurred after that time, general interest was not awakened again until June 24, 1913, when an explosion occurred in a feed grinding plant at Buffalo in which 33 men lost their lives, and over 70 men were injured. This explosion, which occurred during the ordinary process of operation, completely destroyed the milling plant and did considerable damage to surrounding property. As a result of this disaster the millers in and around Buffalo were very desirous of obtaining any possible information relating to the inflammability of grain dust which would help them in taking effective safety precautions in addition to the measures already adopted. An agitation was started which resulted in a cooperation between the millers and the Bureau of Mines for the investigation of questions relating to explosions of grain dusts. This was later taken up by the Government and is being continued as a cooperation between the Bureau of Chemistry and the Bureau of Mines. The laboratory investigations, originally carried on in the laboratories of the Bureau of Mines at Pittsburgh, have recently been transferred to the laboratories of the Bureau of Chemistry at Washington.

SIMILARITY BETWEEN GAS AND DUST EXPLOSIONS

Although the investigations of dust explosions have not been as complete or conclusive as those made on gas explosions—probably because of the great difficulties encountered in maintaining or even obtaining a uniform dust cloud of any desired density—the available data show quite conclusively that the phenomena exhibited by the two types of explosions are very similar. A statement of a few pressures and flame velocities measured in explosions of coal dust and of gases will serve to indicate this fact.

The United States Bureau of Mines¹ reports having

¹ U. S. Bureau of Mines, *Bull.* 56 (1913).

measured in a coal dust explosion an average velocity of 2273 ft. per sec. over a distance of 100 ft. In experiments at the British Experiment Station,¹ Altofts, England, an average velocity of 2014 ft. per sec. has been obtained. Taffanel² obtained a velocity of 3300 ft. per sec.

A pressure of 103 lbs. per sq. in. is reported by the Bureau of Mines. The British authorities report pressure up to 100 lbs. per sq. in., with an estimated pressure in one test of 120 lbs. Taffanel reports having measured pressures of 227 to 270 lbs. per sq. in., while in one test the steel gallery, with an estimated breaking strength of 570 lbs. per sq. in., gave way, pieces of the sheet steel being thrown distances up to 150 meters (472 ft.).

The maximum velocities of propagation of flame in many gas mixtures have been determined with accuracy by Dixon,³ Berthelot,⁴ Emich,⁵ Nernst,⁶ and others.⁷ For certain of these mixtures the following results were obtained:

GASEOUS MIXTURES	VELOCITY PER SECOND	
	Meters	Feet
2H ₂ + O ₂	2830	9280
4 parts coal gas + 5 parts oxygen.....	3700	8876
C ₂ H ₄ + 3O ₂	2364	7724
CH ₄ + 2O ₂	2322	7616
2CO + O ₂	1680	5510

Mallard and LeChatelier⁸ obtained a pressure of 6.5 atmospheres (97.5 lbs. per sq. in.) for a mixture of 1 vol. CH₄ + 2 vol. O₂ + 9 vol. air. Leau and Bone⁹ found a pressure of 20.7 atmospheres (310.5 lbs. per sq. in.) developed in a mixture of 2H₂ + O₂.

It will be noted that as high pressures have been observed in coal dust explosions as in gas explosions. However, the extremely high velocities attained by the flame in certain gas mixtures have not been reported as observed in dust explosions. Such high velocities could not be expected, for even the finest dust particles are many times larger than gas molecules, and so, even in the most dense dust clouds the particles could not be as close together nor as intimately mixed with the oxygen as are gas molecules. Therefore, the heat of combustion of one dust particle cannot be as readily transmitted to the next particle as it can in a mixture of gases. But the finer the dust the more nearly will it approach the size of a gas molecule. Therefore, it might be expected that the velocity of the flame through a cloud of very fine dust would more nearly approach the velocity attained in gas explosions. As a matter of fact, this is true. Taffanel¹⁰ has brought this out in tests made at the French Experiment Station. Results obtained by the Bureau of Mines¹¹ lead to the same conclusion.

The rate at which inflammation travels through a

¹ Report of Committee on British Coal Dust Experiments. Record of first series, 1910.

² "Les expériences françaises sur les poussières de houille." International Congress Dusseldorf 1910. *Berichte der Abteilung für Bergbau.* II. Dixon, *Proc. Trans.* 184, 161, 200, 378. *Chem. News*, 46, 70.

³ M. Berthelot, "Sur la Force des Matières Explosives," 1 (1883), 159.

⁴ Emich, *Ber.*, 42, 2462.

⁵ Nernst, "Theoretische Chemie," *Deutscher Verlag*, p. 638.

⁶ Notably Vieille; Mallard and LeChatelier.

⁷ E. Mallard and H. LeChatelier, *Ann. Mines*, [8] 4 (1883), 379.

⁸ B. Leau and W. A. Bone, *Chem. News*, 66 (1885), 101.

⁹ Taffanel, Fourth Series of Tests.

¹¹ G. S. Rice, "Investigations of Coal-Dust Explosions," *Bull. Amer. Inst. Mining Eng.*, 1914, p. 2476.

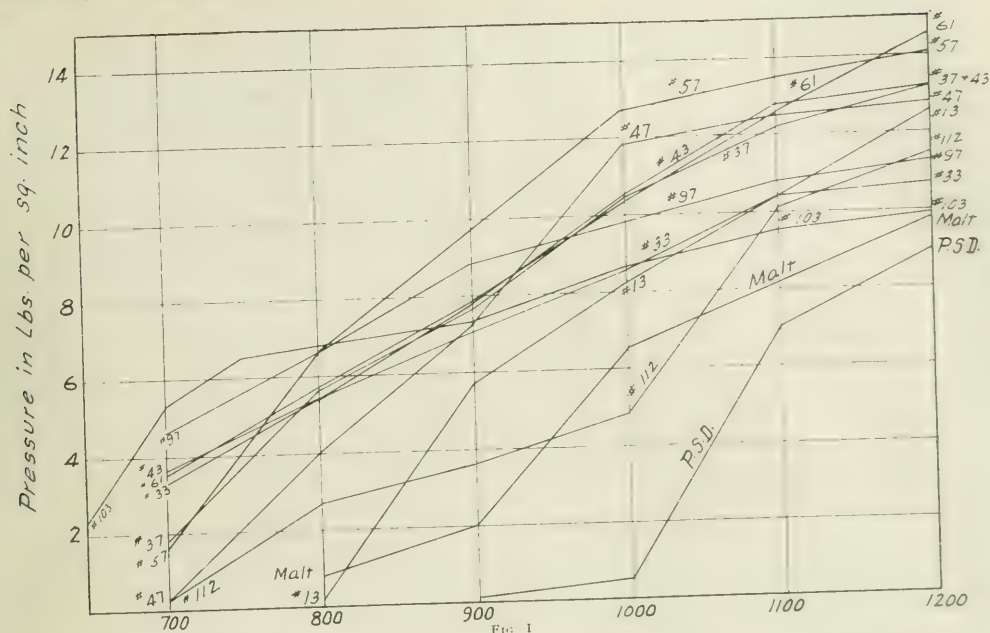


FIG. 1

gas mixture is dependent upon at least two factors, the inflammability of the gas and the percentage of the gases in the mixture. The rate at which inflammation travels through a dust cloud seems to be dependent upon two similar factors, namely, the inflammability of the dust and the amount of dust in suspension. A third important factor is the fineness of the dust.

It will be seen, therefore, that gas and dust explosions are similar in many ways and that a gas explosion is only a limited case of a dust explosion.

A thorough knowledge of the nature of dust explosions and of the accompanying phenomena is necessary in order to devise means for the prevention of such explosions and for the stoppage of explosions if by mischance they should start. It is, therefore, necessary to know how dust ignites, the various means by which it may be ignited, or inflamed, and the chemical processes that take place. Another important factor to know is the ease with which the dust ignites and propagates a flame. This property we may call the "inflammability" of the dust. The term "explosibility" has also been applied in this connection.

DEVELOPMENT OF METHOD FOR TESTING INFLAMMABILITY OF DUSTS

When the present investigation was started to determine the causes and means of prevention of grain dust explosion, one of the first problems undertaken was to devise a method for testing the inflammability of the various dusts, or to adapt some method at present used for testing the same property of coal dusts. The method of Wheeler was tried, but the tests were unsatisfactory. A method for testing coal dusts had been developed by the United States

Bureau of Mines. Preliminary tests showed that it could be adapted. Several kinds of dusts were tested and the results published by the Millers' Committee of Buffalo, New York, as a "Preliminary Report on the Explosibility of Grain Dusts."¹

Further tests were made with the same and other dusts, at the same and at lower temperatures. The results are given in Fig. 1. The temperatures were measured by a thermocouple with its hot junction on the inside of the igniting coil. The pressures given for temperatures from 1000 to 1200° C. are the average of all results given by each dust at these temperatures. But at the lower temperatures ignitions were not obtained in every test, so that the points given are the average of only those where the dust ignited. The results given at 1100 and 1200° C. were referred to Pittsburgh Coal Dust as a standard, but the results at all lower temperatures are those actually obtained. Also, as in the early tests, all the dusts except 61, 112, and malt were tested at 100° C. in a current of dry air.

Tests were also made on a few other tested dusts at two temperatures only. The results at 1000° C. were referred to the coal dust standard.

No.	Dust	Pressure	
		1000° C.	1100° C.
18 A	Wheat	10.5	12.5
4 A	Wheat	10.5	12.5
18 A	Wheat	10.5	12.5
18 A	Wheat	10.5	12.5
18 A	Wheat	10.5	12.5
18 A	Wheat	10.5	12.5
18 A	Wheat	10.5	12.5
18 A	Wheat	10.5	12.5
18 A	Wheat	10.5	12.5
18 A	Wheat	10.5	12.5

¹These results are given as a series of comparisons of the dusts by the method used in testing them and the standard dust.

method to be described. They are given also to show how low a temperature is required to ignite these dusts—a temperature of 700°C . on the inside of the igniting coil showing only a very dull redness at the surface that is scarcely visible in daylight.

VARIABLES AFFECTING RESULTS—The method as used at this time was not at all satisfactory for either coal or grain dusts, as the results were less uniform and reproducible than was desired. There were too many variables. The igniter, with its means of temperature measurement, was unsatisfactory since it did not give the actual temperature at the point of ignition, and did not compensate for the deposition of ash on the coil, or the wearing away of the alundum coating. Probably the most important variable was the manner in which the dust was inserted into the globe and against the coil. This, it appeared, was controlled not only by the amount of air used to force in the dust and by its rate of flow, but also by the size and shape of the funnel which holds the dust. Other variables were the amount of dust used, the temperature used to ignite the dust, and whether or not a screen was used over the funnel through which the dust would be forced.

MEASURING TEMPERATURE OF IGNITER—To overcome the variables in the igniter, a coil of similar construction was used, except that it had, outside the alundum coating, platinum foil fastened tightly around the coil. The temperature at the surface of the coil is measured by a thermocouple. The wires of the thermocouple are not fused together in the usual manner to form the hot junction, but are attached separately to the platinum foil. The platinum rhodium wire is fastened around the coil at the center and the platinum wire about 3 mm. to one side. These were fastened to the foil by means of heat and pressure. The hot junction is then at the immediate surface of the coil and the temperature registered is that of the point of contact between the small platinum rhodium wire and the platinum foil. To reduce to a minimum the loss of heat from the surface of the igniter by conduction along the wires, the ends in contact with the foil are drawn down to a diameter of 0.15 mm. With this arrangement the coil can always be kept clean and the actual temperature at the point of ignition known.

METHOD OF INSERTING DUST—It was early observed that by grading the releasing of the air used to force in the dust, that is, by opening the pinchcock at various rates, a great variation in results could be obtained with any dust. To obviate this a mechanical releasing device was made which would always release at the same rate and very rapidly. With certain dusts this rapid forcing of the dust against the igniting element was found to be too rapid to obtain the highest pressures possible. Therefore, the rate of flow of the air was controlled by a short piece of capillary tubing placed between the releasing device and the funnel.

This method gave much more satisfactory results than had previously been obtained. However, it was observed that the results could be varied by in-

serting the dust into the funnel in different ways, that is, whether it was compact or loose, partly around the bend in the funnel, or entirely in the upright portion, or partially in the bowl. Concordant results were very difficult to obtain with the original funnel. Therefore, an extensive series of tests was started to develop a funnel that would be suitable for all types of dusts, and also a size of capillary which would give consistent results.

In these series of tests seven different types of funnels were tested before one was obtained which was satisfactory. Tests with several different types of dusts were made with each funnel. Capillaries of from 1.0 to 2.5 mm. bore were used in the tests. The two extreme sizes were used in only a few tests as the one of 0.1 mm. bore was found to be too small to allow passage of sufficient air to raise the dust, and the one of 2.5 mm. bore gave results only slightly higher in some cases than were given with the next size smaller. Therefore, only the following sizes were used in most of the tests: 1.5, 2.05, and 2.35 mm. bore, respectively.

The pressure of the air used to force the dust into the globe also affected the results very appreciably. Tests were made with the air under 15 cm. and 20 cm. of mercury. The latter pressure was found the more satisfactory.

The manner in which the dust was inserted was also affected by a 14-mesh screen placed over the funnel. This served to break up the dust and make a more uniform cloud. However, some of the grain dusts were very fibrous, and so did not pass readily through the screen. This gave irregular and low results with some of these dusts so that tests were made using the screen and without it.

AMOUNT OF DUST—In all the early work 50 mg. of the dusts were used in each test except where curves were run with varying amounts of material. These results indicated that a larger amount of material would give more uniform results, therefore series of tests were run with both 50 and 75 mg. of the dusts. The results with 75 mg. were much higher in every case, fully as uniform, and in some cases more uniform than with 50 mg. As 75 mg. was a convenient amount to handle, giving sufficiently high results with the less inflammable materials, and not too high for safe handling of the apparatus with the more inflammable, this amount was used in all later experiments.

EFFECT OF LARGE AMOUNTS OF DUST—The tests with 75 mg. of dusts suggested a study of the effect of large amounts of material. Therefore, a short series of tests was made with four different dusts. That size capillary was used which previous tests had indicated would give highest results. The results of these tests are given in Fig. II. It will be observed that for Samples 47 and 33 the curve had nearly reached its maximum at 150 mg. of material, while the pressures for sugar and starch were still increasing at this point. Higher points were not run because pressures might be obtained beyond the safe working limits of the apparatus.

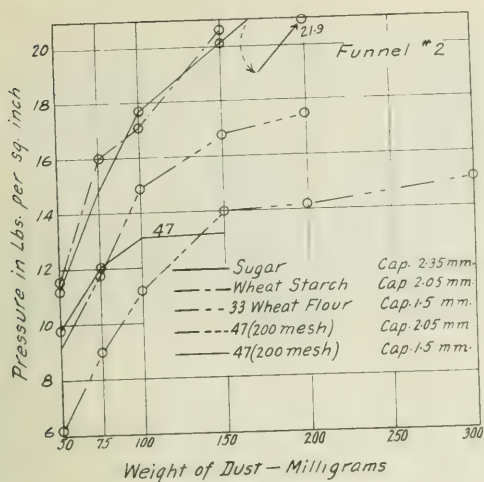


FIG. II

The results indicate that large amounts of the more inflammable materials could not be used in the present type of apparatus, and also that only a certain pressure will be developed even though more material is used. It is possible that these curves would behave as gas curves and begin to decrease if sufficiently large amounts of materials were used.

In running this series of tests it was observed that a slight amount of charring resulted in each test with 100 mg. of Sample 47, while with 150 mg. of material a considerable amount of charred material was found in the flask after ignition. Only very slight charring was noticed with the starch and flour. When 150 mg. of sugar were used, a perceptible odor of formaldehyde came from the flask, while with 200 mg. the odor was quite strong. These observations would indicate incomplete combustion with these amounts of material, and also that the heat of the reaction caused some decomposition of the dust.

INDICATIVE RESULTS—For comparison with previous and later results there is given in Fig. III the results obtained with a few typical dusts, using three different sized capillaries, with and without a screen over the funnel. These results were obtained with the funnel that was found to be most satisfactory. Seventy-five milligrams of material were used and ignited at a temperature of 1100°C ., a temperature approximately the same as 1200°C . on the inside of the coil, which had been used quite satisfactorily in the early work. The results are those actually given, and are not referred to any standard dust.

In these tests it will be observed that the results with dextrin, sugar, and Samples 13 and 47 are higher at certain or all points, when no screen was used over the funnel. No reason can be assigned to the two former, but the latter two contained fibrous material which was held back by the screen. With the other dusts the screen served to break up the dust and form a more uniform cloud.

All these dusts except wheat flour (No. 33), and

Pittsburgh coal dust, gave higher results with the 2.05- and 2.35 mm.-bore capillaries, and in some cases with the 1.5 mm. capillary than were given at the highest temperature in the earlier tests. The 2.05 mm. capillary gave the most concordant results.

OTHER VARIABLES—However, the results at this point were not entirely satisfactory. The only other variables that had not been thoroughly tested were the effect of higher temperature and the action of the valve between the air reservoir and explosion flask. A slight change in capillary was also considered.

EFFECT OF VALVE—Tests were made to determine the effect of the valve. The results obtained without the valves were appreciably lower than when the valve was used. This was expected as the volume of air affected by the ignition was thereby increased by the volume of the air reservoir. However, the valve

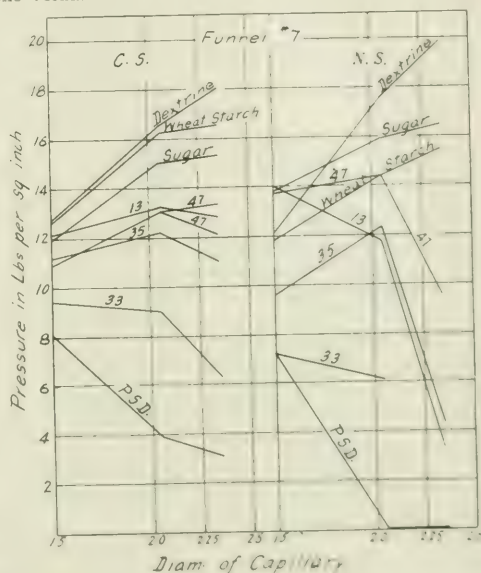


FIG. III

was discarded, as it was shown that it did not always work, and the results without it, though lower, were more uniform.

TEMPERATURE OF IGNITION—To determine the effect of temperature under the new conditions, a series of tests was made at temperatures from 1000 to 1100°C . at 10° intervals. In these tests a capillary of 2.3 mm. bore was used as this was the one used by the Bureau of Mines at that time in testing such dusts, and as it was only slightly smaller than the capillary (2.63 mm. bore) found to give the most satisfactory results with grain dusts.

As some of the dusts had not reached a maximum pressure at 1100°C . they were tested at 1200°C . The results of these tests are given in Fig. IV.

It will be observed that the curves begin to become horizontal at 1100°C . and that the results at 1200 and 1100 are only slightly different in some cases.

results at all these temperatures were quite uniform and concordant. On account of these facts, and because the results at 1200°C. were not much different from those obtained at 1150°C. , which would mean that a slight variation of this temperature would not make any appreciable difference in the results, and since 1200°C. was more convenient to use than a higher temperature, it was taken as a standard temperature.

EFFECT OF CAPILLARY—To determine the most satisfactory size of capillary for all types of dusts, a series of tests was made at 1200°C. , using four different capillaries, 6 cm. long and varying in bore by 0.1 mm. from 1.9 mm. to 2.2 mm. These results are given in Fig. V.

It will be observed that in most cases the size of capillary had no marked effect upon the average results. This was due, probably, to the high igniting temperature, and to the fact that the differences in diameter of the capillaries were not large enough to affect greatly the rate of flow of the air. However, there was a difference in the uniformity of the results obtained. The 2.0 mm. capillary gave the more uniform and concordant results, and these were nearly as high or higher than the results given with other capillaries. So this capillary was chosen as the best for future work.

COMPARISON OF METHODS FOR COAL AND GRAIN DUSTS—During the development of this method, the Bureau of Mines was also perfecting their method for testing coal dusts. As the properties of the two dusts are very dissimilar, a duplication of tests could not be avoided. However, it was thought advisable

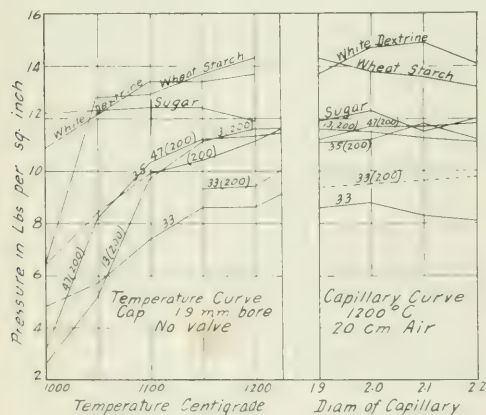


FIG. IV

FIG. V

to have as few differences in the methods as possible. It was partly for this reason, to conform more closely to Bureau of Mines practices, that the valve was discarded, and that a temperature of 1200°C. and a 2.0 mm. capillary was adopted. These conditions gave the best results with coal dust, and practically the same results with grain dusts as slightly different conditions would give. The method as adopted for testing grain dusts is as follows: Temperature,

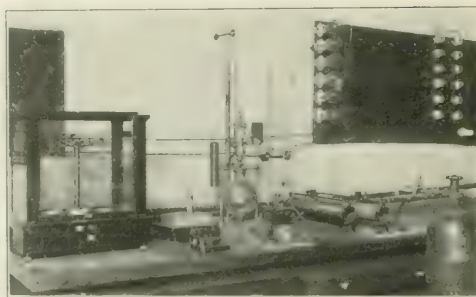


FIG. VI

1200°C. , capillary 6 cm. long and 2.0 mm. bore; air under 20 cm. pressure; no one-way valve between air reservoir and explosion flask, but a pinchcock back of the air reservoir; 75 mg. of material; a coarse screen over the funnel except when very fibrous dust is tested; and a funnel 4.0 mm. internal diameter, with a bowl $\frac{3}{4}$ in. deep and $\frac{5}{8}$ in. across at the top, and the bend in the funnel being a right-angle $\frac{5}{8}$ in. below the bowl and having a small wire screen inside and just back of the bend.

The same type of apparatus is used in testing the inflammability of both the coal and the grain dusts. It is shown in Figs. VI and VII. The only difference in construction is in the funnel. The methods of

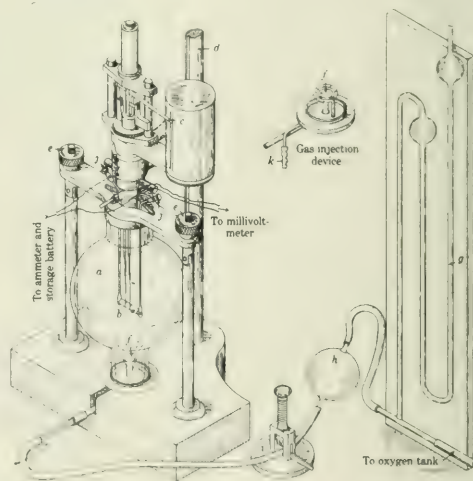


FIG. VII

operation are different, however, in that 75 mg. of grain dust are used as against 100 mg. for the more inflammable coals, and 300 mg. for the less inflammable. The vital difference is that oxygen under 15 cm. of mercury pressure is used to insert the 100 mg. of coal dust, while air at 20 cm. of mercury pressure is used to insert the grain dusts.

RESULTS WITH CARBONACEOUS DUSTS—The method as developed and standardized has been used in test-

ing the inflammability of a large variety of dusts. The results are given in Table I in the order of inflammability:

TABLE I—INFLAMMABILITY OF CARBOACEOUS DUSTS

Sample No.	KIND OF DUST	Pressure Generated Lbs. per Sq. In.
51 A	Lycopodium...	17.5
13 A	Stinking smut of wheat...	15.9
61	Yellow corn dust from first break in dry milling...	15.2
18 A	Dextrin dust from dextrin kiln...	14.6
47 A	Stinking smut of wheat...	14.3
20 A	Powdered wheat starch...	14.0
46 A	Stinking smut of wheat with wheat dust...	13.9
4 A	White dextrin...	13.9
21 A	Starch dust (corn) from dry starch kilns...	13.8
6 A	Canary dextrin...	13.8
43 A (200 mesh)	Tan bark dust...	13.3
5 A	Powdered corn starch...	13.2
11 A	Wheat starch...	13.1
17 A	Starch and dextrin dust from about tray filter...	13.0
35 (200)	Wheat elevator dust, side wall...	13.0
19 A	Dextrin dust from top of reels and mixer...	12.8
3 A (200)	Wood dust from chipper room...	12.8
3 A	Corn starch...	12.7
37 (200)	Oat and corn dust from unloading station...	12.6
2 A	Lump corn starch pulverized to pass 200 mesh...	12.5
112	White corn dust, top of elevator...	12.5
13 (200)	Wheat elevator dust, top of elevator...	12.5
43	Oat and corn dust, top of elevator...	12.4
57 (100)	Oat dust from ground oat hulls...	12.3
1 A	Sugar lump pulverized to pass 200 mesh...	12.2
23 A	Gluten feed dust, from beams, etc., in curing room...	12.1
47 (200)	Oat dust from feed oats...	12.0
7 A	Dark canary dextrin...	11.8
65 (200)	Feed dust from dust collector...	11.8
9 A	Potato flour...	11.7
3 A	Sugar dust from sugar pulverizer...	11.3
12 A	Rice starch...	11.3
33 (200)	Wheat flour from packing room...	11.2
14 A	Powdered wheat starch...	11.0
24 A (200)	Corn elevator dust...	11.0
50 A	Malt dust from discharge of collecting system...	10.6
103	Wheat flour dust, rolls and purifiers...	10.5
48 A (200)	Fertilizer dust, from grinding dry tankage...	10.5
26 A	Tapioca flour...	10.4
34 A	Sugar dust, collector from powder mills...	10.3
13 C	Pittsburgh Standard Coal Dust...	10.1
43 A	Tan bark dust...	10.0
29 A	Tapioca flour...	9.9
32 A	Cocoa dust from cocoa bolters...	9.9
97	Reduction middlings...	9.4
33	Wheat flour from packing room...	9.3
42 A	Cocoa dust from cocoa cooling room...	9.1
8 A	Rice starch...	9.0
41 A	Extra fine sulfur flour...	8.8
44 A	Wheat smut and field dust...	8.8
49 A	Ground cork dust...	8.4
30 A	Rice flour...	5.6
25 A (200)	Arrowroot powder...	3.9
15 A	Potato starch...	3.2
37 A	Gelatin dust from elevator...	1.1

The results in Table I cannot be considered as absolute, as showing that the order as given here is the exact order of ease with which these will ignite. It is, however, the order of inflammability, as given under the conditions used in the tests. A change of any of the conditions might increase the pressure given by some, while it would decrease the pressure given by others. This fact is clearly shown in Fig. III, where increasing the size of capillary caused an increase in pressure with certain dusts, but a decrease with others. However, the results indicate that most of the dusts have a higher degree of inflammability than Pittsburgh coal dust, but in the light of present knowledge it is difficult to interpret the significance of this higher pressure, except that the dust is more easily ignited.

Although these results are only relative, they indicate that all the dusts tested have a high degree of inflammability, and that a dangerous condition exists where a cloud of any one of them is in suspension, or in a position where it can be easily thrown into suspension in the air. The relative degree of danger is approximately in the order of the foregoing results.

Tests on a larger scale are under way which will aid

in the interpretation of these results. These are designed to demonstrate under what conditions each dust will ignite, whether the source can be as small as a static spark, or whether it must be as large as a gas flame, or something between these limits.

ACKNOWLEDGMENTS

The author desires to express his appreciation of the assistance and helpful suggestions given by Dr. G. A. Hulett, consulting chemist, and Dr. J. K. Clement, physicist, U. S. Bureau of Mines.

DEPARTMENT OF AGRICULTURE
BUREAU OF CHEMISTRY
WASHINGTON, D. C.

A STUDY OF COMMERCIAL BEECHWOOD CREOSOTE

By H. K. SMITH AND S. F. ACRELL

Received December 19, 1916

A sample of beechwood creosote, made by a commercial process and furnished by the manufacturer, has been analyzed at the Forest Products Laboratory, Madison, Wisconsin, as a part of the studies on hardwood tars, creosotes and other related substances.

The sample was found to have the characteristics indicated in Table I.

TABLE I—ANALYSIS OF SAMPLE

Fraction No.	Temp. C.	Observed	Per cent. Cumulative	Sp. Gr. 60° C.	Ind. Rel. 60° C.	CHARACTER OF FRACTION
1	205	3.7	3.7			Yellow liquid
2	215	10.1	13.8			Golden yellow liquid
3	225	20.8	34.6	1.003	1.5074	Golden yellow liquid
4	235	8.1	42.7	1.009	1.5083	Golden yellow liquid
5	245	5.5	48.2	1.012	1.5111	Golden yellow liquid
6	255	8.4	56.6	1.019	1.5117	Golden yellow liquid
7	265	13.4	70.0	1.021	1.5123	Golden yellow liquid
8	275	2.7	72.7	1.022	1.5138	Golden brown liquid
9	285	4.8	77.5		1.5138	Red brown paste
Residue		21.6	99.1			Black solid

In the present investigation it was desired especially to determine if any considerable portion of the phenolic constituents have boiling points around 205° C.—that of guaiacol. As the sample contained some tar and pitch it was thought best to remove these before further studies.

The distillation was carried on in an iron still holding about 5 liters. On account of frothing, only about 2 liters could be distilled at one time. There was an overflow attachment to the still so arranged that when frothing became so violent as to cause an overflow, the lead to the condenser could be closed and another passing out of the window opened to prevent the contamination of the distillate with the froth. In the first run there were about 2 liters in the still. This was heated slowly, about 1½ hours being required for the first drops to come over at 45 to 50° C. The temperature rose rapidly to about 215° C. when the first drop of guaiacol came over. The distillate coming over at this temperature was light brown and a small amount of resin was present. Usually the temperature rose to 265° C. and the distillation was

TABLE II—DISTILLATION

Sample	Amount Distilled	Distillate	Residue	Temperature
100 g.	100 g.	100 g.	100 g.	100 g.
100 g.	100 g.	100 g.	100 g.	100 g.
100 g.	100 g.	100 g.	100 g.	100 g.
100 g.	100 g.	100 g.	100 g.	100 g.
100 g.	100 g.	100 g.	100 g.	100 g.
100 g.	100 g.	100 g.	100 g.	100 g.
100 g.	100 g.	100 g.	100 g.	100 g.
100 g.	100 g.	100 g.	100 g.	100 g.
100 g.	100 g.	100 g.	100 g.	100 g.
100 g.	100 g.	100 g.	100 g.	100 g.

observed. The distillate was a mixture of the various components obtained in the distillation.

In No. 2 the part coming over above 260° was apparently a decomposition product; brown fumes came over and the temperature fluctuated.

In No. 3 the pitch left was coked. When cool it was hard and brittle, insoluble in water, would not melt on heating, but decomposed. A small part was soluble in a solution of sodium hydroxide.

In No. 4 the distillation was stopped at 260°. The pitch left was softer and more liquid than those of the previous runs.

SEPARATION OF 215-230° FRACTION INTO NEUTRAL AND ACID PORTIONS

The creosote was shaken up with several portions of 10 per cent NaOH solution until all the acid portion was extracted, the neutral portion floating on the top. The liquids were separated in a separatory funnel. The neutral oil was then shaken up with water until the water was neutral to litmus. The sodium hydroxide solutions of the acid oils were then acidified with dilute HCl. The oil precipitated out and was separated. This was washed with water until neutral to litmus. The amounts of oil extracted by the successive portions of sodium hydroxide are illustrated in Table III.

TABLE III—100 CC. OF 215-230° FRACTION TREATED WITH SUCCESSIVE 50 CC. PORTIONS OF 10 PER CENT NaOH, SEPARATED AND ACIDIFIED

PORTION	I	II	III	IV	TOTAL
Yield of Acid Oil.....	12 cc.	14 cc.	18 cc.	2 cc.	46 cc.
Yield of Neutral Oil.....	38 cc.
Loss.....	16 cc.

TABLE IV—EXTRACTIONS OF 250 CC. PORTIONS OF 215 TO 230° FRACTION

PORTION	I	II	III	IV	TOTAL
Creosote.....	250 cc.	250 cc.	250 cc.	250 cc.	1000 cc.
Acid Oil.....	140	150	125	145	560
Neutral Oil.....	98	100	93	105	396
Loss.....	12	..	32	..	44

Table IV gives the total amounts of acid and neutral oil extracted from 250 cc. portions of the distilled creosote boiling at 215 to 230° C.

FRACTIONATION OF THE NEUTRAL OIL

The distillation was conducted through a 12-in. Hempel column at a rate of about 2 drops per second. The color of the fraction was light yellow, verging toward brown in the higher fractions. From 290° the temperature suddenly jumped to 325°, where practically all the remaining material came over, excepting a small residue of about 9 grams.

TABLE V FRACTIONATION OF NEUTRAL OIL

	12-5 g.	210 to 215°	28-5 g.	240 to 245°	33-0 g.
to 170°	81-0	215 to 220°	56-0	245 to 250°	24-0
170 to 190°	8-0	220 to 225°	70-0	250 to 255°	14-0
190 to 195°	8-0	225 to 230°	26-5	255 to 260°	21-0
195 to 200°	22-0	230 to 235°	35-5	260 to 280°	21-0
200 to 205°	55-5	235 to 240°	42-5	280 to 325°	26-5
205 to 210°	47-5			325 to 330°	15-0
Total Distillate.....					567-0 g.
Residue.....					9-0
Loss.....					19-0

FRACTIONATION OF THE ACID PORTION OF 215-230° FRACTION

The distillation was carried on in a one liter flask with a 12-in. Hempel. The first drops came over at 98°. The fraction was a light brownish yellow which

TABLE VI FRACTIONATION OF ACID PORTION 864 GRAMS OF THE OIL FRACTIONATED

	52-5 g.	215 to 225°	185-0 g.
98 to 190°	95-0	225 to 240°	70-5
190 to 205°	..	240 to 260°	77-0
(Chiefly at 203 to 205°)	..	260 to 265°	24-0
205 to 215°	257-0		
Total Distillate.....			761-0 g.
Residue (above 265°).....			21-0
Loss.....			82-0

changed to a pinkish brown on standing. After standing over a month the fraction was a clear brown liquid.

SUMMARY

It is seen from the above data that this sample of beechwood creosote containing tar and pitch distills rather uniformly from 200 up to 360° C. and leaves a residue of 20 to 25 per cent pitch. If the temperature is not carried above this point the pitch residue is soft and excellent, but above 300° it decomposes, foams over and becomes friable when cold. When the creosote fraction is then redistilled in glass vessels practically no pitch residue is obtained.

When the 215-230° fraction was extracted with 10 per cent sodium hydroxide in excess to remove the phenolic compounds, a yield of about 40 per cent of neutral oil and 56 per cent of acid oil was obtained. These oils distil practically without decomposition and formation of pitch. The acid oil on redistillation gave a yield of about 65 per cent of a guaiacol fraction boiling between 190 and 225° C.

FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN

A METHOD OF PRODUCING CRUDE WOOD CREOSOTE FROM HARDWOOD TAR

By R. C. JUDD AND S. F. ACRREE

Received December 19, 1916

The purpose of this work was to ascertain a practical method of producing on a semi-commercial scale a wood-tar creosote from crude hardwood tar without decomposing part of the material in the still. The requirements to be met are that the method must be rapid, no coke must be left as a residue, and the oil shall contain as little free acid as possible.

METHOD OF CONDUCTING THE WORK

Three methods of distillation were tried:

I—Distillation with steam.

II—Straight distillation.

III—Straight distillation while using steam for stirring.

The two former methods were found to be unsatisfactory and are not reported here.

(I) Distillation with steam gave small yields and a large amount of steam was consumed. Moreover, the length of time necessary to obtain a reasonable amount of oil was excessively long.

(II) Straight distillation gave good yields of oil but there is great danger of deep-seated exothermic decomposition of the tar or pitch into gas and vapor when the temperature is not carefully controlled. This can become so violent that the still can be blown up. Even when great care was taken there seemed to be a slight amount of coking in the still which, with frequent use, would eventually cause trouble and perhaps ruin the still. This is especially true when the temperature of the pitch rises above 300 to 325° C. Work along this line will be reported later in detail.

(III) The last method, *viz.*, stirring with steam, gave good yields of oil, was somewhat more rapid than direct distillation and there were no evidences of coking. It was found that in the early part of the distillation

steam was not necessary as there was already a large amount of water present. The distillation was, therefore, carried on to the point where the distillate came over as a homogeneous liquid. The temperature was slowly raised until 100° C. was exceeded and steam under constant pressure was then injected into the tar.¹ The ratio of oil to water in the distillate gradually decreased until only 25 per cent of the distillate was oil. The distillation was then stopped. The last portion of the distillate on standing solidified to a jelly-like mass because of the presence of paraffin. The residue in the still was liquid when hot and could be easily poured, but on cooling solidified to a hard brittle pitch which could be powdered in the fingers. Special experiments showed that not more than 2 per cent of the tar is lost as gas or vapors.

RESULTS

The following yields were obtained by this method of distillation:

No. 1—1100 g. Tar taken	Total Distillate	Oil	Per cent in Tar
1st Portion of Distillate.....	282 cc.	64 cc.	19.8 Water
Straight distillation.....	29 cc.	29 cc.	8.5 Light Oil
2nd Portion of Distillate			
Stirred with steam.....	1076 cc.	446 g.	40.5 Heavy Oil
Residue (by difference).....			31.2 Pitch
No. 2—1175 g. Tar taken	Total Distillate	Oil	Per cent in Tar
1st Portion of Distillate.....	371 cc.	101 cc.	23 Water
Straight distillation.....			9 Light Oil
2nd Portion of Distillate			
Stirred with steam.....	920 cc.	372 cc.	32 Heavy Oil
Residue (by difference).....			36 Pitch

The heavy oil from No. 1 contained 0.7 per cent acids figured as acetic acid. This was reduced to 0.3 per cent by washing three times with equal volumes of water.

CONCLUSION

In brief, the following method seems to be a desirable one for the production of crude wood-tar creosote on a semi-commercial scale: (1) Distill with direct heat until the distillate comes over as a homogeneous liquid well above the boiling point of water. (2) Raise the temperature and stir the tar with a steam jet; collect this latter portion of the distillate in a separate container and continue until the distillate contains solid paraffin.

If the above procedure is carried out carefully the heavy oil fraction should not contain more than one per cent acid and the pitch can easily be emptied without fear of coking in the still. Furthermore, a slight gain in time of distillation will result from the use of steam.

FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN

SOME OBSERVATIONS ON THE INFLUENCE OF HUMIDITY ON THE PHYSICAL CONSTANTS OF PAPER¹

By OTTO KILBES² AND PHILIP SILVERSTEIN³
Received January 8, 1917

Samples of paper taken for testing purposes at the mill and later at the point of destination may show

¹ This paper represents part of the thesis presented by P. Silverstein in partial requirement for the Degree of Chemical Engineer in the University of Wisconsin.

² In Charge, Section of Pulp and Paper, Madison, Wisconsin.

³ Student Research Assistant, Forest Service.

rather surprising variations in their so-called physical constants. Paper is essentially a network of interwoven cellular fibers which may or may not be sized, loaded, calendered, coated or treated in other ways for special purposes, but the paper will still show the general physical characteristics of the individual fibers which make up the sheet and determine its quality.

INFLUENCE OF HUMIDITY ON STRENGTH

Since the individual fibers of a sheet of paper are hygroscopic, the whole sheet consisting so largely of fibrous material naturally possesses this quality, though to a lesser degree than the individual fibers. It is a common observation that on humid days a sheet of paper is more limp, stretches more and is less resistant to tearing and bursting than on dry days. The relative humidity of the atmosphere varies from 30 per cent in cold, dry weather to almost 100 per cent in foggy or hot, moist weather. Indoors, the relative humidity ranges are not so wide except that on a cold, dry day the relative humidity in a steam-heated room often falls to 20 per cent while in summer, with all the windows open, indoors it may be almost as high as that outdoors.

Herzberg¹ in his treatise on "Papierprüfung" gives data on the effect of varying humidities on the physical properties of paper. From a study of his data, it is evident that variations in the relative humidity of the atmosphere and consequent variations in the percentage moisture in the paper have a decided effect on the strength and stretch of paper. As the humidity falls, the breaking length is increased and the stretch decreased.

Herzberg in quoting from the work of G. Dalén states that for relative humidities between 0 per cent and 80 per cent, paper expands in direct proportion to the amount of moisture present. But when the relative humidity is between 80 per cent and 100 per cent, the expansion is somewhat over this proportion.

G. Dalén, after many experiments on the effect of varying humidities on the breaking length and stretch of papers, constructed a table of factors by which the results for breaking length and stretch obtained at relative humidity are to be multiplied to obtain the correct result for 65 per cent relative humidity. This table of factors has been published in Herzberg's book on page 18.

As a result of the investigations made at the testing laboratories in Germany, all papers for Government use are tested at the Royal Testing Laboratories at Gross Lichterfelde, under a constant relative humidity of 65 per cent.

The Forest Products Laboratory has recently installed a constant humidity room in which to study the effect of variations in humidity on the physical properties of paper. The room is double-walled, 8 ft. x 10 ft. x 9 ft. 6 in. x 7 ft. 6 in. high, and fitted with a constant temperature and constant humidity apparatus. Fig. 1 represents a schematic sketch of the apparatus, which consists essentially of a galvanized iron cabinet 4 in. in diameter at the base and

reaching from the floor through the roof where it is connected with a motor-driven fan *B*. The outlet from *B* leads through heating coils *C* into flue *D* and back into the room. At the bottom of the conduit *A* is a settling tank *E* from which the pump *F* draws its supply of water and pumps it to the sprays *G*, the water dropping down into the tank *E*. Above the sprays are a series of eliminator plates *H*. The air compressor *J* delivers compressed air to the tank *K*, *L* is the humidity regulator, *M* is a thermostat, while *N*₁ and *N*₂ are diaphragm valves. *P* is an air outlet duct. *Q* is a steam supply line in which the steam is reduced to a pressure of 5 lbs. per square inch by means of a reducing valve.

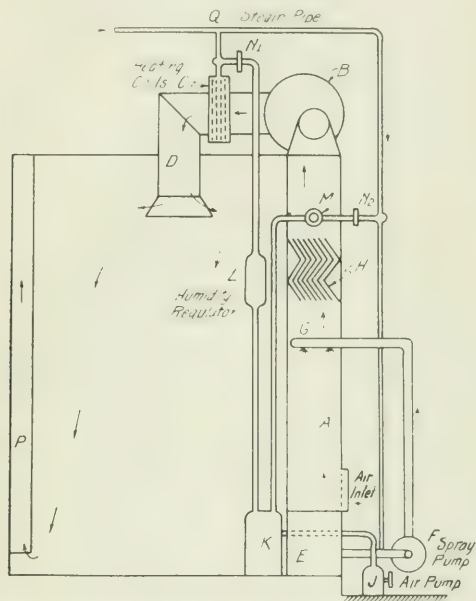


FIG. 1. DIAGRAMMATIC SKETCH OF THE AIR CONDITIONING APPARATUS.

During operation, the pump *F*, sprays *G*, compressor *J* and fan *B* are in constant operation. Air enters the opening in *A* as shown by the arrow, passes up through the sprays *G* and into the eliminator plates *H* where the entrained water is removed, then up through fan *B*, heater *C*, and flue *D* into the room and finally out into the atmosphere through flue *P*.

Before explaining the regulation of the temperature and humidity it is best to review some definitions. The "dew point" of air is that temperature at which it is saturated with a given amount of water vapor. If cooled below this temperature, some vapor will condense and dew will be deposited. The "dry bulb" temperature is the ordinary temperature of the air in the room as given by an accurately graduated thermometer. The "wet bulb" temperature is that given by a thermometer similar to that used for determining the dry bulb temperature, but having the bulb tightly covered with a piece of soft muslin or silk which is thoroughly wet and over which a current of air is passed.

Through the evaporation of water from the cloth, the wet bulb temperature is always lower than that of the dry bulb except at the dew point, when all three temperatures read alike. However, the wet bulb temperature is always higher than the dew point temperature except at 100 per cent relative humidity. The "relative humidity" is the ratio of the amount of water vapor in a given space, to the amount which the same space will hold when fully saturated at the same temperature and is expressed in per cent.

For a given amount of moisture per cu. ft. of air, the dew point is always the same, because at the dew point temperature, only, is the air saturated with that amount of moisture. If this air is heated, both the dry bulb and wet bulb temperature rise, the dry bulb more rapidly than the wet bulb, because the latter is cooled by the evaporation of water from its muslin jacket. As the air is heated, its capacity for water vapor is increased and, therefore, the relative humidity falls. By taking the difference between the wet and dry bulb thermometers, the relative humidity can be found by consulting a humidity chart or a set of tables.

The above-mentioned method of regulation is employed with the apparatus in use. Referring to Fig. 1, the air as it passes from the eliminators *H* is saturated with water vapor, i. e., it is at its dew point. If no heat is added to or taken from the air it will pass through the fan and into the room at the same temperature as that which it had when leaving *H*, and the wet and dry bulb thermometers will both register the same temperature, namely that of the dew point. No evaporation can take place from the wet bulb thermometer because the surrounding air is already saturated and can hold no more moisture.

If now, the humidity regulator *L* is set for say 60 per cent relative humidity, then by means of the diaphragm valve *N*₁, steam is admitted to the heating coils and the air heated. As the temperature rises, the capacity of the air for water vapor increases and the relative humidity decreases. At 60 per cent relative humidity, the humidity regulator shuts off the steam from the heating chamber until the humidity in the room rises above that for which it is set when steam is again admitted to the heaters. The actuating mechanism in the humidity regulator is a silk thread which contracts and expands with the amount of moisture present in the room. Through this regulator the compressed air from *K* being at a higher pressure than the steam keeps the diaphragm valve shut. When the percentage humidity rises above that for which the regulator is set, the silk thread expands and shuts off the air pressure and steam is admitted to the heating coils.

For high relative humidities where it is necessary to keep the temperature of the sprays above that of the water from the supply pipes, the thermostat *M* operates the diaphragm valve *N*₂ which governs the admission of steam to the spray water as it enters the pump *F*.

An automatically operated wet and dry bulb thermometer or psychrometer was used to determine the relative humidity. The extreme ranges of humidity

we were able to secure with the cooling water at our command were 41 to 82 per cent.

TESTS OF COMMERCIAL PAPERS

The laboratory originally planned to include in this work a series of tests on commercial papers made under uniform conditions of mechanical treatment and from the same stock where the only variation would be one of ream weight. For papers made on any given furnish there appears to be a certain thickness (which decides the ream weight) from which the paper of unit maximum strength is produced. Some work has been done by Rehn¹ on the study of the influence of weight on strength of paper, which brings out some interesting points. It was hoped that samples, taken at the time of change in weight, representing papers of different ream weights made with the same mechanical treatment and from the same furnish, could be obtained from the mills. Unfortunately, some of the papers submitted showed such large variation in appearance, texture and color, that we feel sure they represent different runs, and this was substantiated by a study of the strength tests. This necessitated our omitting at this time any study of the effect on the physical constants caused by variation in ream weight.

The physical tests employed in arriving at a basis of comparison of the strengths of the papers studied under varying degrees of humidity were the following:

- 1—Ream weight.
- 2—Thickness.
- 3—Resistance to bursting; points per lb., points per 0.001 in. thickness.
- 4—Tensile strength, breaking length.
- 5—Stretch.
- 6—Resistance to folding.

1—The ream weight was taken on the 500 basis, sheets 24 in. \times 36 in.

2—The thickness was measured by a spring micrometer.

3—The resistance to bursting was measured by the Mullen tester. By "points per lb." is meant the bursting strength in pounds required to burst one sq. in. of surface as determined by the Mullen test divided by the ream weight. By "strength factor" or "points per 0.001 in." is meant the bursting strength in pounds as determined by the Mullen test divided by the number of thousandths of an inch thickness of the paper.

4—The tensile strength in kilograms was determined by the Schopper tensile strength machine. The tensile strength varies with the kind of paper, the width of the strip and the thickness. A numerical expression for the tensile strength of the paper which depends solely upon the nature of the paper is called the "breaking length," and is independent of the thickness and the width of the paper, as these are considered in the calculation by which "breaking length" is determined. By "breaking length" is meant the length of a strip of paper, which if suspended from a support, will break at the point of support due to its own weight.

5—The percentage stretch of the paper is obtained with the Schopper tensile strength machine at the same time as the tensile strength is taken.

6—The resistance to folding is measured by the Schopper folder.

These tests and their significance are, of course, familiar to the paper trade and are only cited to avoid any misunderstanding of the tabulated results. As is well known, machine-made papers are stronger in the machine direction which is indicated in the table by the minus sign (—) than across the machine direction which is indicated in the table by the plus sign (+). The stretch of machine-made paper is less in the machine direction (—) than across the machine direction (+).

In order to obtain average results five tests were made to determine bursting strength and five tests in each direction for tensile strength and stretch, and three folding tests both with and across the machine direction. If variable results were obtained 10 tests were made and the results averaged.

Four sets of commercial papers of totally different properties were examined. These will be designated as Series I, II, III and IV. Series I, known as ground-wood-sulfite papers, was supplied in 25, 30 and 34-lb. weights and was made according to the mill submitting these samples on a furnish of 30 per cent groundwood and 70 per cent sulfite pulp. These papers were of a "wild" formation and showed many shives.

Series II consisted of papers made on an all sulfite furnish in weights of 25, 40, and 60 lbs. These papers showed a "wild" formation, making it difficult to obtain uniform results.

Series III and IV represent kraft papers of two different shipments from the same mill. Series III consisted of samples of 25, 30, 40, and 50-lb. papers while Series IV consisted of 30, 40, and 60-lb. papers. Papers of Series III and IV showed a "wild" formation.

Before beginning the actual testing it was necessary to determine the length of time required for the papers to "season," i. e., to reach the desired moisture content. Herzberg in his "Papierprüfung" states that the strips should be kept under the desired atmospheric conditions for at least 48 hours before testing.

K. Fenchel and K. Cornely¹ state that "experiments on the rate of absorption and loss of moisture when pulp was transferred from an atmosphere of 40 per cent humidity to one of 50 per cent and then back again, showed that two hours were sufficient for the establishment of equilibrium with the atmosphere and papers kept on standing in the first atmosphere, the original weight was not restored in 24 hours or more." In these experiments the humidity was collected by blowing the air through a solution of sodium chloride saturated with it.

In our laboratory a similar test was carried out, carried out under the conditions of the experiments, that of comparing all measurements taken under the same conditions of humidity, paper, type and theory.

TABLE I

Humidity changed from 55 per cent to 70 per cent at 7:05 P.M.
Results given in Grams

Paper	Humidity:			
	55 per cent 6:40 P.M.	70 per cent 9:00 P.M.	70 per cent 10:00 P.M.	70 per cent 10:37 P.M.
News.....	27.54	27.96	27.98	27.96
All Rag.....	17.79	18.00	18.00	18.01
Light Weight Kraft.....	13.18	13.34	13.37	13.37
Heavy Weight Kraft.....	20.28	20.52	20.52	20.56
Light Weight Water Finish.....	27.71	28.14	28.14	28.17
Heavy Weight Water Finish.....	47.48	48.18	48.14	48.09
Aspen Pulp.....	31.46	31.90	31.92	31.90

weights of "water finished" wrapping paper and a sheet of unsized aspen soda pulp were suspended from a string across the room and each sheet was weighed approxi-

mately every half hour on an analytical balance, until the weight became constant.

Table I shows the time required to season the paper when changing from 55 per cent relative humidity to 70 per cent. The change from 55 per cent to 70 per cent relative humidity was made at 7:05 P.M. The data show that in two and one-half hours all the papers had practically attained equilibrium. A striking feature of this test is that the heavily sized all-rag paper reached a state of constant weight about half an hour before the unsized aspen pulp. The light

TABLE II

PAPER	Humidity Per cent	Weight per ream Lbs.	Thickness in.	Bursting Strength	Points per sq. ft. Lb.	Points per 0.001 in. Thickness	TENSILE STRENGTH		BREAKING LENGTH		STRETCH		NUMBER OF FOLDS					
							— Kilograms	— Av.	— Meters	— Av.	— Per cent	— Av.	— Double					
													+	Av.				
SERIES I—GROUNDWOOD-SULFITE PAPERS																		
25-lb.....	41	26.5	0.00300	12.8	0.482	4.25	3.7	1.8	2.75	5860	2820	4340	1.24	2.12	1.68	17	10	13
	53	26.5	0.00286	12.2	0.478	4.36	3.5	1.72	2.61	5450	2700	4075	1.25	2.27	1.76	15	11	41
	64	26.5	0.00343	12.0	0.447	4.09	3.48	1.61	2.35	5210	2500	3885	1.45	2.32	2.12	92	82	5
	65	28.0	0.00312	12.8	0.457	4.10	3.36	1.48	2.42	5190	2400	3795	1.32	2.96	2.14	80	10	45
	77	28.0	0.00326	12.0	0.429	3.68	3.08	1.44	2.26	4750	2220	3485	1.78	3.87	2.82	104	14	59
	82	27.5	0.00298	9.4	0.342	3.15	2.64	1.16	1.90	4100	1860	2980	1.72	3.90	2.81	41	11	17
30-lb.....	41	32.5	0.00354	17.0	0.523	4.80	4.60	2.62	3.61	6040	3340	4690	1.16	2.14	1.65	60	17	38
	53	32.5	0.00364	16.6	0.511	4.56	4.55	2.52	3.53	5940	3270	4580	1.24	2.52	1.88	72	15	82
	64	32.0	0.00358	14.6	0.456	4.08	4.12	2.24	3.18	5370	2760	4065	1.38	2.66	2.01	114	33	73
	65	33.0	0.00316	16.0	0.485	4.42	4.38	2.36	3.37	5700	2980	4340	1.38	2.52	1.95	126	18	72
	77	34.5	0.00368	14.4	0.417	3.92	4.26	2.04	3.15	5110	2600	3855	1.58	3.02	2.30	170	25	97
	82	32.0	0.00369	11.8	0.369	3.47	3.35	1.66	2.41	4080	2120	3270	1.58	3.72	2.90	107	19	60
34-lb.....	41	35.0	0.00404	17.0	0.486	4.21	5.08	2.86	3.97	5810	3460	4635	1.30	2.42	1.86	68	25	46
	53	36.5	0.00410	17.5	0.479	4.27	5.00	2.70	3.85	5660	3300	4345	1.30	2.44	1.87	78	30	54
	64	35.5	0.00400	15.75	0.444	3.94	4.38	2.50	3.44	4940	2820	3880	1.42	3.14	2.28	86	42	64
	65	37.0	0.00400	16.20	0.438	4.05	4.72	2.58	3.65	5520	3040	4280	1.42	2.90	2.16	80	34	56
	77	39.5	0.00412	13.2	0.518	4.20	4.24	2.44	3.34	4690	2760	3645	1.64	3.28	2.46	136	43	64
	82	38.5	0.00416	14.4	0.374	3.41	4.44	1.94	2.69	4080	2120	3270	1.58	3.72	2.90	107	19	60
SERIES II—ALL SULFITE PAPER																		
25-lb.....	41	23.5	0.00182	12.8	0.545	7.04	4.24	2.06	3.15	7320	3580	5450	0.96	1.56	1.16	17	10	13
	53	25.5	0.00194	13.2	0.518	6.80	4.24	2.06	3.15	7330	3210	5270	1.24	2.35	1.76	15	11	41
	64	26.0	0.00194	13.6	0.523	7.01	3.88	1.90	2.89	6890	3220	5055	1.28	2.60	1.95	92	82	5
	65	22.5	0.00184	12.2	0.550	6.63	3.87	1.96	2.91	6700	3240	4970	1.00	2.60	1.95	80	10	45
	77	25.5	0.00164	13.2	0.518	0.505	5.25	2.44	3.34	3150	1695	2475	1.42	2.32	1.76	104	14	59
	82	22.0	0.00162	11.0	0.500	6.80	3.20	1.68	2.44	5520	2820	4170	1.52	3.48	2.81	41	11	17
30-lb.....	41	31.5	0.00314	23.8	0.756	7.93	5.82	3.87	4.34	7650	3780	5715	1.75	2.90	2.26	60	17	38
	53	32.0	0.00304	23.2	0.725	7.64	5.52	3.10	4.31	7290	3920	5605	1.84	3.48	2.60	72	15	82
	64	32.0	0.00312	25.6	0.800	8.24	5.62	3.08	4.35	7050	3860	5455	2.12	4.52	3.40	92	82	5
	68	33.0	0.00322	26.5	0.803	8.24	5.62	3.08	4.35	7050	3860	5455	2.12	4.52	3.40	92	82	5
	77	35.0	0.00302	26.5	0.758	8.77	5.48	2.76	4.12	6490	3580	4935	2.26	4.82	3.64	104	14	59
	82	34.0	0.00304	25.2	0.741	8.29	4.84	2.44	3.64	5800	2910	4355	2.44	5.68	4.32	41	11	17
40-lb.....	41	40.5	0.00382	33.8	0.833	8.84	7.30	4.16	5.73	7550	4275	5912	1.50	4.72	3.56	60	17	38
	53	40.0	0.00374	32.8	0.820	8.77	7.60	3.78	5.69	7830	3770	5800	1.72	4.66	3.56	72	15	82
	64	40.5	0.00371	30.7	0.758	8.28	6.78	4.20	5.49	7030	4200	5615	1.81	5.23	4.00	92	82	5
	68	41.0	0.00384	29.75	0.725	7.75	5.48	3.78	5.16	6840	3585	5385	1.86	4.92	3.72	104	14	59
	77	43.0	0.00391	27.0	0.628	6.89	6.10	3.68	4.89	6150	3720	4935	1.90	5.84	4.52	41	11	17
	82	43.5	0.00382	25.6	0.589	5.92	5.92	3.34	4.63	5870	3270	4570	2.32	6.20	4.88	41	11	17
60-lb.....	41	63.0	0.00576	56.0	0.889	9.71	10.81	6.50	8.65	6900	4410	5655	2.00	3.88	2.96	17	10	13
	53	61.5	0.00556	54.5	0.886	9.80	10.34	6.86	8.50	6650	4430	5540	1.97	4.34	3.36	15	11	41
	64	61.5	0.00572	48.5	0.787	9.11	10.00	6.42	8.10	6310	3860	5085	2.11	4.47	3.40	92	82	5
	68	65.0	0.00610	55.5	0.853	9.10	10.60	6.32	8.46	6980	4170	5530	2.48	5.64	4.32	104	14	59
	77	71.0	0.00636	5	0.828	9.10	10.60	6.32	8.46	6980	4170	5530	2.48	5.64	4.32	104	14	59
	82	71.0	0.00636	5	0.828	9.10	10.60	6.32	8.46	6980	4170	5530	2.48	5.64	4.32	104	14	59

weight papers also tend to approach equilibrium somewhat sooner than the heavier papers.

The papers for each day's run were hung loosely from a cord strung across the room so that the air had free play around them and were left to season for at least 3 hours. Each set of papers was tested without interruption on the same day and all the conditions of testing were kept as nearly constant as possible.

RESULTS OF THE EXPERIMENT

The results of the tests under varying humidities are shown in detail in Table II, and graphically by means of curves. Keeping in mind the shifty character of the groundwood-sulfite papers and the wild formation of all of the samples of papers examined, these results can be considered only as indications. However, certain conclusions may be drawn which should be of interest.

Table II shows the average of the results obtained

CONCLUSIONS

I—The value of points per pound increases with the decrease in relative humidity. The increase between 40 and 65 per cent is fairly regular but the increase of the relative humidity above 70 per cent causes a large reduction in strength. Foreexample, on the groundwood-sulfite mixture, Series I, taking the strength at 65 per cent relative humidity as standard, the average variation for the three papers was 8 per cent for the humidity change from 41 per cent to 65 per cent while from 65 per cent to 82 per cent the drop was 21.5 per cent, giving a total variation in strength of almost 30 per cent from the strength at 65 per cent relative humidity. On the Series IV, No. 1 kraft, the variation from 44 per cent to 64 per cent relative humidity was 13.7 per cent, while from 64 to 82 per cent the difference in

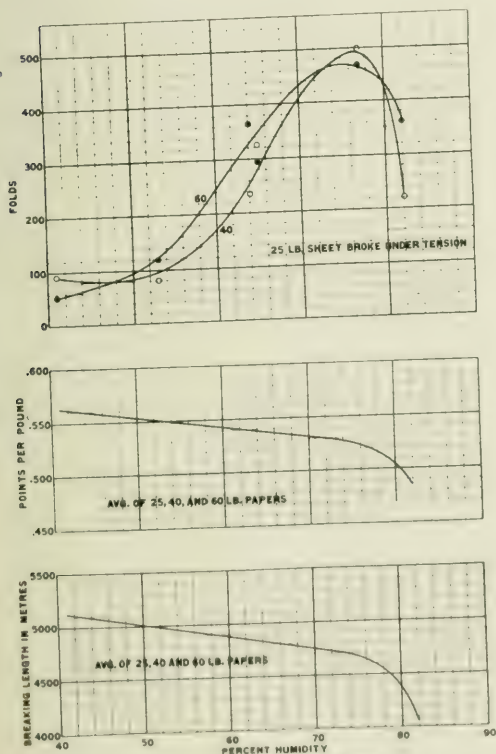


FIG. 2. SERIES II. ALL SULFITE.

in testing the different papers of Series I, II, III and IV at 41, 55, 64, 68, 77 and 82 per cent humidities. In order not to show too many curves only those for Series II on the all sulfite papers, and for Series IV on kraft papers are included in Figs. 2 and 3. The results for all the different weights of the papers in each of Series II and IV, for both the "points per pound" and for "breaking length," are plotted and the curves are practically parallel and form a composite curve.

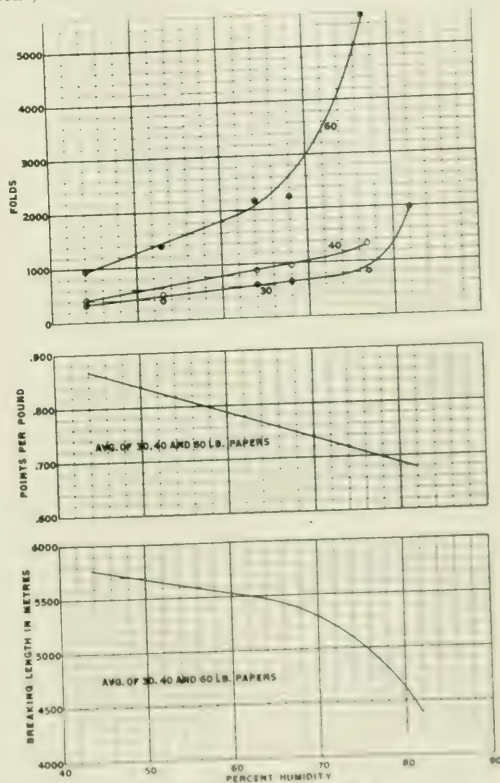


FIG. 3. SERIES IV. No. 1 KRAFT.

strength was 11.5 per cent, the total variation in strength being nearly 25 per cent from that at 64 per cent relative humidity.

II—The same results seem to hold for the breaking length. Above 60 to 75 per cent relative humidity the strength falls more rapidly than between 40 per cent and 60 per cent. For the groundwood-sulfite mixture, Series I, again taking the value at 64 per cent as standard, the variation in breaking length between

41 per cent and 65 per cent relative humidities is 10 per cent, while an increase in humidity from 65 per cent to 82 per cent caused a reduction in the breaking length of 27.2 per cent, a total variation of over 37 per cent. For Series IV, No. 1 kraft, the variation in breaking length for the humidity change from 44 per cent to 64 per cent was 6.4 per cent, while with an increase in humidity from 64 per cent to 82 per cent the drop in breaking length was 10.3 per cent, a total variation of 25.7 per cent.

III—The stretch of the paper increases with increase in relative humidity, the variation being rather more regular than with points per pound and breaking length. For the groundwood-sulfite mixture, Series I, the stretch increased 17.0 per cent, with increase in relative humidity from 41 per cent to 65 per cent, and 31 per cent with increase in humidity from 65 per cent to 82 per cent. For the Series IV, No. 1 kraft, the stretch increased 20.4 per cent with increase in relative humidity from 44 per cent to 64 per cent, and 18.7 per cent with increase in humidity from 64 per cent to 82 per cent.

IV—The folding properties seem to be affected to a greater degree than any other property. For the groundwood-sulfite mixture and the all sulfite papers, the resistance to folding increased tremendously between 55 and 77 per cent relative humidity, a further increase in the moisture content, however, causing the folding strength to break sharply. With the kraft papers, the folding strength increased with the increase in humidity and at the most saturated condition used, *viz.*, 82 per cent, the papers showed far greater folding strength than at 77 per cent. For the groundwood-sulfite paper, Series I, the number of folds increased 153 per cent with a humidity increase from 41 per cent to 77 per cent. Above 77 per cent relative humidity the folding strength decreased, showing that the per cent of relative humidity giving greatest folding strength had been passed. For Series IV, 30-lb. paper, the number of folds increased from 348 at 44 per cent relative humidity to 1980 folds at 82 per cent humidity, an increase of 470 per cent, while the 60-lb. paper showed an increase of 588 per cent in the folding strength in varying the relative humidity from 44 to 82 per cent.

The results obtained are sufficient to show that when paper is bought and sold on strength specifications, more uniform results would be obtained if the relative humidity at the time of testing were specified.

FOREST PRODUCTS LABORATORIES
MADISON, WISCONSIN

FURTHER STUDIES ON A NUMERICAL EXPRESSION FOR COLOR AS GIVEN BY THE IVES TINT PHOTOMETER

By OLEO KRUESS AND C. C. MCNAUGHTON
RECEIVED FEBRUARY 22, 1917.

In a previous paper by the authors¹ we described the results of some experiments in attempting to determine a numerical expression for color of paper as given by the Ives Tint Photometer. These experiments were made, (1) to determine if color indica-

tions as shown by the Ives Tint Photometer could be employed as a means of measuring the progress of beating, and (2) to observe the relation between the numerical expression for depth of color as read by the instrument, as compared with the grading for depth of color as observed by visual inspection. As reported in the previous paper we found it was possible to give a numerical expression for depth of color of papers comparable to visual grading where the variations were produced by either varying the amount of color or by holding the amount of dyestuff constant and varying the depth of color by variation in the hydration of the stock. The matter of scientifically and accurately recording color both as to hue and intensity is one of especial interest to those interested in paper research. A numerical expression for color is of value for purposes of scientific record and description, and for comparison and classification of papers and paper stocks. The best prepared papers may change in shade in a comparatively short time, due to changes of the paper stock itself or the fugitive character of the dyestuff.

Further experiments were made in order (1) to determine whether any shade matched visually in both hue and intensity with a different combination of dyestuffs would give the same tint photometer reading, (2) to study the darkening action caused by calendering of paper and whether such progressive darkening action could be numerically recorded, and (3) to study if there is a definite relation between the readings of the tint photometer and the glarimeter for successive increases in darkness and finish as produced by progressive calendering.

For description of the Ives Tint Photometer reference is made to our previous paper.

Through the courtesy of the Badische Company, New York City, some paper dyeings made on a furnish of 80 per cent groundwood and 20 per cent unbleached sulfite stock and sized with rosin size were obtained.

A paper which will be designated a "brown shade" using per 1000 pounds of stock,

Vesuvine BPX 4 lbs. Auramine Conc 12 oz. Safranine T extra Conc 4 oz.

was accurately matched both for shade and depth of color by a dyed paper using per 1000 pounds of the same stock,

Auramine Conc 3 lbs. 2 1/2 oz. Safranine T extra Conc 2 lbs. 1 1/2 oz. Victoria Green BF 1 1/2 oz.

and this dyeing will be designated as "brown match." These two dyeings matched well under both natural and artificial light and gave the following readings under the Ives Tint Photometer, the results being the average of 5 readings:

PARTS	TINT PHOTOMETER READINGS			
	Red	Green	Blue	Black
Brown shade	75	31	31	158.2
Brown match	73.8	37.2	30.9	158.1

A "blue shade" was prepared using per 1000 pounds paper stock, consisting of 80 per cent groundwood and 20 per cent unbleached sulfite.

Methyl Violet N 3 lbs. 10 1/2 oz. Victoria Blue BC Conc 1 lb. 10 1/2 oz.

This was matched with a "blue match" using per 1000 pounds of the same stock,

Methyl Violet N
3 lbs. 10 $\frac{1}{2}$ oz.Methylene Blue BGN
1 lb. 5 $\frac{1}{2}$ oz.

These two dyeings are fair matches under natural light whereas under artificial light the combination with Victoria Blue is, of course, decidedly redder. On comparing these dyed samples under the Ives Tint Photometer the following average readings were obtained:

PARTS:	TINT PHOTOMETER READINGS			
	Red	Green	Blue	Black
Blue shade	28.9	27.3	49.5	197.9
Blue match	27.1	27.8	47.2	197.3

The readings as given for both the brown and the blue matches check within the allowable experimental error showing that matches made with different com-

of Safranin T extra Conc. (Samples Nos. 1, 2b, 3a, and 7) are shown in plotted form. The curves are typical of all the dyeings examined, in so far as they show the increase in parts black and the decrease of the parts red, blue, and green produced by successive calendering. The three sets of curves marked parts black, red, blue, and green show the tint photometer readings of the dyed samples with practically no finish, with an intermediate finish and with a high finish.

In order to measure the per cent glare of the samples use was made of the glarimeter which was invented by Prof. Ingersoll at the Forest Products Laboratory. The per cent glare for the three degrees of finish of

No.	Sample Description	Amount and Kind of Dye Used	TINT PHOTOMETER READINGS				GLARE READINGS			
			1. No Finish	2. Low Finish	3. High Finish	4. Very High Finish	1. No Finish	2. Low Finish	3. High Finish	4. Very High Finish
1	Natural	None	88.2	80.2	72.0	59.6	83.2	74.5	68.9	73.4
2a		4 lbs. Vesuvine BPN	72.0	42.7	32.1	158.7	71.5	37.5	31.1	159.9
2b		1 oz. Safranin T extra Conc.	87.0	57.7	65.1	90.2	83.1	55.0	61.5	100.4
3		12 oz. Auramine Conc.	86.8	81.3	49.8	82.1	79.9	47.7	47.7	78.1
3a		Mixture of 2a, b, and c	73.7	37.1	31.0	158.2	71.3	37.1	30.5	161.1
3b		Mixture of 3a, b, and c	73.8	37.2	30.9	158.1	71.6	36.1	30.1	162.2
4		2 lbs. 1 $\frac{1}{2}$ oz. Safranin T extra Conc.	85.3	34.1	48.5	132.1	79.9	32.4	44.5	143.2
4a		3 lbs. 2 $\frac{1}{2}$ oz. Auramine Conc.	87.3	77.0	34.4	101.3	81.0	72.9	35.4	110.7
4b		1 $\frac{1}{2}$ oz. Victoria Green B. F.	64.8	76.3	70.8	88.1	60.2	71.6	66.8	101.4
5		1 lb. 10 $\frac{1}{2}$ oz. Methyl Violet N	37.3	27.9	48.4	186.4	36.0	26.9	48.5	191.6
5a		1 lb. 10 $\frac{1}{2}$ oz. Victoria Blue B Conc.	31.2	45.9	61.5	161.4	30.1	44.8	58.7	166.8
5b		Mixture of 4a and 4b	28.9	27.3	49.5	194.3	28.1	26.2	46.5	200.4
5c		Mixture of 5a and 5b	27.1	27.8	47.2	197.9	26.6	27.2	44.8	201.4
6		1 lb. 5 $\frac{1}{2}$ oz. Methylene Blue BGN	33.8	61.8	64.3	140.1	33.2	60.6	62.2	144.0
7		5 lbs. Vesuvine BPN	70.7	35.2	28.8	165.3	69.3	35.0	28.8	166.9
8		5 lbs. Safranin T extra Conc.	79.3	26.1	36.3	158.3	77.1	26.0	35.6	161.3
9		5 lbs. Victoria Green B. F.	84.6	75.5	32.2	107.7	82.8	72.9	32.1	112.2
10		5 lbs. Methylene Blue BGN	24.6	46.6	54.4	174.4	23.4	44.5	51.7	179.5
11		5 lbs. Victoria Green B. F.	23.8	46.3	46.2	183.7	23.3	45.1	44.9	186.7
12		5 lbs. Victoria Blue B Conc.	24.4	35.2	54.3	186.1	24.0	35.2	51.4	189.4
13		5 lbs. Methyl Violet N	34.5	28.7	45.3	195.0	34.1	28.4	45.0	195.5
14										
15										
16										
17										
18										
19										
20										
21										
22										
23										
24										
25										
26										
27										
28										
29										
30										
31										
32										
33										
34										
35										
36										
37										
38										
39										
40										
41										
42										
43										
44										
45										
46										
47										
48										
49										
50										
51										
52										
53										
54										
55										
56										
57										
58										
59										
60										
61										
62										
63										
64										
65										
66										
67										
68										
69										
70										
71										
72										
73										
74										
75										
76										
77										
78										
79										
80										
81										
82										
83										
84										
85										
86										
87										
88										
89										
90										
91										
92										
93										
94										
95										
96										
97										
98										
99										
100										

binations of dyestuffs, if they match visually, will give comparable readings with the Ives Tint Photometer. The blue shade and blue match do not check as well as the brown dyeings either visually or under the tint photometer. Individual dyeings were made on the same stock and with the same proportion of dyestuffs as were used in the brown and blue dyeings in the hope that some relation could be discovered between the tint photometer readings of the component colors and the mixture. This we have not been able to do but the tint photometer readings on these various dyed samples are given in the above table, and may enable some reader to discover a relation which will hold consistently for different colors.

It is common knowledge in the paper mill that calendering and supercalendering will darken the paper. Some experiments were made to determine whether the progressive darkening of either dyed or undyed paper as produced by calendering could be observed and numerically recorded by means of the tint photometer. The sample papers, prepared in identical manner with little or no finish, were successively calendered to give various degrees of finish, the colors were read by the tint photometer and the per cent glare determined by the Ingersoll glarimeter after each calendering. Complete tint photometer and per cent glare readings are given in the table for conditions of (1) no finish, (2) low finish, and (3) high finish. We have no supercalendered or plaster at the laboratory and Methylene Blue, were obtained on the samples studied through the courtesy of the Hammermill Paper Company, Erie, Pennsylvania.

Data from the tint photometer and glarimeter readings made on the first dyed sample are shown in the

various samples examined are given in the preceding table and are shown graphically at the top of the accompanying figure.

A brief description of the general principles on which the use of the glarimeter is based, may be of interest; for a full description the reader is referred to the original article describing the instrument.¹

Light reflected from a sheet of paper may be considered as belonging to one of two general types. First there is diffusely reflected light which means that the light is reflected uniformly in all directions. A matte surfaced paper diffusely reflects the bulk of the light falling on it and may be considered as a typical example of this case. Secondly, part of the light may be "specularly" reflected which is the case of all light where the angle of incidence equals the angle of reflection. The bulk of the light reflected from a highly supercalendered paper may be considered as being "specularly" reflected. Practically, light reflected even from the dullest matte finished paper is a mixture of diffusely and "specularly" reflected light.

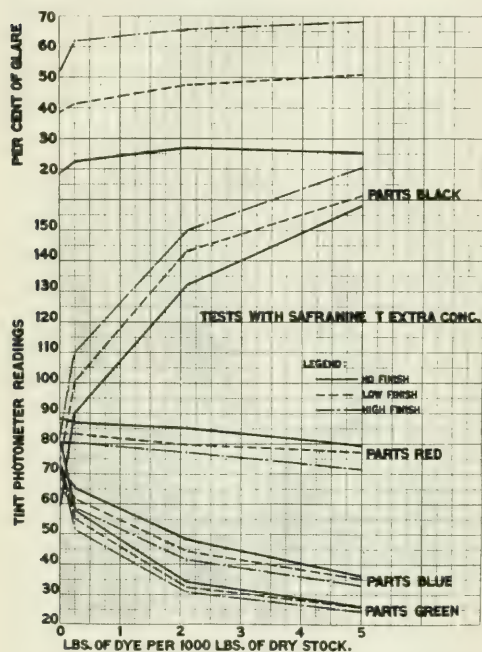
The "specularly" reflected light which is characterized by being concentrated in one direction, is called "specular" light. It is the portion of the light which is reflected in one direction, and is the portion of the light which is reflected in one direction. The portion of the light which is reflected in one direction, is called "specular" light. It is the portion of the light which is reflected in one direction, and is the portion of the light which is reflected in one direction.

All papers, whether matte or supercalendered, reflect a portion of the light which is reflected in one direction, and is the portion of the light which is reflected in one direction. The portion of the light which is reflected in one direction, is called "specular" light. It is the portion of the light which is reflected in one direction, and is the portion of the light which is reflected in one direction.

The portion of the light which is reflected in one direction, is called "specular" light. It is the portion of the light which is reflected in one direction, and is the portion of the light which is reflected in one direction.

reflected light is unaffected by the depth of color of the paper, while the amount of diffusely reflected light is diminished, depending on the depth of the shade of the paper.

The increase in per cent glare caused by calendering is shown by the typical glare curves, as plotted in the figure for dyeings made with various amounts of Safranine T extra Conc., on a furnish of 80 per cent groundwood and 20 per cent unbleached sulfite. The per cent glare of the blank made from the same furnish as the dyed samples increased from 18.8 to 38.7 to 51.4 per cent with the successive calenderings. The effect of the color in increasing the per cent glare reading by causing absorption of some of the light is evident from a study of the curve.



We have shown that it is possible to give a numerical expression for both shade and depth of color by means of the tint photometer and that two dyeings which match visually, will, within the allowable experimental error, match under the Ives Tint Photometer even though the two matches were dyed with different dyestuffs. For white sheets it is possible to follow the progress of calendering both by the tint photometer in recording the increase in parts black of the paper or by the decrease in parts red, blue, or green, and by the glare meter in recording the increase in per cent glare.

For colored papers the tint photometer will record the increase in parts black for successive production of finish by calendering, but the per cent glare will increase, not only due to the finish of the paper itself, but also due to the fact that with darkening of the paper the amount of diffusely reflected light is decreased without changing the amount of light "specularly"

reflected. With the same finish but with increase in color, this causes an apparent increase in per cent glare. With the present design of the glare meter, uniform lighting conditions are secured by an incandescent light within the light-proof interior of the instrument, while lighting conditions for the tint photometer are secured from daylight. In trying to check relations between the two instruments, the color screens of the tint photometer were later attached to the objective of the glare meter while readings were being taken but the results secured were very erratic. Thus while the glare meter might be found of value in determining the finish of white papers, in the light of our data it could not be recommended for colored papers of different hues and intensities.

FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN

THE CHEMISTRY OF WOOD DECAY PAPER I—INTRODUCTORY

By ROBERT EVSTAFIEFF ROSE AND MARTIN WILLIAM LISSE¹

Received November 27, 1916

During the decay of wood the composition of the material obviously undergoes profound alteration. By slow changes the structure of the wood is destroyed, the macroscopic changes being accompanied by a corresponding chemical disintegration. The highly complex compounds originally present pass into others of increasing simplicity until at last all passes into carbon dioxide, water, perhaps also hydrogen and methane. Between wood and its ultimate dissolution products must lie a whole range of intermediate substances. The chemistry of the process has received but scant attention, though it should prove of interest, as a scientific study, and as a prerequisite to discovering possible uses for a waste product occurring in great quantity. The subject has been merely touched upon in the work of Omelianski,² while the efforts made to determine the nature of humus and its components bear only distantly upon the question of wood decay, although the results obtained should prove valuable in determining the nature of the substances in very rotten wood.³ The very nearest approach to the subject has been made by Schreiner and Sullivan,⁴ who have identified some products obtained from rotten wood and peat.

It is clearly no easy task to determine the chemical changes undergone during the disintegration of wood under natural conditions; the transition of the material is a slow one unsuited to laboratory study; the accompanying conditions vary very greatly, and the products formed are largely lost as gases or as water-soluble compounds. Moreover, inasmuch as decay is due to the activity of lower vegetative forms, the nature of the bacteria, fungus or fungi responsible will largely modify the outcome.

¹ Used by M. W. Lisse in part fulfillment of the requirements for the M.S. degree in the University of Washington.

² *Compt. rend.*, **121** (1895), 658; **125**, 970, 1141; *Archiv. Science biologic.*, **7**, 411; **9**, No. 3; *Centr. Bakt.*, **8** (II), 193; **11**, 370 and 703.

³ Compare Czapek, "Die Biochemie der Pflanzen," Vol. I, pp. 226-229.

⁴ Sullivan, *This Journal*, **6** (1914), 919, and **8**, 1027; O. Schreiner and E. C. Shorey, U. S. Dept. Agr., Bureau of Soils, *Bull.*, **74**, 1914; Sullivan, *Science*, **38** (1913), 678.

Realizing the many uncontrolled, not necessarily uncontrollable, variables, it yet seemed desirable to us to attempt to apply a chemical method of analysis to a study of the problem. The present paper is the outcome of the very superficial survey of the field, attempted in order to find whether the work would show any promise of success.

For this first attempt it was unnecessary to take into account everything known of the composition of wood; to regard wood as a complex consisting of moisture, cellulose, lignocellulose, with smaller quantities of fats, starches, acid, tannins, etc., was sufficient for the purpose.

In adopting a method of analysis the following considerations had weight:

I—The decrease in cellulose content should be determined directly by such a method as the chlorination process of Cross and Bevan.

II—Inasmuch as decay is associated with increasing molecular simplification, the solubility of the material should prove worthy of determination. For this reason the amounts extracted both by cold and by hot water were determined. Quite evidently the first of these could hardly be reliable because with increasing solubility in cold water there would be an increasing tendency towards loss by leaching out.

III—The lignin complex gives a variety of characteristic hydrolysis products. It yields furfural and methyl furfural with strong hydrochloric acid, methyl iodide with strong hydriodic acid, and acetic acid when treated with dilute sulfuric acid. This being so it should be better for the present purpose to determine each product separately than to establish the amount of lignin present, though the latter should form a part of a more exact analysis. The reason for preferring a determination of the hydrolysis products of lignin was simply that to do so would make it perhaps possible to distinguish between the fate of different portions of the lignin complex. This hope was realized as will be apparent.

IV—During its decay, wood becomes more and more similar to "humus," which is itself the result of partial vegetable decomposition. Humus is largely soluble in alkali and it, therefore, seemed desirable to determine the amount of alkali-soluble material in the wood.

V In addition to the above determinations, the moisture content was found, in order to allow the calculation of all results to a moisture-free basis. Also, it was thought advisable to determine the percentage soluble in ether, and the ash.

While the methods to be employed were being discussed, the authors were very fortunate in receiving, through the courtesy of the Director of the Forest Products Laboratory at Madison, Wisconsin, a preliminary outline of a method for wood analysis, due to the work of Dr. A. W. Schorger. This proved almost ideal for the purpose of this research and was very largely adopted. The method is to be published in the near future and we feel that no description of methods should be entered upon in the present paper and will, therefore, confine ourselves to giving enough

detail to make clear the meaning of the analytical results. The minutiae will be taken up, if necessary, at a date subsequent to the publication of the contribution of the Forest Products Laboratory. The authors wish to take this occasion to thank Dr. Schorger for his kindness.

No attempt was made to identify the fungi responsible for the decay. In future work some effort must be made to do this, because even a superficial examination shows that the course of disintegration may be very different under nearly similar conditions. The difference is probably due to a variation in the type of fungi present. Thus the spongy products of extreme decay are sometimes very white and consist of masses of fibers having the appearance and properties of cellulose, which is, therefore, the last portion of the wood to be attacked. On the other hand, the samples analyzed showed the lignin complex to be the most resistant. Evidently different fungi produce very different cytases.

EXPERIMENTAL

The samples analyzed were three, all Douglas Fir:

(1) Sound heart wood.

(2) Heart wood softened by decay to an extent which made the annular rings rather less distinct than in the sound specimen, which had changed the color to a whitish yellow (sound wood is reddish), and had made the wood much less resistant to strain at right angles to the grain. The last may be better characterized by saying that on chopping the wood with the grain a clean blow would cause it to split readily in perfect pieces, but that a less violent stroke would frequently cause pieces 2 in. \times 2 in. to break at right angles to the grain. The sample was taken from a fallen tree whose diameter was about 4 feet at the base. The portion taken must have been 15 feet from the ground when the tree was standing. The trunk was still covered with bark. How long the tree had been dead, it was, of course, impossible to determine. The upper end was in a state of advanced decay under the bark, the wood being quite spongy.

Sample 2 could not have lost very extensively by leaching of water-soluble breakdown products, because it was taken from near the center of the log which was freshly cut. The wood was wet but sufficiently sound to protect the inside portions from any rapid removal of soluble products of decay.

(3) Heart wood in the last stages, taken from what remained of a standing stump. This sample was porous, dark red brown in color, and could be crushed readily between the fingers. Care was taken to avoid the material excreted by the larvae of wood borers.

PREPARATION OF SAMPLES. The wood was reduced to particles which would pass a 40-mesh sieve, and this powder was used for all determinations except that of cellulose. In the latter case fine wood shavings, equivalent in particles to the size of particles of the wood powder, were used. Care was taken to obtain as representative a sample as possible. The material for analysis was kept in airtight containers in order that, with the moisture and dissolved portions used in analyses, only the results obtained on a moisture-free basis.

TABLE I. PERCENTAGES OF ANALYSES OF SOUND, PARTIALLY ROTTEN AND COMPLETELY ROTTEN DOUGLAS FIR WOOD

Sample No.	I. Heart Wood			II. Partial Rot			III. Complete Rot			COMPARISONS OF RESISTES		
	I	II	Av.	I	II	Av.	I	II	Av.	Heart Wood	Partial Rot	Complete Rot
Cold Water-Soluble.....	3.94	4.12	4.03	1.77	1.75	1.76	1.27	1.06	1.16	4.03	1.75	1.16
Hot Water-Soluble.....	2.31	2.18	2.23	4.36	3.02	3.19	7.72	7.82	7.77	2.33	4.19	7.77
Alkali-Soluble.....	10.66	10.56	10.61	38.16	38.04	38.10	65.34	65.29	65.31	10.61	38.10	65.31
Cellulose.....	58.81	59.12	58.96	41.64	41.69	41.66	8.51	8.43	8.47	58.96	41.66	8.47
Acid Hydrolysis.....	0.72	0.71	0.71	0.28	0.28	0.28	0.17	0.18	0.17	0.71	0.28	0.17
Pentosan.....	2.26	1.09	1.16	6.73	6.85	6.79	2.92	3.00	2.96	7.16	6.79	2.96
Methyl Pentosan.....	2.81	2.47	2.64	3.71	3.42	3.56	6.12	6.00	6.06	2.64	3.56	6.06
Methoxy Group.....	3.96	3.92	3.94	5.15	5.18	5.16	7.72	7.89	7.80	3.94	5.16	7.80
Moisture (40-mesh).....	9.85	9.77	9.81	10.63	10.64	10.63	9.10	9.08	9.09	9.81	10.63	9.09
Moisture (sawdust).....	10.26	10.17	10.22	9.09	9.10	9.09	8.97	8.98	8.97	10.22	9.09	8.97
Ether Extract.....	2.67	2.76	2.71	2.00	2.11	2.05	2.12	2.12	2.12	2.71	2.05	2.72
Ash.....	0.18	0.12	0.15	0.15	0.15	0.15	0.64	0.67	0.65	0.15	0.15	0.65

(a) Percentages for "Hot Water-Soluble" are the Total, less the "Cold Water-Soluble."

ANALYTICAL METHODS

MOISTURE—3 to 4 g. dried at 105° C. for 6 hours.

COLD WATER EXTRACTION—2 to 3 g. digested with 300 cc. cold water for 48 hours. Weight of washed and dried residue determined.

HOT WATER EXTRACTION—2 to 3 g. extracted with boiling water under reflux for 3 hours. Weight of residue after washing with hot water and drying gives loss, from which cold water-soluble is deducted.

CELLULOSE—Determined by Cross and Bevan's chlorination method.

PENTOSAN AND METHYL PENTOSAN—Determined by the Tollen phloroglucide method.

ACID HYDROLYSIS—2 g. treated with boiling 2.5 per cent sulfuric acid during 3 hours. The volatile acid produced is distilled off and titrated. Result calculated as acetic acid.

METHOXY—Determined by Zeisel's method.

ETHER EXTRACT—3 to 4 g. extracted in a Soxhlet apparatus for 16 hours. Residue left on evaporation of solvent is weighed.

ALKALI-SOLUBLE—2 g. are treated with 100 cc. of 1 per cent NaOH in a boiling water bath for one hour. Loss in weight of sample, less percentage removed by extractions with hot and cold water, ether and acid hydrolysis, is calculated on moisture-free basis.

ASH—5 g. ignited in muffle. The results as obtained by us are probably too low, owing to lack of a suitable muffle.

DISCUSSION

An examination of the results in Table I makes it evident that the composition of wood, as roughly gauged by the inadequate preliminary tests performed, does indeed alter sufficiently during decay to allow of the application of analytical methods of study. The changes taking place are progressive and very profound, even in wood which has altered little in structural appearance.

As was foreseen, the ether-soluble materials vary but little. The cold water-soluble portion actually decreases regularly, while the value for the solubility in hot water increases. The tendency towards the production of acidic breakdown products is very evident from the rapid increase in alkali-soluble material. That these are formed largely at the expense of the cellulose follows from the surprisingly rapid fall in the cellulose percentage.

Turning to the lignin, the evidence is more conflicting but also more interesting. It will be noticed that two of the lignin values, those for acid hydrolysis and pentosan fall, while two rise, those for methyl pentosan and methoxy, the latter two rising at the same

rate, thus leaving the ratio between them nearly constant. This result is surprising, and highly instructive; it shows that the method of investigation may well throw some light on the chemical structure of wood. It is too early to theorize, but if a guess may be allowed, it would seem very probable that the part of the lignin complex which furnishes methyl furfural, that is, the methyl pentosan, also contains the methoxy group, and that the pentosan and the complex yielding acetic acid on hydrolysis are associated. This is to be surmised from the fact that the values for methyl pentosan and methoxy show a like ratio throughout and also represent an increasing percentage of the whole, that is, appear to represent the most resistant complex in the wood. Pentosan and the hydrolyzable group diminish in percentage progressively though their ratio does not remain constant, and it can only be said that both belong to a complex or complexes less stable towards decay than that of methyl pentosan and methoxy.

It should be emphasized that the above analyses are merely in the nature of a preliminary attack. They have served to show the value of the method, but will need a great deal of amplification. For instance, it will be necessary to determine the distribution of the lignin characteristics between the alkali-soluble material and the residue; direct lignin determinations are required; some attempt should be made to isolate products sufficiently pure to permit of analysis from the alkali-soluble substances. Were the last to succeed it would throw much light on the vexed question of the nature of humus. Another point requiring study is the elementary analysis of the wood in each stage, because that will determine whether the changes are accompanied by oxidation as it is reasonable to suppose that they are. Furthermore, the gaseous products should be analyzed. It is hoped to make these and several other questions the subject of future papers.

SUMMARY

I—Analysis of a sound sample of Douglas Fir heart wood is given.

II—Analyses of a partially and of a totally rotten portion of fir are compared with that of the original wood.

III—The progress of decay is readily followed by the use of chemical methods. Indeed, the change is so marked that a comparative cellulose determination might well serve to detect insipient decay.

IV—In the cases studied, decay is accompanied by a very rapid fall in cellulose content.

V—The lignin is far more resistant than the cellulose. If lignin is a definite compound, then its mole-

cule does not appear to decay uniformly, the portion first attacked being that which yields acetic acid and furfural on hydrolysis. The more resistant portion of the complex is that which yields methyl furfural on treatment with concentrated hydrochloric acid, and methyl iodide when heated with concentrated hydriodic acid.

VI—The results obtained tend to show that the method described may well be used in attacking the problem of the chemical composition of wood and of such substances as are found in humus, *i. e.*, humins, ulmins, huminic, ulminic and hymalomelanic acids.

VII—Attention is drawn to desiderata of further work.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF WASHINGTON, SEATTLE

THE EFFECT OF EXPOSURE ON COMMERCIAL LIMES

By J. CLYDE WHETZEL

Received September 22, 1916

INTRODUCTION

The object of this investigation has been to determine the effect of exposure to the atmosphere on the carbon dioxide and water contents of commercial limes, or the effect of what is commonly known as "air-slaking" on the chemical analysis. It was undertaken to fix more accurately the causes of complaints on high-grade lime shipments and to determine whether these are due to the quality of lime leaving the plant or to deterioration on the road. So far as lime manufacturers are aware, no work has been done on this subject, although it is of importance in the lime trade especially in the shipment of high calcium lime for chemical use.

METHOD AND EXPERIMENTAL DATA

Obviously the best way of carrying out the tests would have been to expose under the exact conditions obtained in practice, but this was not practicable, owing to the expense and difficulties of using such large quantities.

Accurate sampling is an important factor in the analysis of lime shipments and is even more troublesome than in the case of coal. The lime is in the form of large lumps, through which may be scattered comparatively large pieces of unburned stone or core, making it very difficult to obtain a representative sample unless the lime is afterwards ground. In order to prevent errors in sampling, due to the presence of core, the lime used in the tests was carefully selected by hand. It was impossible to use one large sample, quartering and sampling at certain periods, for as the lime slaked the sampling operations would break it up until finally it would become completely pulverized. This rubbing-off of the coating of slaked lime and exposure of quicklime would also affect the rate of absorption of carbon dioxide and water.

The containers for the bulk lime samples were boxes, having six compartments, 6 in. \times 6 in. \times 6 in., in each of which was placed a sample. The barrel selection gave lime uniformly uniform so that the samples were of the same composition at the start. Each box was open at the top, but a lid was suspended about 6 in. above the box in order to exclude dust and

dirt. In order to compare the results obtained by exposure in boxes with exposure under conditions more closely approaching actual practice, 6 open barrels were filled about $\frac{3}{4}$ full of large lumps carefully selected and exposed simultaneously. The samples of ground and hydrated lime were contained in boxes 6 in. \times 6 in. in cross-section but varying in depth in order to determine the protective effect of the upper layers of finely divided material. All the samples were placed for exposure in a small building and were probably in a more exposed position than would be found in actual practice as the building was very loosely constructed and in addition had two open windows. Several samples were prepared by quartering from a large pile. One was reserved for analysis at the start and the others were placed in the containers, exposed and analyzed at the intervals indicated in the tables.

Available calcium oxide was determined by the direct Solvay method of liberating the ammonia from an ammonium chloride solution and titrating with normal hydrochloric acid. Total calcium oxide was determined volumetrically by precipitation as oxalate and titration with standard permanganate. In determining carbon dioxide, the well-known method of absorption in a Geissler bulb was used. Water was found by difference between loss on ignition and carbon dioxide.

EXPOSURE OF HIGH CALCIUM LUMP LIME—This test consisted in the determination of the rate at which high calcium lump lime takes up carbon dioxide and water. Two sets of samples were exposed simultaneously: one set containing lump lime $\frac{3}{4}$ in. to 2 in. in size and placed in the boxes, the other 5 in. to 6 in. in size and contained in the barrels. The analyses and other data are given in Tables I and II, the latter giving the results obtained with the barrel samples.

TABLE I—HIGH CALCIUM LUMP LIME (BOXES)

Date Analyzed (1915)	Days Exposed	Per cent Avail.	Total	CO ₂	H ₂ O	Per cent Available CaO Dry Basis	Complete Analysis before Exposure
6/17	0	95.6	96.2	0.2	1.6	97.2	SiO ₂ 0.20%
6/24	7	84.8	86.5	0.8	11.6	96.0	SiO ₂ 0.28%
7/2	15	81.1	83.1	1.0	13.6	93.9	CaO 96.17
7/17	30	76.2	79.4	1.7	18.5	90.3	MgO 1.01
8/1	45	68.0	72.0	2.4	21.4	86.6	CaO 0.16
8/16	60	64.7	70.3	3.1	22.7	83.6	H ₂ O 1.50

TABLE II—BARRELS

Date Analyzed (1915)	Days Exposed	Per cent Avail.	Total	CO ₂	H ₂ O	Per cent Available CaO Dry Basis	Complete Analysis before Exposure
6/17	0	94.9	98.4	0.5	1.7	96.7	SiO ₂ 0.20%
6/24	7	87.2	88.9	0.5	9.3	96.0	SiO ₂ 0.28%
7/2	15	85.1	87.1	1.0	10.4	94.5	CaO 95.58
7/17	30	82.4	83.8	1.1	13.7	94.3	MgO 1.01
8/1	45	81.0	83.8	1.2	14.6	94.6	CaO 0.16
8/16	60	73.0	78.1	1.8	19.4	90.8	H ₂ O 1.50

TABLE III—MAGNESIUM LUMP LIME (BOXES)

Date Analyzed (1915)	Days Exposed	Per cent Avail.	Total	CO ₂	H ₂ O	Per cent Available CaO Dry Basis	Complete Analysis before Exposure
6/17	0	0.3	3.2	..	SiO ₂ 0.21%
6/24	7	1.2	8.3	..	SiO ₂ 0.28%
7/2	15	3.8	11.3	..	CaO 95.58
7/17	30	1.9	14.8	..	MgO 1.01
8/1	45	2.9	17.9	..	CaO 0.16
8/16	60	4.6	17.6	..	H ₂ O 1.50

TABLE IV—HIGH CALCIUM LUMP LIME (BARRELS)

Date Analyzed (1915)	Days Exposed	Per cent Avail.	Total	CO ₂	H ₂ O	Per cent Available CaO Dry Basis	Complete Analysis before Exposure
6/17	0	94.9	98.4	0.5	1.7	96.7	SiO ₂ 0.20%
6/24	7	87.2	88.9	0.5	9.3	96.0	SiO ₂ 0.28%
7/2	15	85.1	87.1	1.0	10.4	94.5	CaO 95.58
7/17	30	82.4	83.8	1.1	13.7	94.3	MgO 1.01
8/1	45	81.0	83.8	1.2	14.6	94.6	CaO 0.16
8/16	60	73.0	78.1	1.8	19.4	90.8	H ₂ O 1.50

TABLE V—HIGH CALCIUM LUMP LIME (BOXES)

Date Analyzed (1915)	Days Exposed	Per cent Avail.	Total	CO ₂	H ₂ O	Per cent Available CaO Dry Basis	Complete Analysis before Exposure
6/17	0	95.6	96.2	0.2	1.6	97.2	SiO ₂ 0.20%
6/24	7	84.8	86.5	0.8	11.6	96.0	SiO ₂ 0.28%
7/2	15	81.1	83.1	1.0	13.6	93.9	CaO 96.17
7/17	30	76.2	79.4	1.7	18.5	90.3	MgO 1.01
8/1	45	68.0	72.0	2.4	21.4	86.6	CaO 0.16
8/16	60	64.7	70.3	3.1	22.7	83.6	H ₂ O 1.50

TABLE VI—HIGH CALCIUM LUMP LIME (BARRELS)

Date Analyzed (1915)	Days Exposed	Per cent Avail.	Total	CO ₂	H ₂ O	Per cent Available CaO Dry Basis	Complete Analysis before Exposure
6/17	0	94.9	98.4	0.5	1.7	96.7	SiO ₂ 0.20%
6/24	7	87.2	88.9	0.5	9.3	96.0	SiO ₂ 0.28%
7/2	15	85.1	87.1	1.0	10.4	94.5	CaO 95.58
7/17	30	82.4	83.8	1.1	13.7	94.3	MgO 1.01
8/1	45	81.0	83.8	1.2	14.6	94.6	CaO 0.16
8/16	60	73.0	78.1	1.8	19.4	90.8	H ₂ O 1.50

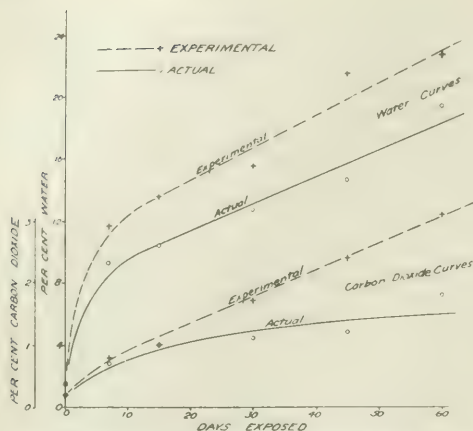


FIG. I—COMPARISON OF EXPERIMENTAL CONDITIONS WITH THOSE APPROACHING ACTUAL PRACTICE. ABSORPTION OF CARBON DIOXIDE AND WATER

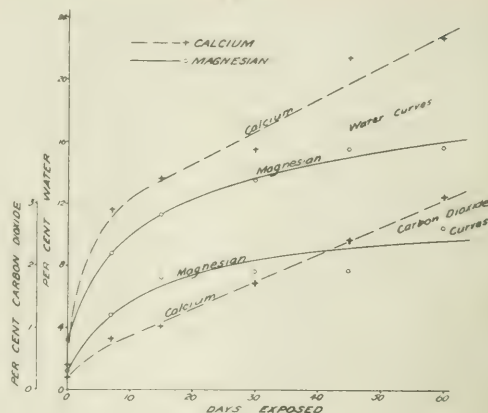


FIG. III—EFFECTS OF EXPOSURE ON HIGH CALCIUM AND MAGNESIAN LIMES. ABSORPTION OF CARBON DIOXIDE AND WATER

EXPOSURE OF A MAGNESIAN LUMP LIME—Samples of a magnesian lump ($\frac{3}{4}$ in. to 2 in. in size) lime were prepared by careful selection, placed in 6 in. \times 6 in. \times 6 in. boxes and exposed under the same conditions as the previous test with the results given in Table III.

EXPOSURE OF HIGH CALCIUM LUMP LIME UNDER WINTER AND SUMMER CONDITIONS—All the tests, except the one indicated in Table IV, were carried out in typical summer weather, while the present one had been carried out as a preliminary run during the previous winter, the only variable being the weather.

EXPOSURE OF A HIGH CALCIUM HYDRATED LIME—Three open boxes, 6 in. \times 6 in. \times 3 in., 6 in. \times 6 in. \times 6 in. and 6 in. \times 6 in. \times 9 in., the varying dimension being the depth, were filled with hydrate. After 20 days' exposure, the contents of the boxes were analyzed as indicated in Table V.

EXPOSURE OF A HIGH CALCIUM 10-MESH GROUND LIME—This test was merely a duplication of the previous test, using commercial 10-mesh ground lime such as is sold for agricultural purposes instead of the hydrate. The results are given in Table VI.

RESULTS

In order to discuss more conveniently the results

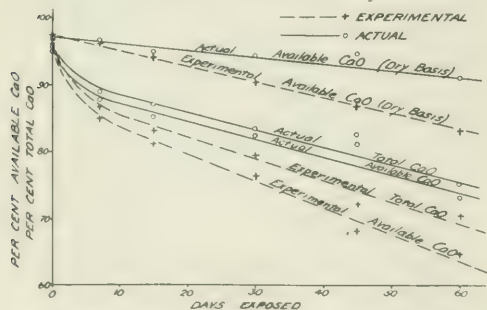


FIG. II—COMPARISON OF EXPERIMENTAL CONDITIONS WITH THOSE APPROACHING ACTUAL PRACTICE. DECREASE IN CALCIUM OXIDE CONTENT

obtained in the previous investigations, they have been expressed graphically. Days exposed are plotted as abscissae for all curves, while the factors affected by exposure are plotted as ordinates. It will be noticed that the best line representing average conditions misses quite a few of the experimental points. Most of these discrepancies can probably be explained as due to sampling and variation in the weather conditions of the different periods.

COMPARISON OF EXPERIMENTAL CONDITIONS WITH THOSE APPROACHING ACTUAL PRACTICE (Figs. I and II)—Owing to the greater surface exposed in the boxes in relation to their volume and the lumps of smaller size, the box samples indicate a greater deterioration than the barrel samples. The question arises as to a comparison between the barrels and commercial bulk lime shipments. The size of lumps is practically the same in both cases, but in actual shipments the ratio of the surface exposed to the air to the total volume is probably less than in the case of the barrels. Also the air does not have such free access to the lime under actual conditions as it had in the experimental tests. From these considerations, it is indicated that deterioration in commercial shipments is less than that indicated by the barrel samples. In the statement of final results (Figs. VI and VII), the data obtained from these barrel samples are used since these represent conditions more closely approaching actual practice than the box samples.

EFFECTS OF EXPOSURE ON HIGH CALCIUM AND MAGNESIAN LIMES (Fig. III)—The deterioration of magnesian limes in shipment has little importance in practice as these find their chief use in plastering and are usually barreled or made into hydrate. It is interesting, however, to compare the rates of absorption of carbon dioxide and water for high calcium and magnesian limes. As indicated, the absorption of water is less in the case of magnesian limes. The water is probably absorbed by the calcium oxide present and the magnesium oxide acts merely as a filler, since it has been shown that the magnesium in commercial hydrated mag-

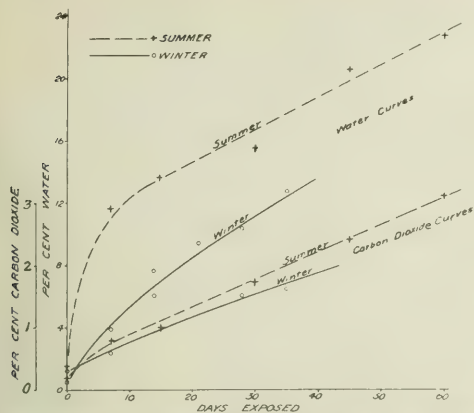


FIG. IV—EFFECTS OF EXPOSURE ON LIME IN WINTER AND IN SUMMER. ABSORPTION OF CARBON DIOXIDE AND WATER

nesian limes exists not as the hydrate but as magnesium oxide. The carbon dioxide increases at the start more rapidly with the magnesian lime than with the high calcium lime. Whether this is due to the greater porosity of the magnesian lime, as the high calcium lime was very dense, or to an inherent quality of magnesian limes, it cannot be stated. If this is a general characteristic of magnesian limes, it may throw some light on their superior plastering qualities.

EFFECTS OF EXPOSURE ON LIME IN WINTER AND IN SUMMER (Figs. IV and V)—It is commonly recognized among those who have to deal with lime that its deterioration is far more rapid in summer than in winter. This variation between the two seasons is shown quantitatively by the curves in the figures indicated. There is a very great difference in the absorption of water in summer and winter, but less difference in the absorption of carbon dioxide. These results would have been predicted from the fact that a far greater amount of water exists in the atmosphere in summer than in winter and that the carbon dioxide content is almost constant.

EFFECTS OF EXPOSURE ON GROUND LIME AND HYDRATED LIME—The analyses in Tables V and VI indicate that there is little difference in the rates of carbonation of ground lime and hydrated lime although the apparent effect of "air-slaking" is much more marked with ground lime because of hydration. The

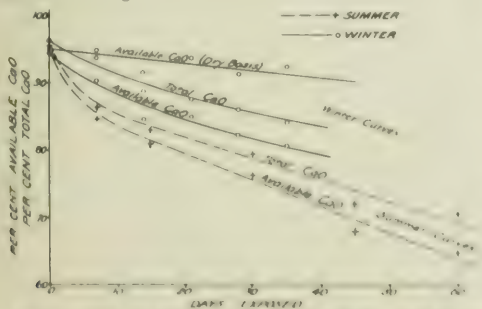


FIG. V—EFFECTS OF EXPOSURE ON LIME IN WINTER AND IN SUMMER. INCREASE IN CALCIUM OXIDE CONTENT

carbonation of hydrate is of little importance commercially as it is packed in tight bags. Ground lime is often sold in bulk and although the results obtained may not be applied directly because of the greater depth in actual practice, it is of interest to determine the approximate thickness of the layer affected by "air-slaking."

The depths of the boxes vary as 1 : 2 : 3. From the analyses in Table VI, the carbon dioxide absorbed varies as

$$(2.5-1.7) : (2.0-1.7) : 4.0-1.7$$

or as

$$0.8 : 1.2 : 2.3 = 1 : 1.5 : 2.9$$

These results show that carbonation in bulk ground lime will not penetrate to a greater depth than approximately 3 in. in 20 days of summer weather since the weight of carbon dioxide absorbed was almost the same in each box.

The foregoing conclusions evidently do not hold for hydration as the conditions are quite different. The absorption of water is so much greater that the top

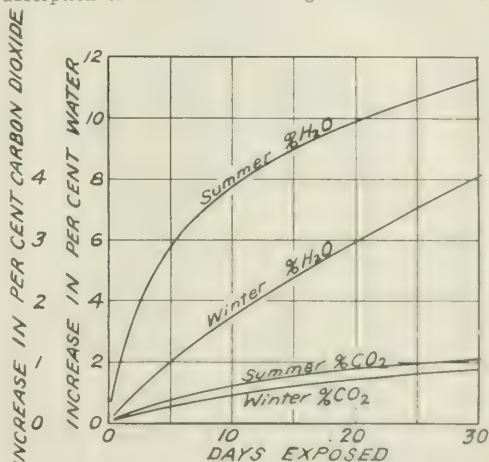


FIG. VI—ABSORPTION OF CARBON DIOXIDE AND WATER BY BULK LIME IN WINTER AND IN SUMMER

layer becomes completely hydrated, thus allowing any additional water to pass on to the lower part of the mass. The amount of carbon dioxide absorbed is comparatively small, so that only a thin layer is necessary to protect the remaining portion from carbonation.

The results obtained with hydrate likewise indicate that carbonation is very superficial.

CURVES FOR THE PREDICTION OF THE DEGRADATION OF HIGH CALCIUM RPL LIME (Figs. VI and VII) It is essential that some curves should represent actual conditions as far as possible. Therefore, the barrel tests, which approached the real conditions more nearly than the box tests, were made the basis of the curves. It must be realized that the predictions are only approximate, but they are of this nature and are likely to indicate some "air-slaking" about the right place. It should not be forgotten that changes in weather conditions will cause the curves to increase "air-slaking."

These tests were carried out in summer.

it became necessary to reduce the box tests carried out in winter to barrel conditions. This was done by assuming that the ratios of the ordinates of the barrel curves to the box curves, obtained in summer, would remain the same during the winter.

In the construction of the curves, the initial carbon dioxide, water and calcium oxide contents were taken as zero. This renders them more easily used; it then becomes necessary in order to determine the analysis after "air-slaking" only to add the water and carbon dioxide percentages from the curves to the corresponding initial percentages as found by analysis. Similarly, the calcium oxide decrease as found from the curves is subtracted from the initial calcium oxide content. Exposure in shipment is usually for a short time so the time of exposure is indicated only up to 30 days.

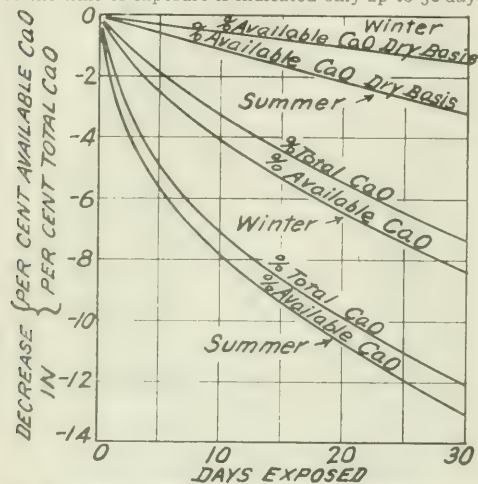


FIG. VII—EFFECT OF EXPOSURE ON CALCIUM OXIDE CONTENT OF BULK LIME IN WINTER AND IN SUMMER

In addition to the curves for total and available calcium oxide, curves giving the decrease in available calcium oxide on the dry basis are added. The calculation of analyses on the dry basis, *i. e.*, assuming the only loss in availability as being due to carbonation, is a method satisfactory to both the consumer and manufacturer of lime. The consumer pays only for the weight of lime as it leaves the lime plant when it contains practically no water. If it absorbs water on the road, it is merely converted into the hydrate, giving the same amount of available alkali. This slaking is of little consequence in many industries as the lime must be slaked before use. However, the carbonation represents a distinct loss, but as indicated on the curves calculated on the dry basis, there is a relatively small decrease in the available calcium oxide content due to this cause. Total calcium oxide, calculated on the dry basis, will show almost no decrease; the decrease in this case is simply due to the additional weight of the material in consequence of the absorption of the small amount of carbon dioxide.

BURKELEY LABORATORY
SOUTHERY CEMENT AND LIME COMPANY
MARTINSBURG, WEST VIRGINIA

STUDIES ON THE PHENOLDISULFONIC ACID METHOD FOR DETERMINING NITRATES IN SOILS¹

By CHARLES W. DAVIS

Received March 27, 1916

According to Tiemann^{18*} the estimation of no substance has so constantly occupied the attention of analytical chemists ("literally 'enchained' them") as the determination of nitric acid; and Gill¹² says, "No determination requires more care, or occasions more trouble in its execution, or is more unsatisfactory when finished, than the one in question."

Three general methods are used:

I—The Zinc-Iron Method.

II—The Tiemann-Schulze Method.

III—The Colorimetric Method.

The last two are direct methods. Other direct methods that have attracted attention are those of Schlessing-Reichardt,¹⁷ Crum-Lunge,¹⁸ and Marx-Trommsdorf.¹⁹ These methods are best suited only when relatively large amounts of nitrates are present, and in water analysis this would necessitate the evaporation of a large quantity of water.

The phenoldisulfonic acid method is another direct method that has received much attention from soil chemists and soil bacteriologists during the past ten years. It originated with Sprengel²⁰ in 1863, then for some time fell into disuse, but in 1885 it was revived by Grandval and Lajoux.²¹ Afterwards articles appeared by Fox,²² Johnson,²³ Lind,²⁴ Smith,²⁵ Bartram,²⁶ and Hazen and Clark.²⁷

Hazen and Clark²⁷ as well as the German chemists have criticized the method severely. On recommendation of the Association of the German Experiment Stations,²⁸ the Halle Station, after an investigation as to the most reliable method for the determination of nitrates in soils and fertilizers, selected the Zinc-Iron Reduction Method as being the most accurate.

SOURCES OF ERRORS MENTIONED BY VARIOUS INVESTIGATORS

Leeds,³² Fox,²² and Gill¹² have found losses of nitrates on the water bath. Chamot and Pratt⁴ report losses small on a water bath except when chlorides are present.

Many writers have found interference in determinations in the presence of organic matter due in part to the masking of the yellow tint, besides certain flocculents as carbon black, potash alum,³ aluminum cream, copper sulfate, etc., used to precipitate clay and organic matter occasions considerable loss in nitrates.

Gill¹² and Weston³³ found losses in the presence of carbonates, while Chamot and Pratt⁴ claim losses of nitrates insignificant except when the quantities of nitrates are low or the alkalinity of the solution very high.

Lipman and Sharp,³ and Kelly⁷ call attention to great losses in the determination due to presence of sulfates either in the solutions, or when sulfates as potash alum are used as a flocculent.

¹ Part of Thesis submitted in partial fulfillment of the requirement for the Degree of Doctor of Philosophy in Agronomy in the graduate school of the Iowa State College, 1916.

* Numbers refer to Bibliography at end of article.

Chlorides seem to be the greatest interfering salt as evidenced by the investigations of Gill,¹² Stewart and Greaves,¹⁰ and Chamot and Pratt.⁴

The latter investigators also point out the interference of chloroform when used in soil solution to prevent denitrification. They also show that the presence of iron produces a brown or red solution, thus affecting the desired yellow color of the nitrophenoldisulfonate.

REAGENTS AND APPARATUS

1—All reagents were tested for purity before using.

2—The standard nitrate solutions were made up according to the U. S. Bureau of Soils,¹ and used in the determination of nitrates in the first eight tables of results shown herein. The standard solution for the remainder of determinations was made after Hill's procedure.⁶

3—Throughout the whole work Chamot and Pratt's⁵ modified phenoldisulfonic acid reagent was used.

4—The color was always developed with a concentrated potassium hydroxide solution.

5—Colors were compared in the regulation comparing tubes. The Sargent-Kennicott colorimeter was used occasionally as a check on the work.

In obtaining results as shown in Tables XV and XVI, the writer used a colorimeter manufactured by Lenz and Naumann, New York.

Known amounts of nitrates were measured from standard potassium nitrate solution by means of pipettes.

EFFECT OF AMMONIA FUMES ON THE DETERMINATION

It was thought advisable to ascertain if ammonia fumes in the laboratory would affect the results in the evaporating process on the water bath. Shallow dishes containing ammonium hydroxide were placed in the hood. Here samples of known nitrate content were evaporated and compared with samples evaporated in the laboratory. The ammonia fumes did not affect the results. In a second experiment ammonium hydroxide was boiled in the hood with other samples, so that the fumes were given off profusely, and these samples were evaporated; nitrates were determined and compared with samples evaporated away from the presence of ammonia. In this second experiment no loss of nitrates was obtained.

EFFECT OF DELAY IN APPLICATION OF PHENOLDISULFONIC ACID AFTER EVAPORATION

A series of nitrate solutions was evaporated to dryness, and after a delay of 24, 48 and 72 hours, the phenoldisulfonic acid was added. The results showed that the delay in the application of the phenoldisulfonic acid had no effect whatever.

A second series was prepared and equal quantities of the acid were applied immediately after evaporation and left in contact unequal periods of time. Table I shows the results of this experiment:

TABLE I

Time in contact	10 min.	30 min.	1 hr.	24 hrs.
Nitrates Added (cc.)	0.004	0.004	0.004	0.004
Nitrates Found (cc.)	0.004	0.004	0.0035	0.0035

EFFECT OF LIGHT AND TIME ON COLOR MATERIAL

Three solutions were prepared and the color developed. No. 1 was read immediately. No. 2 was left on the laboratory desk for 24 hours. It was thus exposed to light for about 12 hours. No. 3 was placed in the dark room for 24 hours. From the results (Table II), we conclude that readings should be made without delay after the color is developed.

TABLE II

No.	TREATMENT	Mg. Nitrates	
		Added	Found
1.....	Immediate reading	0.0040	0.0040
2.....	Left on laboratory desk 24 hours	0.0040	0.0025
3.....	Left in dark room 24 hours	0.0040	0.0036

METHODS OF APPLYING THE ACID

The next experiment was planned for the purpose of finding the effect of method of applying the phenoldisulfonic acid to the dry residue in the nitrate determination. The acid was applied to the salt as follows: (1) without stirring; (2) while stirring with a glass rod; (3) while hot. No variation was found in the results.

EFFECT OF TEMPERATURE WHILE POTASSIUM HYDROXIDE IS BEING ADDED

At various times we observed that in the application of potassium hydroxide for the purpose of developing the color much heat was evolved and sometimes violent action occurred. A series of experiments was carried on to find the influence of temperature during the time the alkali was being added, with the results given in Table III.

TABLE III

No.	TREATMENT OF SOLUTION	Mg. Nitrates	
		Added	Found
1.....	Kept at room temperature	0.010	0.010
2.....	Heated by reaction	0.010	0.010
3.....	Heated to 80° C.	0.010	0.010
4.....	Heated to 100° C.	0.010	0.010
5.....	At freezing temperature (on ice)	0.010	0.0096

EFFECT OF CONCENTRATED SOLUTION WHEN POTASSIUM HYDROXIDE IS ADDED

After the application of phenoldisulfonic acid, when the salt is taken up with water, if the solution is highly concentrated, a precipitate is sometimes formed on the addition of KOH. This phenomenon suggested a series to find whether the concentration of the solution at this point affected the results. Table IV shows no variation in results whether the solution just before the addition of potassium hydroxide was dilute or concentrated.

TABLE IV

No.	SOLUTION	Mg. Nitrates	
		Added	Found
1.....	Concentrated	0.004	0.004
2.....	Concentrated	0.004	0.004
3.....	Dilute	0.004	0.004
4.....	Dilute	0.004	0.004

EFFECT OF VARIOUS SALTS

The writer carried on experiments to ascertain the effects of NaCl, Na₂SO₄, Na₂CO₃, and mixed alkali salts on the loss of nitrates. These results confirm in a general way the results of Liptman and Sharp¹¹ in experiments with these same salts.

EFFECT OF Na₂CO₃

Since Liptman¹¹ as well as the writer found no effect of sodium carbonate and potassium carbonate in

the order mentioned, the latter producing slight loss, if any, it was believed a weak acid with a strong base might not occasion any loss whatever. From 1 to 20 mg. of sodium acetate were used in a solution containing 0.025 mg., no loss of nitrates being noticed.

EFFECT OF VARYING AMOUNTS OF STANDARD NITRATE SOLUTION AND UNIFORM AMOUNTS OF PHENOL-DISULFONIC ACID

A series with a nitrate content from 0.0125 to 0.200 mg. was now analyzed using uniform amounts of phenoldisulfonic acid (2 cc.) throughout and compared with standard of 0.025 mg. having been treated with 2 cc. of phenoldisulfonic acid. The loss here with the sample lowest in nitrates was 4 per cent; the sample highest in nitrates lost 30 per cent. (See Table V.)

TABLE V—2 CC. PHENOLDISULFONIC ACID ADDED IN EACH CASE

Mg. Nitrates Added.....	0.0125	0.0250	0.0500	0.0750	0.1000	0.2000
Mg. Nitrates Found.....	0.0120	0.0250	0.0446	0.0625	0.0832	0.1388

EFFECTS OF VARYING AMOUNTS OF NITRATE WITH VARYING AMOUNTS OF PHENOLDISULFONIC ACID

It was then decided to increase the amount of phenoldisulfonic acid in proportion to the amount of nitrates used: 2 cc. of this acid were used for every 0.025 mg. of nitrate. In this way a greater per cent of nitrates was recovered from the artificial solution. Here the maximum loss was only 10 per cent as compared with a loss of 30 per cent in Table V.

TABLE VI

Cc. Disulfonic Acid	1	2	4	6	8	16
Mg. Nitrates Added.....	0.0125	0.0250	0.0500	0.0750	0.1000	0.2000
Mg. Nitrates Found.....	0.0125	0.0250	0.0500	0.0695	0.0892	0.1800

MEANS OF PREVENTING LOSS OF NITRATES BY THE PHENOLDISULFONIC ACID METHOD

The results of the last two experiments demonstrated the fact that when the nitrate solution approaches 100 parts per million, or more, the loss of nitrates is great even when there are no interfering salts present, such as chlorides, sulfates, etc. On further investigation the writer was convinced that much loss took place on the water bath as had been suggested by Lipman² and others.

Three things suggested dissociation of KNO_3 on the water bath: (1) Slight or no loss of nitrates when sodium carbonate was added before evaporation; (2) recovery of more nitrates in soil solution when CaO is used as a substitute for alum in precipitating the clay in a soil solution. Not only does the use of CaO prevent the loss occasioned by the SO_4 radical, as in the case when alum is used as a flocculent, but the fact that CaO is an alkali prevents the loss of nitrates when the KNO_3 dissociates by uniting and forming $\text{Ca}(\text{NO}_3)_2$. An excess of alkali prevents the formation of nitric acid; (3) a bit of blue litmus paper was placed in the KNO_3 solution and it was noticed to have turned red just before the solution became dry. This was the first clue that furnished a solution for the prevention of loss of nitrates on the water bath.

EFFECT OF ADDING AMMONIA TO THE POTASSIUM NITRATE SOLUTION BEFORE EVAPORATION

Since it had already been found that ammonia fumes did not affect the loss or gain of nitrates, a series

was run in which each sample was kept ammoniacal during evaporation. The results were as anticipated as will be seen in Table VII.

TABLE VII

Mg. Nitrates Added.....	0.0125	0.0250	0.0500	0.0750	0.1000
Mg. Nitrates Found.....	0.0125	0.0250	0.0500	0.0760	0.1010

In the last experiment the five samples were compared to a standard containing 0.025 mg. of KNO_3 , to which no ammonia had been added before evaporation as in case with the samples above.

EFFECT OF POTASH ALUM $[\text{K}_2\text{Al}_2(\text{SO}_4)_4]$

It was desired, if possible, to prevent loss occasioned by the use of potash alum as a flocculent in preparing the soil solutions for analysis.

Lipman and Sharp,² in speaking of the phenoldisulfonic acid method in determining nitrates, say: "So that while we deem it unsafe in the presence of considerable quantities of salts containing chlorides and sulfates to determine nitrates by the phenoldisulfonic acid method, and would therefore recommend the Street modification of the Ulsch method³⁵ in such cases, it is likewise clear that many of the nitrate determinations made in soil laboratories, as is especially the case in soil bacteriological work, would not be interfered with by salts. In such cases the method can be safely depended upon if potash alum, aluminum cream and bone-black are not used to coagulate the clay and organic matter, since they have been found in the researches above described to be productive of very serious errors."

Since ammonia is highly volatile, potassium hydroxide was substituted in keeping the solution alkaline on the water bath. This prevented the loss of nitrates on the water bath, so that we were able to recover all nitrates when the samples contained from 5 to 150 mg. of potash alum before evaporation. Lipman and Sharp,² however, lost as high as 38 per cent of nitrates when they used the same amounts of potash alum without the addition of alkali. Table VIII shows a comparison of the writer's and Lipman and Sharp's results.

TABLE VIII

Mg. $\text{K}_2\text{Al}_2(\text{SO}_4)_4$ ADDED		Mg. NITRATES ADDED		Mg. NITRATES FOUND	
Davis	Lipman	Davis	Lipman	Davis	Lipman
	5.0		0.050		0.040
12.5	12.5	0.025	0.050	0.025	0.036
25.0	25.0	0.025	0.050	0.025	0.033
50.0	50.0	0.025	0.050	0.025	0.031
100.0	100.0	0.025	0.050	0.025	0.034
150.0	150.0	0.025	0.050	0.025	0.040

In the previous experiment we have shown conclusively that potash alum may be used as a flocculent in preparing the soil solution without incurring any loss of nitrates; then, since potash alum is undoubtedly the best flocculent in precipitating clay and organic matter, soil chemists and soil bacteriologists may safely continue its use as a flocculent, provided the solution is kept alkaline on the water bath.

EFFECT OF POTASSIUM CHLORIDE BY NEW METHOD

We now attempted to recover all nitrates in the presence of the chlorine radical. A series was prepared using from 1 to 20 mg. KCl and evaporated down with excess of potassium hydroxide as in the previous experiment. Here equal amounts of phenol-

disulfonic acid were applied, but rather violent action took place. Hydrochloric acid fumes were noticeable. The results as shown in Table IX were startling.

	TABLE IX			
Mg. KCl Added	1	5	10	20
Mg. Nitrates Added.....	0.025	0.025	0.025	0.025
Mg. Nitrates Found.....	0.0125	0.100	0.0050	0.0035

This loss of nitrates, of course, did not take place on the water bath, but at the time the phenoldisulfonic acid was added. There was a noticeably large residue of potassium salts since potassium hydroxide had been added to keep the solution alkaline and potassium chloride had been added to the series. This was responsible for the violent action, thus liberating much hydrochloric acid which in turn brought about losses of nitrates at this point.

EFFECT OF $\text{Ca}(\text{OH})_2$ IN PREVENTING THE LOSS OF NITRATES IN THE PRESENCE OF CHLORIDES AT THE POINT WHEN THE PHENOLDISULFONIC ACID IS APPLIED

To avoid the violent action when phenoldisulfonic acid is applied it was decided to substitute saturated calcium hydroxide solution for potassium hydroxide before evaporation. Potassium chloride was added in amounts as before. When the solutions went to dryness the residues were found to be small, and we hoped the difficulty had been overcome, but we were much disappointed as the results in Table X will show.

	TABLE X			
Mg. KCl Added	1	5	10	20
Mg. Nitrates Added.....	0.025	0.025	0.025	0.025
Mg. Nitrates Found.....	0.0250	0.0220	0.0195	0.0140

Here with 20 mg. of KCl we obtained a loss of 44 per cent. This was better than in the previous experiment, yet the loss was still too great. In the last experiment the chemical action was slight, but HCl fumes were still noticeable when the acid was applied.

Another trial was carried out as previously, except that the phenoldisulfonic acid was added, slowly, drop by drop, in an effort to reduce the action. The results were as follows:

	TABLE XI			
Mg. KCl Added	1	5	10	20
Mg. Nitrates Added.....	0.025	0.025	0.025	0.025
Mg. Nitrates Found.....	0.023	0.023	0.019	0.014

Still another trial was made. Nos. 1, 2, 3, and the standard were treated as before, i. e., 4 cc. of phenoldisulfonic acid were applied to each, but in No. 4 an excess of phenoldisulfonic acid was used (about 12 cc.), and instead of adding the acid slowly it was flooded over the dry residue quickly. The results were as follows:

	TABLE XII			
No.	1	2	3	4
Mg. KCl Added	1	5	10	20
Mg. Nitrates Added.....	0.025	0.025	0.025	0.025
Mg. Nitrates Found.....	0.0225	0.0220	0.0200	0.0250

The treatment of No. 4 in Table XII shows means of preventing loss of nitrates at the time of application of phenoldisulfonic acid. We now decided to apply treatment of No. 4 in the above table to a whole series. This was done and gave results free from loss of nitrates.

EFFECT OF SODIUM SULFATE BY NEW METHOD

Kelly⁷ made a study of the effects of sulfates on the determination of nitrates, using Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, and CaSO_4 . Since his greatest loss occurred in the presence of Na_2SO_4 we carried out an experiment with this same salt by our new method. A comparison of our results with those of Kelly's is given in Table XIII below.

		TABLE XIII			
		Mg. Na_2SO_4 Added		Mg. Nitrates Found	
Davis	Kelly	Davis	Kelly	Davis	Kelly
1	1	0.025	0.275	0.025	0.275
5	5	0.025	0.275	0.025	0.265
10	10	0.025	0.275	0.025	0.225
20	20	0.025	0.275	0.025	0.180
..	40	...	0.275	...	0.140

The writer recovered all nitrates, while Kelly lost from 0 to 32 per cent when 20 mg., and 48 per cent when 40 mg. of sodium sulfate were used.

BAER'S METHOD—COPPER SULFATE AS FLOCCULENT

Baer¹⁴ used copper sulfate as a flocculent in preparing soil solutions for nitrate determinations. After the solution was clarified with copper sulfate, aliquot parts were measured out into Erlenmeyer flasks and the copper removed by adding one gram of manganese oxide. The flasks were stoppered and gently warmed, and then filtered and washed, the filtrate was evaporated to dryness and the nitrates determined by the ordinary method. While CuSO_4 is an excellent flocculent the writer has never been able to recover all nitrates even by the modified method. Since potash alum can be used as a flocculent and all nitrates recovered regardless of what other salts may be present, it seems that there is no use of attempting to use copper sulfate since it is necessary to remove the copper before the determination can be made.

APPLYING NEW METHOD TO THE DETERMINATION OF NITRATES IN SOILS

As lime, copper sulfate and alum are considered good flocculents, a comparison of these was made by the new method. Three 50-gram samples were prepared and placed in Mason jars with 240 cc. of distilled water. Ten cc. of normal solutions of CaO , CuSO_4 , and $\text{K}_2\text{Al}_2(\text{SO}_4)_4$ were added, respectively. The samples were placed in a shaker for 30 minutes and the determinations made by the modified method.

		TABLE XIV	
		FLOCCULENT USED	Mg. Nitrates Found in Soil Solution
No.	1	CaO	0.1144
2	2	CuSO_4	0.113
3	3	$\text{K}_2\text{Al}_2(\text{SO}_4)_4$	0.1114

Another sample of soil was taken and lime and alum were used as flocculents. The acid solution with the alum was tried both by new and old method.

		TABLE XV	
		FLOCCULENT USED	Mg. Nitrates Found in Soil Solution
No.	1	CaO	0.1144
2	2	$\text{K}_2\text{Al}_2(\text{SO}_4)_4$ (New Method)	0.1144
3	3	$\text{K}_2\text{Al}_2(\text{SO}_4)_4$ (Old Method)	0.1144

It was now suggested that a comparison of the old colorimetric and modified colorimetric method be tried on several soils of varied nitrate content. Alum was used as a flocculent in each case. Samples of soil were taken from the following plots: Corn, fallow, oat stubble and alfalfa. The results are given in Table XVI.

TABLE XVI

No.	Kind of Soil	Mg. Nitrates in 100 Grams of Soil	
		Old	New
1.....	Corn	1.1639	1.3403
2.....	Fallow	0.8798	1.1639
3.....	Oats	1.1060	1.1245
4.....	Alfalfa	2.0382	2.0382

You will observe that by the modified method greater amounts of nitrates were found with each soil except in case of that from the alfalfa plot; here the results were the same. Perhaps a heavy application of lime to the soil before seeding the alfalfa rendered this soil strongly alkaline and the presence of the alkali in the soil prevented loss of nitrates on the water bath.

Since in the last experiment the highest amount of nitrates found in the soil was over 2 mg., we tested the reproducibility of the method in artificial solutions of known nitrate content, using samples from 0.55 mg. to over 2 mg. All nitrates were recovered.

Many investigators have asserted that the colorimetric method is unreliable when large amounts of nitrates are to be determined. This objection prompted an experiment to find if as much as 4 mg. of nitrate could be recovered in artificial solutions. All nitrates were recovered, thus showing the reproducibility of results.

APPLICATION OF THE MODIFIED PHENOLDISULFONIC ACID METHOD TO SOIL BACTERIOLOGICAL WORK

Frequently large amounts of nitrates are obtained in the nitrification experiments in soil bacteriology. We decided to test the applicability of the method to work of this kind.

NITRIFICATION EXPERIMENT

Soil samples were taken from the soil plots of the Iowa Experiment Station. The plots were as follows:

Soil No. 101 from timothy sod. The timothy had just been cut.

Soil No. 102, peat plot. Two and eight-tenths tons of peat had just been added and kept fallow.

Soil No. 107, check plot which had also been kept fallow.

Two hundred-gram samples of each soil were placed in tumblers in duplicate: 200 mg. of $(\text{NH}_4)_2\text{SO}_4$ were dissolved in 60 cc. water and added to each tumbler. The incubation was carried on for three weeks at room temperature. The tumblers were weighed every six days, and the water lost by evaporation was restored. At the end of three weeks the nitrates were determined as follows: The samples were placed in shaker bottles with 800 cc. of water. Alum was used as the flocculent. After the samples had been shaken 30 minutes, 25-cc. portions, in duplicate, were evaporated to dryness with 15 cc. of saturated $\text{Ca}(\text{OH})_2$ solution. The samples were treated with 5 cc. portions of phenoldisulfonic acid and compared with standard. Table XVII shows the large amounts of nitrate found.

That large amounts of nitrates can be determined by the phenoldisulfonic acid method is here demonstrated. In Table XVII from 6 to 15 times as much

TABLE XVII

Soil No.	Plot	Mg. N Found as Nitrate per 100 g.	
		Old	New
101.....	Timothy	62.774	58.250
102.....	Peat	66.086	57.564
107.....	Check	35.786	29.016

nitrate was determined as in the preceding experiments where known amounts of nitrates were used. Should soils contain larger amounts of nitrates than those used in Table XVII one need only to reduce the amount of aliquot part of soil solution taken for the determination.

SUMMARY

I—STUDIES ON THE OLD METHOD

1—Ammonia fumes in the laboratory do not affect the result in the determination of nitrates by the phenoldisulfonic acid method.

2—Light affects the color material and readings should be made without delay.

3—Applying phenoldisulfonic acid without stirring, stirring with a rod, or applying while hot shows no difference in results.

4—The temperature of the solution at the time alkali is added to develop color shows no variation in results except at freezing temperature when a loss of 4 parts per million is found in a 100-part-per-million solution.

5—In checking up Lipman and Sharp's work, "Studies on the Phenoldisulfonic Acid Method for Determining Nitrates in Soils," we found the loss of nitrates occasioned by the addition of various salts to correspond with the results of these investigators, the maximum loss being caused by the chlorine radical, and decreasing with sulfates and carbonates—the latter producing no loss. The addition of a weak acid (sodium acetate) produced no loss of nitrates whatever.

6—Potassium chloride added just before and just after the developing of the color by potassium hydroxide produced no loss of nitrates.

7—When uniform amounts of phenoldisulfonic acid (2 cc.) were used the maximum loss of nitrates was 30 per cent; when proportional amounts of phenoldisulfonic acid were used (i. e., 2 cc. for each 0.025 mg.), the maximum loss was reduced to 10 per cent.

II—PREVENTING LOSS OF NITRATES BY A MODIFIED METHOD

1—Loss of nitrates was found to take place on the water bath, and this loss was prevented by keeping the solution alkaline during the process of evaporation.

2—The addition of two drops of HCl in a solution containing 25 parts per million of nitrates caused a loss of all nitrates.

3—By the modified method we were able to prevent the loss of nitrates in the presence of chlorides, sulfates and carbonates.

4—When chlorides were present, a loss of nitrates was found to take place on the addition of the phenoldisulfonic acid. This loss was overcome by evaporating the solution to dryness with excess of $\text{Ca}(\text{OH})_2$,

and flooding an excess of phenoldisulfonic acid quickly over the salt.

5—All nitrates in a soil solution can be recovered regardless of the salts present therein.

6—Potash alum may be used as a flocculent in preparing the soil solution without producing a loss of nitrates. By the old method the loss of nitrates in the presence of certain salts was often as high as 50 per cent.

7—Since potash alum is an excellent flocculent, soil chemists and soil bacteriologists need not hesitate to employ its use, provided they use the modified phenoldisulfonic acid method.

BIBLIOGRAPHY

- ¹ Schreiner and Failyer, "Colorimetric, Turbidity and Titration Methods Used in Soil Investigations," Bureau of Soils, U. S. Dept. Agri., *Bull.* **31**.
- ² C. B. Lipman and L. T. Sharp, "Studies on the Phenoldisulfonic Acid Method for Determining Nitrates in Soils," *Univ. Cal. Pub. in Agr. Sci.*, Vol. 4, No. 2.
- ³ E. M. Chamot and D. S. Pratt, "A Study of the Phenoldisulfonic Acid Method for the Determination of Nitrates in Water—The Composition of the Yellow Compound," *Jour. Am. Chem. Soc.*, Vol. **33**, pp. 630-637.
- ⁴ E. M. Chamot, D. S. Pratt and H. W. Redfield, "A Study on the Phenoldisulfonic Acid Method for the Determination of Nitrates in Water—the Chief Sources of Error in the Method," *Jour. Am. Chem. Soc.*, Vol. **33**, pp. 366-381.
- ⁵ E. M. Chamot, D. S. Pratt and H. W. Redfield, "A Study of the Phenoldisulfonic Acid Method for the Determination of Nitrates in Water—A Modified Phenoldisulfonic Acid Method," *Ibid.*, Vol. **33**, pp. 381-384.
- ⁶ H. H. Hill, "The Determination of Nitrates in Soil and Soil Extracts," *Annual Report of the Va. Expt. Sta.*, **1911-12**, p. 133.
- ⁷ W. P. Kelly, "The Effects of Sulfates on the Determination of Nitrates," *Jour. Am. Chem. Soc.*, **35** (1913), 775.
- ⁸ Robert Stewart, "The Occurrence of Potassium Nitrate in Western America," *Jour. Am. Chem. Soc.*, **33** (1911), 1952.
- ⁹ R. Stewart and J. E. Greaves, "The Influence of Chlorine on the Determination of Nitrates by the Phenoldisulfonic Acid Method," *Jour. Am. Chem. Soc.*, **35** (1913), 579.
- ¹⁰ R. Stewart and J. E. Greaves, "The Influence of Chlorine upon the Determination of Nitric Nitrogen," *Ibid.*, **33** (1910), 756.
- ¹¹ E. M. Chamot and D. S. Pratt, "A Study of the Phenoldisulfonic Acid Method for the Determination of Nitrates in Water—The Composition of the Reagent and the Reaction Product," *Jour. Am. Chem. Soc.*, **31** (1909), 922.
- ¹² A. H. Gill, "On the Determination of Nitrates in Potable Water," *Jour. Am. Chem. Soc.*, **16** (1894), 122.
- ¹³ King and Whitson, *Wis. Agri. Exp. Sta. Bull.* **85** and **93**.
- ¹⁴ Baer, Thesis (unpublished) for M.S. in Agriculture, Univ. of Wisconsin (1914).
- ¹⁵ Tiemann-Gaertner "Wasseranalyse," 3rd Ed., p. 168.
- ¹⁶ Schulze-Tiemann, *Ber. d. chem. Ges.*, **6**, 1041.
- ¹⁷ Schlössing-Reichardt, *Z. anal. Chem.*, **9**, p. 24.
- ¹⁸ Crum-Lunge, *Phil. Mag.*, [3] **30**, 426.
- ¹⁹ Marx-Trommsdorff, *Z. anal. Chem.*, **9**, 171.
- ²⁰ Sprengel, *Fogg. Ann.*, **121**, 188.
- ²¹ Grandval and Lajoux, *Compt. rend.*, **10**, 1, 62.
- ²² Fox, *Tech. Quart.*, **1**, 1.
- ²³ Johnson, *Chem. News*, **61**, 15.
- ²⁴ Lind, *Chem. News*, **58**, 1, 15, 28.
- ²⁵ Smith, *Analyst*, **10**, 197.
- ²⁶ Hartman, *Jour. Frank Inst.*, March 17, 1891.
- ²⁷ Hansen and Clark, *J. Anal. Appl. Chem.*, **5**, 1.
- ²⁸ *Exp. Sta. Record*, **5**, 401.
- ²⁹ Fox, *Tech. Quart.*, **1**, 54.
- ³⁰ Andrews, *Jour. Am. Chem. Soc.*, **26**, 388.
- ³¹ Montferrat, *Gen. chim. ind.*, **32**, 1, 87, 1902.
- ³² Leeds, *Am. Jour. Sci.*, [4] **7**, 197.
- ³³ Weston, *Lab. Univ. of Ill.*, 1909.
- ³⁴ Merelle, *Am. Chem. Anal.*, **14** (1909), 303.
- ³⁵ Uebel, *New Jersey Expt. Sta. Rept.*, **1892**, 188, 193.

A NOTE ON THE DETECTION AND ESTIMATION OF SMALL AMOUNTS OF METHYL ALCOHOL

By ELIAS ELOVSE

Received January 24, 1917

In applying the Denigès¹ test for methyl alcohol to its colorimetric estimation, Simmonds² recommends that the solution be always made up to contain 10 per cent³ ethyl alcohol. In studying this method with the view of applying it to the detection and estimation of methyl alcohol vapor in air it was found, however, that the test can be made more sensitive by reducing the proportion of ethyl alcohol from 10 to 0.5 per cent. That this is so may be seen from the following experiment:⁴ To 2.5 cc. of an aqueous solution of methyl alcohol containing 0.3 mg. methyl alcohol (No. 1), in a 50 cc. Erlenmeyer flask, there were added 2.5 cc. of a one per cent aqueous solution of ethyl alcohol. To another equal volume of this methyl alcohol solution (No. 2), there were added 2.5 cc. of a 20 per cent aqueous solution of ethyl alcohol. Each solution was then treated with 2.5 cc. of a 2 per cent potassium permanganate solution and 0.2 cc. concentrated sulfuric acid and allowed to stand 3 minutes. The excess of the permanganate was then reduced by mixing each solution with 0.7 cc. of a 9.6 per cent⁵ oxalic acid solution. Each solution was then further acidified by mixing with one cc. of concentrated sulfuric acid, allowed to cool to room temperature, and finally mixed with 5 cc. of Schiff's reagent. After standing 40 minutes, they were compared in the narrow form 50 cc. Nessler tubes and it was found that whereas No. 1 had developed a very decided color, No. 2 was almost completely colorless in comparison. After standing an hour, this difference was even more pronounced, the color

¹ *Compt. rend.*, **150** (1910), 832.² *Analyst*, **37** (1912), 16.³ All percentages of ethyl alcohol mentioned in this paper refer to percentage by volume.⁴ The details of this experiment also give the essentials of the procedure which was finally adopted. To apply this for estimating the methyl alcohol in its aqueous solution, such as may be obtained by suitably passing through water a definite volume of air carrying methyl alcohol vapors, proceed as follows: Ascertain by a preliminary experiment the approximate amount of methyl alcohol in the solution. If this shows that 5 cc. of it contain more than 1 mg. of methyl alcohol, dilute so as to bring it within this limit. Mix 4.5 cc. of this diluted solution with 0.5 cc. of 5 per cent ethyl alcohol. Similarly prepare several 5 cc. portions of methyl alcohol solutions by diluting the proper amounts of a 0.1 per cent (0.1 g. to 100 cc.) aqueous solution of methyl alcohol to 4.5 cc. with water and then adding 0.5 cc. of 5 per cent ethyl alcohol to each. These standard methyl alcohol solutions are made to vary by 0.1 mg. methyl alcohol and the limits are chosen so as to bring the unknown within their range. The unknown and the standards are then subjected exactly alike, preferably in 50 cc. Erlenmeyer flasks, to the permanganate treatment and the subsequent mixing with Schiff's reagent as described above. The solutions are finally transferred into the narrow form 50 cc. Nessler tubes and the resulting colors are compared after the solutions have stood 40 minutes.⁵ Simmonds used 0.8 cc. of the oxalic acid solution but this amount was found insufficient to reduce readily the excess permanganate when the proportion of ethyl alcohol was reduced to 0.5 per cent and hence 0.7 cc. was used in each case in order to make them exactly comparable. That this slight difference in the amount of oxalic acid used was not an important factor was proven by making a third comparison in which the two cases differed only in the respect, why there was no appreciable difference in the result.⁶ This strength was used in order to demonstrate that a very small amount of a 10 per cent solution of the reagent was sufficient to give a decided color and for the purpose of making the comparison of the colors of the unknown with the standard more accurate. It was found, however, that the color of the standard was not affected by the use of a larger amount of the reagent.

of No. 1 having increased while No. 2 still remained almost completely colorless in comparison.

According to Simmonds, with "properly sensitive" Schiff's reagent 0.3 mg. of methyl alcohol in 5 cc. can be detected but the best depths of color for comparison are obtained when the 5 cc. taken for the test contain from 1 to 4 mg. The standards for the colorimetric comparisons are made to vary by whole units of a milligram, containing 1, 2, 3, etc., mg. of methyl alcohol, respectively. By reducing the proportion of ethyl alcohol from 10 to 0.5 per cent, however, and applying the test as outlined above, even as little as 0.1 mg. of methyl alcohol in 5 cc. showed a coloration on standing 40 minutes.¹ A suitable series of standards for the colorimetric comparisons may, therefore, be obtained by varying the amounts of methyl alcohol in fractions of a milligram as 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 mg., respectively.

PREPARATION OF THE REAGENT

As has already been indicated above, Simmonds refers to a "properly sensitive" Schiff's reagent. He does not, however, say anything descriptive about it, either as to its composition, mode of preparation or keeping qualities. According to Schaffer,² the reagent should be prepared from fuchsine and sulfur dioxide, using the proportion of 0.5 g. of the former to 1 g. of the latter in 400 cc. When more than 1 g. of SO₂ was added to 0.5 g. of fuchsine, Schaffer found the reagent valueless after standing 2 days; but when prepared in the above proportion, he found it to keep well for 10 days, although he recommends not to use a solution over 7 days' old. In this connection, it was thought that probably an improvement in the preparation of this reagent could be introduced by substituting an equivalent amount of anhydrous sodium sulfite for the sulfur dioxide. The advantage in such a change is apparent, since it enables one to weigh out directly the amount required whereas with the sulfur dioxide it probably would be necessary to prepare first an aqueous solution of it, determine its strength, and then calculate how much of it would be required in order to have the proper proportion of SO₂ to fuchsine. As a matter of fact, Denigès in his communication³ refers to the variety of procedures which have been given for the preparation of Schiff's reagent and then states the one he adopted which calls for a certain volume of a sodium bisulfite solution of a certain degree Baumé. Since, however, sulfite in solution is not very stable while the anhydrous sodium sulfite is quite stable⁴ even when kept under ordinary conditions, it appears preferable to base the formula for the fuchsine bisulfite (Schiff's) reagent on the latter rather than on the former. The following reagent was found to give satisfactory re-

sults and it appears to be at least as good, if not better, in keeping qualities¹ than the reagent in the preparation of which sulfur dioxide was used as recommended by Schaffer: 0.2 g. finely powdered fuchsine² dissolved in about 120 cc. hot water and cooled to room temperature; 2.0 g. anhydrous sodium sulfite³ dissolved in about 20 cc. water and added to the fuchsine solution; then add 2.0 cc. HCl (sp. gr. 1.19) and dilute to 200 cc. with water. After standing for about an hour, this solution is ready for use as a reagent for formaldehyde or methyl alcohol by the procedure referred to above.

EFFECT OF TEMPERATURE

Since there is a rise in temperature when the solution is mixed with the concentrated sulfuric acid, it was thought desirable to determine whether or not this rise in temperature affects the color produced on mixing with the fuchsine bisulfite reagent. The following experiment was, therefore, carried out: Two 5 cc. portions of an aqueous solution of methyl alcohol, each containing 0.3 mg. of methyl alcohol and 0.5 per cent of ethyl alcohol, were treated by the permanganate procedure referred to above.⁴ After mixing with the 1 cc. concentrated sulfuric acid, No. 1 was allowed to cool to room temperature before it was treated with the 5 cc. of fuchsine bisulfite reagent while No. 2 received the fuchsine bisulfite immediately after the solution had been mixed with the sulfuric acid. After both mixtures had stood 40 minutes, the resulting colors were compared. It was found that they were not alike but that the one (No. 2) which was treated with the reagent immediately after the mixing with the sulfuric acid had a deeper color. It appears, therefore, that when a quantitative result is desired the solutions to be compared should all have the same temperature before the fuchsine bisulfite reagent is added. In most cases this can probably be more advantageously attained by allowing all the solutions to cool to room temperature after the final mixing with the concentrated sulfuric acid.

EFFECT OF THE PRESENCE OF FORMALDEHYDE

According to Simmonds, when the solution to be examined for methyl alcohol also contains formaldehyde, "its effect must be determined and allowed for." From this brief and unexplained statement one might get the impression that all that is necessary is to determine the effect of the formaldehyde on the reagent previous to the oxidation of the methyl alcohol to formaldehyde and then allow for this by subtracting the amount of formaldehyde found before the oxidation from that found after the oxidation. Such a procedure, however, would lead to erroneous results, since it appears that the oxidation of the methyl alcohol to formaldehyde in the procedure outlined above is not quantitative but that some of the formaldehyde

¹ In working with these smaller quantities of methyl alcohol, the color develops more slowly, so that while 40 minutes was sufficient to show a coloration in comparison with the control even when dealing with only 0.1 mg. in 5 cc., an hour or even two hours should be allowed for the color to develop when the problem is the detection of methyl alcohol, since under these circumstances it is, of course, desirable to obtain a fairly intense coloration.

² U. S. Naval Medical Bull., 6 (1912), 392.

³ Compt. rend., 150 (1910), 830.

⁴ Elvove, Am. J. Pharm., 82 (1910), 211.

¹ A fuchsine bisulfite reagent prepared as here described, which had stood in a closed bottle for about six weeks, was found at the end of that time to be as useful a reagent for formaldehyde as one which had been freshly prepared.

² The fuchsine used had the label of G. Grübler & Co., Leipzig.

³ Commercial anhydrous sodium sulfite which complies with the requirements of the U. S. Pharmacopoeia may be used for this purpose.

⁴ See details of experiment at beginning of article and also the accompanying foot-note.

is still further oxidized and does not show up in the final reaction with the fuchsin bisulfite reagent. In the presence of formaldehyde, therefore, it appears necessary to proceed somewhat as follows: Determine the amount of formaldehyde in the solution colorimetrically by means of the fuchsin bisulfite reagent and a suitable series of standards containing known amounts of formaldehyde. Then make up the methyl alcohol standards so that they will also contain formaldehyde in the same concentration as that in the solution to be examined. After this has been done, the procedure referred to above for estimating the methyl alcohol may be followed and the figures for methyl alcohol obtained directly by comparison with these modified standards.

HYGIENIC LABORATORY, U. S. PUBLIC HEALTH SERVICE
WASHINGTON, D. C.

RELATION OF THE FAT IN MILK TO THE SOLIDS-NOT-FAT

By LUCIUS P. BROWN AND CLARENCE V. EKROTH
Received December 1, 1916

In the year 1910 the New York State standard for the chemical composition of milk was placed by the Legislature at its present figures, to wit: 3 per cent fat and 11.5 per cent total solids. No standard for solids-not-fat was mixed.

In making municipal standards the City of New York was empowered under the law to enact additional legislation but could enact no legislation conflicting with that of the State. In endeavoring to secure a good milk supply for the city and, at the same time, to make figures which would be useful in the detection of adulteration, the only additional legislation which the city could enact was to set a standard for solids-not-fat, which was accordingly placed at the difference between the State's standards for fat and total solids, namely 8.5 per cent. When a rigid enforcement of this standard was attempted it was objected by dealers that the standard was an impossible one and that the cattle in the city's milk shed could not supply it. An investigation was, therefore, set on foot to determine whether these claims were justified. In the course of this some very interesting facts developed.

In looking into the experiences of the several states as (presumably) set forth in legislation, it developed that apparently the standards for the different states had been made entirely without system. For instance, one state requires a minimum of 12 per cent total solids, but only 2.5 per cent of this need be fat. Whether any normal cow could be found in that state (or anywhere else) giving milk containing 9.5 per cent solids-not-fat and 2.5 per cent butter-fat is not only open to at least a reasonable doubt but it is quite certain that no unadulterated herd milk would even approach such figures. Another state requires 9.75 per cent solids-not-fat. We venture to say that a literal enforcement of this standard would leave the state without a milk supply.

The legal standards furnishing no help, nothing re-

mained except to consult actual analytical figures. We were able to obtain the figures of herd milk and of that of a large number of individual cows of known purity in papers by Lythgoe¹ and Sherman² and from our own work. The results of all three of these sources, about 1,600 samples, were separately plotted. Using the fats as ordinates and the solids-not-fat as abscissae, curves of the same general shape but on different portions of the chart were obtained. The making of a zone with the extreme curves as boundaries suggested itself to Mr. Ekroth, giving the interior zone bounded by the lines *K-K* and *P-P* as shown in Fig. 1 herewith.

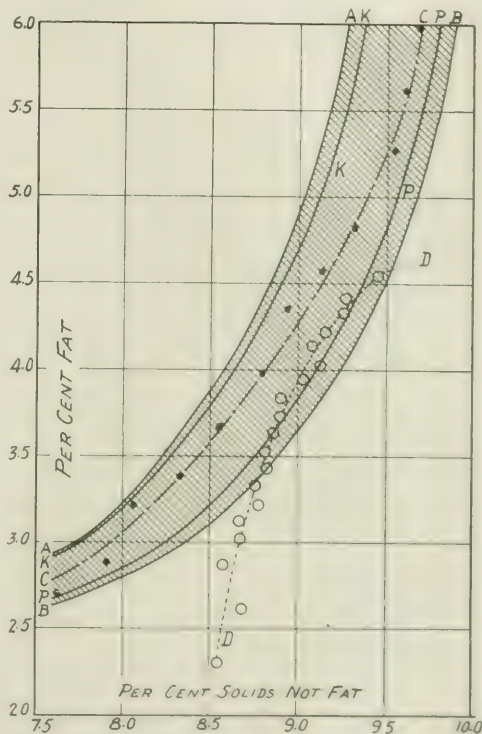


FIG. 1

This seemed promising but it was recognized that with such a small number of samples the influence of the many factors of variation in the composition of the milk might not be eliminated, these factors being: difference in breeds, the season of the year, feeding practice in different sections of the country and in different countries, etc. The available literature furnished a large number of analyses of milk, the sources drawn upon being Richmond, Leach, Haecker, Woodward and Lee, and others. Altogether the figures from over 200,000 samples, including approximately 40,000 New York City samples (unpublished), were used. We prepared the zone diagram in which

¹ Lythgoe, *Trans. Roy. Soc. Edinb.*, 5, 171 (1871), 88.
² Sherman, *Trans. Roy. Soc. Edinb.*, 20, 110 (1887), 131.

nating samples apparently adulterated and it is our belief that the influence of adulteration in the large number of samples examined is negligible. The result was the zone, bounded by the lines *A-A* and *B-B*, of the greater area as shown. It is significant that in no portion of its boundaries does this zone exclude the smaller one. It is believed that this larger zone offers a practical means of determining, at least presumptively, whether or not a given sample of herd milk or other mixed milk is adulterated. Thus, if a given milk in its fat and solids-not-fat falls within the zone it can, in the absence of other facts, be fairly considered to be unadulterated but if the junction line of these two constituents falls outside the zone the milk is at least suspicious and the burden of proof is then to show that it is unadulterated.

There will, of course, be individual animals whose milk at times or continuously will not show the composition herein indicated, but inasmuch as milk supplies are made up of the milk of a number of individuals, it is believed that this chart will be of value not only to governmental milk controls but to dealers as well.

The curve *C-C* shown about the middle of the larger zone represents a smoothed curve obtained from 1,000 analyses of individual cows made by Dr. Lythgoe and placed by him in 12 groups according to the total solids. In plotting this curve, however, total solids were disregarded by us and were separated into fat and solids-not-fat.

At the time this paper was read no method of treatment of the chemical composition of milk, having to do with the limiting values of unadulterated milk, had been found by either of the authors in the literature but we have since seen Dr. A. G. Woodman's table on page 135 of his work on "Food Analysis," published in 1915. While the two methods are not strictly comparable, Dr. Woodman's idea of limiting values is that which we had already adopted independently in this treatment of the subject. It will be noted, however, that Woodman's table referred to is calculated from certain assumptions and analyses while we have endeavored to confine ourselves only to published tables. Inasmuch as this represents a somewhat considerable departure from ordinary methods of treating the matter, we do not wish to be considered as suggesting that the zone in its present form represents absolutely true conditions but we present it in the hope that it may be tested out by workers interested in these lines to the end that, if possible, a graph may be finally obtained which may be used to give us absolute results in testing the composition of any sample of milk. It is hoped, in addition to the use above suggested, that this figure may serve as a guide to our law-making bodies so that they shall not make the impossible standards we have noted above.

In making this chart we attempted to use analytical results from some 5,000 samples of milk produced in New York State as cheese factory supplies, but the average composition of these milks, when plotted according to the solids-not-fat, gave the curve *D-D* in Fig. 1, of an entirely different form from any normal

milk curve which we have been able to obtain, being convex to the ordinate. The conclusion is irresistible that a considerable portion of these samples had been skimmed.

A study of the proportions of the two milk constituents mentioned, as indicated by this figure, shows some very interesting inter-relations. In order to bring this out more clearly, Tables I and II have been made. In making both these tables, the fat has been used as

TABLE I

FAT Per cent	SOLIDS-NOT-FAT Av.	(PER CENT) Extremes	TOTAL SOLIDS Per cent
3.00	8.05	7.75-8.35	11.05
3.25	8.30	8.05-8.65	11.55
3.50	8.55	8.20-8.90	12.05
4.00	8.90	8.55-9.25	12.90
4.50	9.20	8.85-9.50	13.70
5.00	9.35	9.05-9.65	14.35
5.50	9.50	9.20-9.80	15.00
6.00	9.60	9.30-9.90	15.60

the fixed point and the solids-not-fat and total solids corresponding thereto have been sought. For the lower percentages, fat has been selected in differences of $\frac{1}{4}$ of 1 per cent. The zone shows that corresponding to 3 per cent of fat, there may be from 7.75 to 8.35 per cent solids-not-fat. The average of these gives the figure in Col. 2, Table I, while the total solids are, of course, the sum of this average and the fat. The limiting figure in this table should be of value to legislators.

In Table II the difference apparent by an examination of the chart in the increment of fat and solids-not-fat is reduced to figures. Thus, it will be seen that in the lower ranges the average fat increments are about the same as those for the solids-not-fat but with about 3.5 per cent of fat the increment of the solids-not-fat begins to decrease until on reaching the higher figures for fat the latter increment is less than one-third that of the fat. The difference between extremes, as shown by Cols. 7 and 8 of Table II, is also of interest, showing

TABLE II

PER CENT FAT		PER CENT SOLIDS-NOT-FAT		INCREMENTS Per cent		DIFFERENCE BETWEEN EXTREMES Per cent	
Aver.	Approx. Extremes	Aver.	Approx. Extremes	Fat	Solids- Not- Fat	Fat	Solids- Not- Fat
3.00	2.85-3.30	8.05	7.75-8.35	0	0	0.45	0.60
3.25	2.95-3.60	8.30	8.05-8.65	0.25	0.25	0.65	0.60
3.50	3.15-3.95	8.55	8.20-8.90	0.25	0.25	0.80	0.70
4.00	3.50-4.65	8.90	8.55-9.25	0.50	0.35	1.15	0.70
4.50	3.90-5.40	9.20	8.85-9.50	0.50	0.30	1.50	0.65
5.00	4.20-6.25	9.35	9.05-9.65	0.50	0.15	2.05	0.60
5.50	4.50-7	9.50	9.20-9.80	0.50	0.15	?	0.60
6.00	4.75-7	9.60	9.30-9.90	0.50	0.10	?	0.60

the fat to be much the more variable constituent. For any given average percentage of fat, it will be noted that the maxima and minima of the corresponding figures for solids-not-fat have a comparatively limited range, these figures in no case being more than 0.7 nor less than 0.6 of 1 per cent. For the higher average percentages of fat, on the contrary, the difference between maxima and minima may be over 2 per cent.

It will be apparent from these facts that standard requirements embracing only fat and solids are illogical because it is possible so to water or skim a milk with high fat as to benefit considerably the dealer and, at the same time, leave the milk well within the requirements of the legal standard for both fat and total solids.

Table II likewise seems to show that the practice of paying for milk on the fat percentage basis will,

when the cattle predominating in any given milk supply are of breeds or strains having a comparatively low percentage of fat, probably have the effect of markedly raising the "solids-not-fat" but that this effect will not be so marked with percentages of fat above about 4.50. Inasmuch as possibly most city milk supplies in the United States are now furnished by cattle having milk of low fat percentages, this method of payment is to be commended if a milk of given moderate nutritive value is desired; but, as has been pointed out by others, this method of payment is unfair to the man furnishing a low or medium grade milk, in that his cattle produce relatively higher total solids than cattle with a high fat content.

It will further appear, from an examination of the tables and figures, that in legislating, unless due regard is had to the inter-relations of the constituents of the milk, legislators will make trouble for administrators by suggesting such a composition for milk as is not normally produced by the cows themselves. Thus, for a standard of 3 per cent fat an average of 8 per cent solids-not-fat would be proper and for 8.5 per cent solids-not-fat, the fat should be placed at 3.5 per cent.

It is thus seen that the standard proposed by the Federal Government and in use by them of 3.25 per cent fat and 8.5 per cent solids-not-fat is open to criticism, the corresponding figure as shown by this curve being 8.3 per cent solids-not-fat as an average and the same thing is apparently true of the standards of most of the states.

It is worth while here to note Fig. II of our accompanying paper on the "Chemical Quality of New York City Market Milk." This figure shows the percentage of the samples in certain groups of known purity milk, arranged according to the same scheme of percentages as indicated by the tables in this paper. It will be noted by reference to that paper that the groups of the higher fat content and of the corresponding solids-not-fat show a marked parallelism, tending to show the accuracy of the relationship indicated by the zone chart presented herein. This is further indicated by Fig. III of that paper.

SUMMARY

I—The zone chart devised appears to show the approximate chemical composition of normal milk.

II—This chart appears to be capable of use as a guide in fixing legal standards.

III—It appears also to be capable of use as a guide in detecting adulterated milk.

IV—A milk standard having regard only for the total solids is illogical.

V—Most of the legal milk standards in force in the several states of the Union as well as that of the Federal Government are unbalanced and, therefore, incapable of enforcement.

We desire to acknowledge our indebtedness to the sources of reference given herewith and to Dr. L. L. Van Slyke, J. B. Newman, Assistant Food Commissioner of Illinois, and others for valuable information furnished in private communications.

BUREAU OF FOOD AND DRUGS
DEPARTMENT OF HEALTH, NEW YORK CITY

CHEMICAL QUALITY OF NEW YORK CITY MARKET MILK

BY LUCIUS P. BROWN AND CLARENCE V. EKROTH

Received December 1, 1916

The size of the problem presented in an endeavor to control the quality of milk supplied to New York City is one which is, of course, equalled nowhere else in the United States and probably in only one other city of the world. The population of the city is 5,500,000. It consumes daily about 2,000,000 quarts of fluid milk and as much or a little more milk in other forms. The fluid milk is collected at about 1200 country creameries and pasteurizing plants and supplied by some 45,000 dairy farms located in 7 different states and in Canada. When it arrives in the city, it is distributed by about 600 dealers using more than 7,000 delivery wagons and by 12,000 retail stores.

It is axiomatic that the cow producing the largest flow of milk will be the one favored by the dairyman dealing with a city milk supply, other things being equal. Unfortunately, this tendency can be pushed to extremes and it is conceivable that cattle may be so bred, with an eye single to the flow of milk, as to reduce greatly and injuriously the food-value of this milk. For the past ten years the chief efforts of the New York City Health Department have been devoted to securing a safe milk supply rather than one furnishing a maximum of nutrients. It is obvious that the tendency to reduce the quality of the milk supply must have limits set to it lest the community suffer from too great a reduction in the actual amount of food furnished by it.

In an attempt to get together, in an easily demonstrable form, information gathered during the past 40 years, we have made an exhaustive analysis of certain available data, hoping it may be of use to other food officials. Space, obviously, will not permit of detailed presentation of many of the facts which could be brought out.

In the years 1904 and 1905 this Department conducted a survey of the country creameries supplying the city, which resulted in the establishment in 1906 of a regular country inspection service. These investigations indicated that a considerable amount of skimming had been practiced in the country. A comparison of inspections in 1909 with those of 1905 showed that there had resulted, as the effect of closer supervision, a marked increase in the content of both fat and solids-not-fat, as shown by Charts *a*, *b*, *c* and *d* of Fig. I and as further indicated by Fig. III. Up to that time the standard for total solids of New York State milk had been 12 per cent. The Legislature of 1901 reduced this to 11.5 per cent, the fat being left unchanged at 3 per cent. Immediately on a proportion of the milk supply had been running below the standard for a number of years, and in this time no marked change is indicated by Charts *b* and *c* of Fig. I, for 1904, except a slight drop in the content of fat. This is significant, however, only because the figures for 1904, when the lower milk requirements had been in effect for 3 years, indicated a still further dropping of the content of this constituent, and resulted in

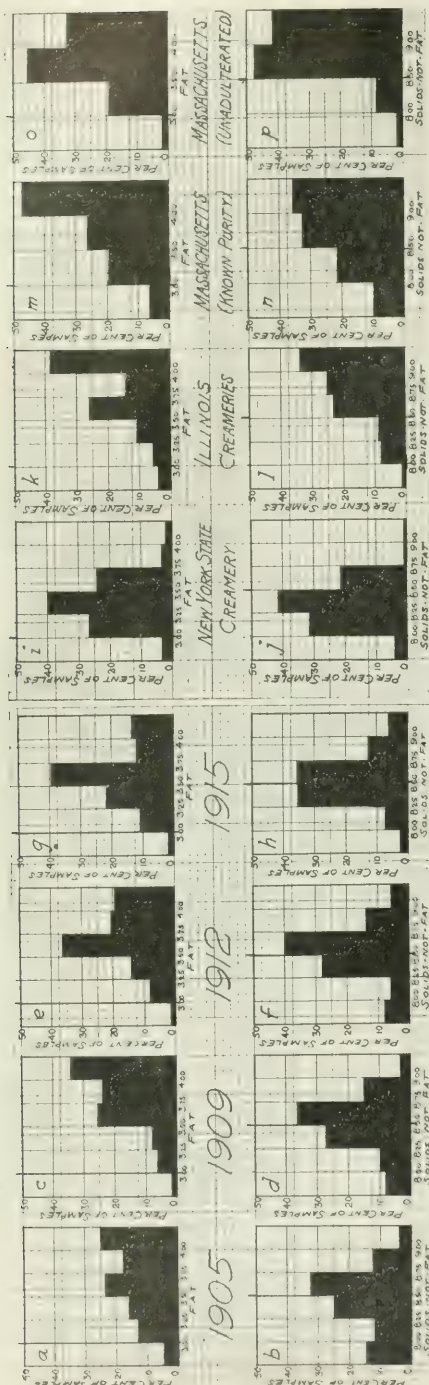


FIG. I. CHARTS SHOWING THE CHEMICAL QUALITY OF NEW YORK CITY MILK FOR FOUR YEARS

FIG. II. CHARTS SHOWING THE CHEMICAL QUALITY OF MILK FROM VARIOUS SOURCES

compared with the fat curve for 1909, the year when the maximum effect of the former high standards was observed.

An interesting feature of Fig. I is that the milk, as a rule, for the 4 years plotted, ran very much above the standard in fat. The solids-not-fat curves of this figure further indicate that during the greater part of these years, the milk was below the standard in solids-not-fat, an indication of the unbalanced character of this standard and the fact that the dealers in endeavoring to live up to such a standard were forced to give more fat than the standard called for. It also appears to indicate that the 3 per cent standard for fat is unneces-

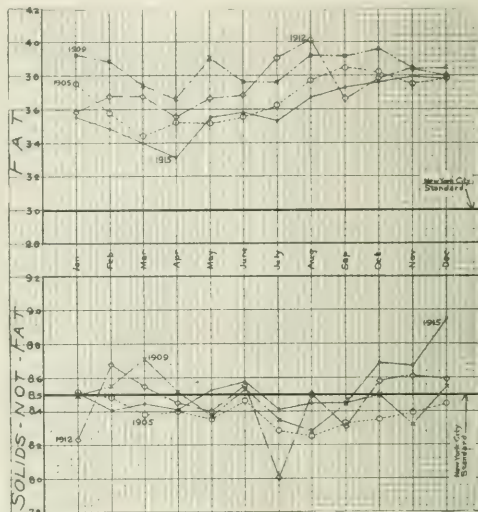


FIG. III—CHARTS SHOWING THE AVERAGE MONTHLY PERCENTAGES OF FAT AND SOLIDS-NOT-FAT IN NEW YORK CITY MILK FOR THE YEARS 1905, 1909, 1912 AND 1915

sarily low but, despite this fact, it is only natural to suppose that there was no great straining of the possibilities in this attempt, the effort being simply to get just within the standard. This is further indicated by Charts *k* to *n* of Fig. II, which are all of "known purity" samples and which all indicate a great preponderance of the higher percentages. Charts *o* and *p* are from routine milk supply samples but are supposed to be pure samples, and show the same thing.

In Fig. III the curve for solids-not-fat for 1915 is interesting, showing, as it does, a decided rise in the latter part of the year, coincident with the announcement by the Department of Health that a greater effort on the part of the dealers must be made to live up to the solids-not-fat standard. When compared with the corresponding curve for the fat the fact that the latter curve shows no perceptible change would lead to the supposition that an appreciable number of cows furnishing milks of higher fat content had been added to the milk shed, but that their milk had been partly skimmed and then added to lower grade milk in such a way as to increase the solids-not-fat alone.

Charts *i* and *j* of Fig. II are of interest as representing about 150 samples taken from the herds furnishing one of the lowest grade milk supplies of the state and of known purity. They indicate what the result of lack of attention to the quality of the milk supply may result in.

SUMMARY

I—The diagrams shown indicate a considerable betterment of the milk supply as a result of more rigid enforcement of the standards.

II—The fat standard of 3 per cent is a very easy one to live up to but will not result in a betterment of the nutritive value of the milk.

III—The suggestion in our other paper of this date as to the unbalanced character of the ordinary milk standard in effect in the United States is further indicated by these diagrams.

IV—As a corollary to the conclusions of both papers in question, it would appear that it is time that the chemical standards for milk in the United States were placed on a more rational basis.

BUREAU OF FOOD AND DRUGS
DEPARTMENT OF HEALTH, NEW YORK CITY

RED PEPPERS

By FRANK M. BOYLES
Received November 9, 1916

In the trade the hot red peppers are divided into or classed as "capsicums" and "chillies." The larger pods are usually called "capsicums" and the smaller pods, varying in size from about $\frac{1}{2}$ to $1\frac{1}{2}$ inches in length, "chillies."

The term Cayenne or Cayenne Pepper is applied only to the ground product which is made from either or both the capsicums and chillies. The capsicums and chillies vary greatly in flavor and pungency. Contrary to general belief some of the capsicums are more pungent than some of the chillies.

During the past few years the writer has examined a large number of shipments of commercial grades of red pepper of various varieties, both domestic and imported, and has been impressed by the number that do not comply with the requirements for this class of products as laid down in *Circular 19*, Office of the Secretary, U. S. Department of Agriculture, which circular serves as a standard for the Department in the enforcement of the Food & Drugs Act of 1906.

This condition obtains not only with the imported peppers but also in a striking degree in the case of peppers of domestic origin, which are now being produced in such quantities as to be of considerable commercial importance.

Louisiana and Texas produce a considerable amount of capsicums and chillies and in South Carolina the industry has forged ahead considerably; in 1915 the production in this state was approximately 150,000 lbs.

The South Carolina capsicums average about $2\frac{1}{2}$ in. in length and are of a bright red color. They are free of stems, very bright in appearance, carry no extraneous dirt, and altogether present an appearance not excelled by any variety of capsicum. Upon grinding, they produce a bright powder of excellent appearance, equal in flavor and pungency to most and much better than many of the imported capsicums.

The writer has had the opportunity of examining samples from a number of shipments of these capsicums, the data being compiled in Table I. These capsicums were ground under the supervision of the writer and the samples were composites, representing the regular

TABLE I—PERCENTAGE ANALYSES OF SOUTH CAROLINA CAPSICUMS

No.	Moisture	Ash		Crude Fiber	ETHER EXTRACT		
		Total	Insoluble		Total	Volatile	Non-Vol.
1	6.02	5.37	0.67	28.36	12.90	1.15	10.75
2	7.38	4.82	0.25	27.62	11.90	0.72	11.18
3	6.65	5.83	0.48	24.45	13.22	0.85	12.37
4	5.67	7.75	0.65	29.29	14.22	1.88	12.34
5	4.40	7.04	1.20	27.27	14.22	1.88	12.34
6	5.37	7.14	0.96	30.48	14.22	1.88	12.34
7	5.90	6.27	0.71	24.34	14.22	1.88	12.34
8	6.17	7.19	1.07	25.12	15.24	0.35	14.89
9	5.31	7.10	1.10	25.27	14.85	0.20	14.65
10	5.55	4.95	0.55	25.37	14.85	0.15	14.70
11	5.65	5.51	0.77	28.95	13.44	0.42	13.02
12	5.60	5.82	0.86	28.37	15.10	0.32	14.78
13	5.72	1.20	21.27	16.32	0.62	15.70	15.70
14	5.22	0.73	22.65	16.20	0.55	15.65	15.65
15	5.35	0.62	23.27	15.98	0.49	15.49	15.49
16	5.96	5.47	0.77	21.01	15.00	0.40	14.60
17	7.08	5.03	0.77	20.07	15.00	0.40	14.60
Max.	7.38	7.75	1.20	30.48	16.32	1.85	14.47
Min.	4.40	4.82	0.25	20.07	11.90	0.15	11.75
Average	5.90	5.98	0.78	25.48	14.55	0.60	13.95

factory run and were taken at frequent intervals during the grinding. Each sample represents the composition of lots of about 2200 lbs. They were not previously sieved because of their apparent freedom from extraneous dirt and because a number of preliminary trials showed that only a negligible quantity of dust (from 0.03 per cent to 0.08 per cent) could be removed; the total ash and acid-insoluble ash in this small amount of dust were 14.5 per cent and 4.8 per cent, respectively. All lots were free from stems.

These peppers were grown under the indirect supervision of the Bureau of Plant Industry of the U. S. Agricultural Department, from Hungarian Paprika Seed. In this climate peppers grown from these seed become very much hotter than the imported Paprika, so hot indeed that in the trade they are classed as Capsicums, and when ground constitute Cayenne pepper. This industry was begun in South Carolina about 10 years ago.

A study of the results obtained on these peppers shows that 29.4 per cent exceed the standard of not more than 6.5 per cent for Total Ash as given in *Circular 19*, the maximum being 7.75 per cent; that 88.2 per cent exceed the standard of not more than 0.5 per cent for HCl-Insoluble Ash; that 23.5 per cent contain more than double the standard amount of Insoluble Ash; that 29.4 per cent exceed slightly the standard of not more than 28 per cent for Crude Fiber, the maximum being 30.48 per cent; and that 76.4 per cent fall below the standard for Non-Volatile Ether Extract of not less than 15 per cent, the lowest being 10.75 per cent. These data show that the South Carolina peppers, though of a very desirable quality, are, to a large extent, not in accord with any of the requirements of *Circular 19*.

In Table II are given the results of a study of twenty-five samples of these peppers, each of these samples representing a kind of representative two-ounce sample. The samples are composites taken at frequent intervals.

As in the case of the capsicums, these peppers were not found to be uniformly hot being found that less than a per cent consisting of organic products matter could be removed by all of the processes.

TABLE II—BOMBAY CAPSICUMS

No.	PER CENT Total	ASH Insoluble	No.	PER CENT Total	ASH Insoluble	No.	PER CENT Total	ASH Insoluble	CRUDE FIBER	PER CENT Total	ETHER Volatile	EXTRACT Non-Vol.
1	5.96	0.35	12	8.43	0.65	23	6.92	0.94	15.28
2	7.50	0.77	13	6.00	0.33	24	6.96	1.14	14.60
3	7.40	0.86	14	8.72	0.57	25	6.61	0.82	15.79
4	5.58	0.32	15	6.84	0.65	26	5.77	0.47	18.71
5	6.17	0.43	16	7.07	0.28	27	6.00	0.60	17.21
6	6.16	0.79	17	7.08	0.81	28	7.20	1.30	29.87	17.47	0.72	16.75
7	9.84	0.95	18	6.77	0.51	29	8.16	1.30	27.15	16.72	0.38	16.37
8	6.06	0.31	19	7.07	0.14	30	6.80	1.22	25.00	18.27	0.40	17.87
9	6.14	0.51	20	7.42	0.71	31	7.67	1.75	29.00
10	5.50	0.74	21	5.75	0.23	32	7.67	1.57	28.30	20.87	0.47	20.40
11	5.95	0.96	22	7.28	0.34	33	8.25	1.10	27.80	12.85	0.50	12.35
						34	6.42	0.51	32.30	18.25	0.50	17.75
						35	9.355	1.50	25.25	16.10	0.25	15.85

Maximum of 35 samples..... 9.35 1.75 32.30 20.87 0.72 20.40
 Minimum of 35 samples..... 5.56 0.14 25.00 12.85 0.25 12.35
 AVERAGE of 35 samples..... 6.95 0.76 28.08 17.22 0.45 16.57

TABLE III—JAPAN CAPSICUMS

No.	PER CENT Total	ASH Insol.	No.	PER CENT Total	ASH Insol.	No.	PER CENT Total	ASH Insol.	CRUDE FIBER	PER CENT Total	ETHER Volatile	EXTRACT Non-vol.
1	4.9	0.20	6	5.76	0.28	10	6.75	0.20	15	5.70	0.32	23.90
2	5.7	0.50	7	5.80	0.18	11	6.41	0.15	16	5.77	0.60	16.65
3	5.17	0.42	8	6.20	0.26	12	6.15	0.21	17	6.82	0.33	15.97
4	6.32	0.78	9	5.90	0.14	13	6.61	0.26	18	6.84	0.36	19.45
5	6.07	0.30				14	5.93	1.17	19	6.32	0.36	22.50

Maximum of 19 samples..... 6.84 1.17
 Minimum of 19 samples..... 4.9 0.14
 AVERAGE of 19 samples..... 6.05 0.39

TABLE IV—MOMBASSA CHILLIES

No.	PER CENT Total	ASH Insoluble	CRUDE FIBER	PER CENT Total	ETHER Volatile	EXTRACT Non-volatile
1.....	6.70	1.62	29.75	15.75
2.....	5.95	0.85	30.45	16.85
3.....	4.57	0.50	22.63	28.71	0.22	25.49
4.....	6.25	1.77	25.44	20.97	0.32	20.65
5.....	9.45	1.78	25.56	16.16
6.....	5.38	0.35
7.....	4.36	0.61	23.69	21.65	0.15	21.50
Maximum.....	9.4	1.77	30.45	25.49
Minimum.....	4.36	0.35	22.63	15.75
AVERAGE.....	6.08	1.06	26.25	20.06

TABLE V—MISCELLANEOUS

CAPSICUMS	PER CENT Total	ASH Insol.	CRUDE FIBER	PER CENT Total	ETHER Volatile	EXTRACT Non-vol.
Korean, highest type.....	7.70	0.60
Korean.....	6.20	0.20
African, highest type.....	5.05	0.95	28.76	19.45
Korean, highest type.....	6.75	0.75	26.02	22.70	0.45	22.25
Korean, highest type.....	7.10	0.30	25.85	20.37	0.60	19.77
Niger.....	5.72	0.60	24.20	18.65	0.25	18.40
Niger, highest type.....	5.27	0.62	27.77	21.96
Niger.....	6.17	1.27	22.82	19.07	0.85	18.22
Bombay Cheries.....	5.35	0.65	29.20	15.60
(highest type) }	5.67	0.82	27.45	17.85	0.30	17.55
Bright Japan Chillies.....	4.63	0.18	24.02	22.50

ties treated in this paper the sifting experiments were not performed with a few pounds of the product taken from the center of the bale, as is sometimes done, but one or more whole bales were sifted on a mechanical sieve. These capsicums usually carry a small amount of stems. In these 35 lots the stems averaged less than $\frac{1}{2}$ inch in length.

It is seen that 62.8 per cent of the Bombay Capsicums exceed the standard for Total Ash, the maximum being 9.35 per cent; that 45.7 per cent contain more than 7 per cent Total Ash; that 71.4 per cent exceed the standard for HCl-Insoluble Ash, and that 22.7 per cent contain more than 1 per cent Insoluble Ash.

While the Crude Fiber and Non-Volatile Ether Extract were not determined on all of these lots still it is apparent that in this variety of Red Peppers the Crude Fiber will often exceed the standard while the Non-Volatile Ether Extract will almost always be higher than the standard.

Table III shows the results on 19 lots of Japan Capsicums. On the whole these peppers are well within the limits of the standards but occasionally shipments come in which are high both in Total and Insoluble Ash. Notwithstanding that these capsicums generally come within the standards, they are not superior either in color, flavor or pungency to the other varieties. These samples are composites and represent grinds of about 5000 lbs. The stems on these lots averaged less than $\frac{1}{4}$ in. in length.

The results on 7 lots of Mombassa Chillies are recorded in Table IV. These samples are composites representing grinds of about 3000 lbs. These peppers frequently exceed the standard for Total Ash and in the majority of lots the Insoluble Ash is very much above 0.50 per cent. These chillies are practically

always free of stems. Only a negligible amount of inorganic matter could be removed by sifting, consequently they were not sifted.

Table V lists the results on a number of different varieties of red peppers which are not so often met in commerce. Some of these lots, it will be noted, are of the very highest type obtainable.

The Korean Capsicums and so-called Bombay Cheries, which latter are small peppers about the size and shape of an ordinary cherry (carrying no stem and exceptionally bright and free from extraneous dirt), are almost invariably higher than the standard in either Total or Insoluble Ash or both.

These samples represent the factory run on lots of about 2 tons. These peppers were not sieved because of their apparent freedom from dirt and also because experience had shown that practically no mineral matter could be removed by this means.

CONCLUSIONS

These data show clearly that the present standards for Red Peppers are sadly in need of revision. Indeed, there are very few red peppers entering into commerce to-day that will comply with all of the requirements of Circular 19.

The standard for Total Ash should be increased to 7.50 per cent.

The standard for HCl-Insoluble Ash should be increased to 1.00 per cent.

The standard for Non-Volatile Ether Extract should be lowered to 14 per cent.

The standard for Crude Fiber should be increased to 29 per cent.

CHEMICAL LABORATORIES, McCORMICK & COMPANY
BALTIMORE, MARYLAND

LABORATORY AND PLANT

THE MANUFACTURE OF PICRIC ACID FROM THE MEDICAL STANDPOINT

By F. O. Wessr, M.D., Resident Surgeon

New England Manufacturing Company, Woburn, Massachusetts

A study of the medical complaints of workmen engaged in the manufacture of picric acid has furnished much material that is interesting, and some of which, I trust, will be of value to others. Although this investigation has covered the short period of nine months, a report is made at this time because, owing to the excellent system of manufacture recently installed, the number of accidents from this trade will be greatly reduced. A subject as many-sided as this cannot be fully discussed in a short paper; therefore, as the chief danger arises from the fumes of nitric and mixed acids, this particular part will be more fully treated.

The conditions under which our men work, and the vigorous medical supervision, have been important factors in minimizing the accidents of a dangerous trade. The building devoted to making picric acid was erected especially for this purpose and is a modern, substantial structure. The systems of lighting and ventilating are adequate; exits are numerous and of easy access. The new method of manufacture has almost eliminated the escape of fumes in the building, and has markedly reduced the number of acid burns. Our hospital department, described in a recent publication,¹ is thoroughly organized and completely equipped.

The examination of all new men, and the reexamination of the older employees at frequent intervals, have much to do with preventing accidents by weeding out the unfit and discovering intercurrent disease. This work has given much valuable information, and has been the means of rejecting 9 per cent of all men applying for employment. The reasons for rejection include: heart lesions, albumin and casts in the urine, asthma, bronchitis, aortic aneurysm, mediastinal tumor, arteriosclerosis, and alcoholism.

PHYSICAL EXAMINATIONS

Realizing that a permanent and well-trained force of able-bodied men is of great value in preventing accidents and illness, much attention has been given to accomplishing this thing. As a result there have been many changes in the employees of this department; signs of unfitness and inborn carelessness soon show themselves. Our records give the interesting information that we have had the representatives of 18 nationalities and 4 races among the men working with picric acid; moreover, we have recruited from 32 different occupations, varying from laborers to college graduates. None of these men were familiar with this particular trade before coming to this plant. No class or race of men seem to be especially sensitive to the dangers of the trade; a strong, healthy, non-alcoholic man, free from arteriosclerosis, has proved a good risk, even in regard to fume poisoning.

¹ *Boston Medical and Surgical Journal*, December 11, 1916.

The information concerning fume poisoning has been obtained from 398 cases reported at our hospital, and we make a strenuous effort to have all men so affected come for treatment.

No. of Men.....	50	29	28	13	7	2	4	3	2	2	2	Total Cases
No. of Attacks...	1	2	3	4	5	6	7	8	9	10	13	398

Twenty-nine cases were serious enough to require bed treatment in our hospital ward, for periods varying from 1½ day to 3 days. The absence of any deaths in this series of 398 cases is due, we believe, to the vigorous method of handling such accidents.

DELAYED ACTION OF FUMES

Our experience is in accord with that of other observers in that mild and apparently insignificant attacks may result in serious consequences, which, at the time, could not be foreseen, and also, that fume poisoning may have a delayed action. The following case will illustrate both points. One of the older employees, having become careless and believing himself immune to fumes, neglected to report at the hospital after two very slight attacks. When he left work some time later, there was absolutely nothing to indicate that he was not perfectly well. He ate supper and went to bed in his usual good health. On being called to breakfast, about twelve hours after the last attack, he was found to be semiconscious and breathing with great difficulty. He remained in this condition three days, but finally recovered and soon reported back to work. Since then, about three months, he has worked here but in another department, and as far as we are able to see, has not suffered from his experience.

The symptoms given by our cases do not vary from those already stated by other observers, and will not be taken up in this paper.

AFTER-EFFECTS OF FUME POISONING

As to serious complications and sequelae of fume poisoning, our observations do not include a large enough number of cases or extend over a long enough period to warrant making any positive statements. Our investigation, however, has not disclosed any cases of pneumonia or any predisposition to affections of the respiratory apparatus. Although we have had 398 cases of fumes, there have been only 7 cases of coryza and 7 of bronchitis in this series treated at the hospital, and the men having the greatest number of attacks of fumes were not more susceptible than the others. Neither do repeated examinations of the urine show any evidence of renal irritation. It has been noticed that men working with fumes are generally slow in recovering from headache, constipation and indigestion. How much of these can well be attributed to fume poisoning, or how much to the fact that these men have worked more frequently than those in other departments of the plant, and many "new recruits" among them who cannot hold a job for any length of

time can easily be blamed on something else besides employment.

METHODS OF TREATING "FUMES"

The method of handling "fumes" is the same in all instances regardless of the mildness of the attack, or whether we believe it due to apprehension or malingering. Foremen are instructed to send to the hospital all men affected, and the hospital department sees to it that such men do not leave the plant till they have again reported. Treatment, whether the man is coughing or complains simply of a slight oppression in the chest, is started with the lungmotor, which we have modified somewhat to suit our needs (see Fig. 1).

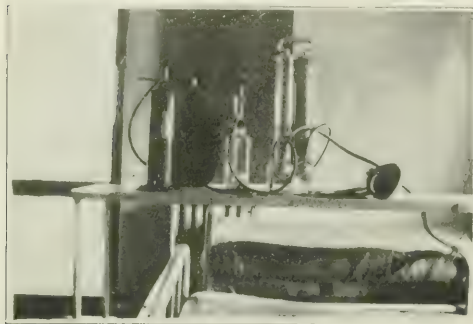


FIG. 1.—LUNG MOTOR MODIFIED TO TAKE UP AMMONIA FUMES

Instead of using simply air or oxygen, we have so arranged that the air takes up ammonia fumes by being drawn over the surface of aromatic spirits of ammonia. This mixture is so regulated that the ammonia fumes can be forced into the lungs without causing any great inconvenience to the patient, and can be kept up indefinitely. Prolonged treatment, however, has not been necessary, as the relief is almost immediate. If oxygen is used, it is supplied from a small cylinder, and not taken from the generator that accompanies the apparatus. When cough and substernal distress are relieved, the patient is kept under observation for some time before being allowed to return to work, and from time to time inhales ammonia fumes from a small bottle of ammonium carbonate cubes. Internal treatment consists of aromatic spirits of ammonia and a saline laxative. Chloroform has not been used. The men are also instructed to refrain from smoking and the use of alcohol. Bed treatment in our hospital is insisted upon in cases that cause any anxiety, or when the man lives away from this vicinity and under unfavorable home surroundings.

There has been one case of chronic fume poisoning in a man who had frequent slight acute attacks, and was indifferent to the methods used for self-protection. This man showed a slight cough and bluish lips. He did not report till forced to by a severe attack and was thus discovered. These symptoms cleared up when he was put to work outside and he shows no ill effects.

EYE BURNS

There are other ailments worthy of note that affect men in this employment. The next most serious class of injuries that we have to deal with are mixed acid burns of the eyes; and these are difficult to prevent as the men will not use the goggles provided. It is not uncommon, on calling a man to account for not wearing his goggles, to have him state he had them in his pocket. The gambling instinct to "take a chance" is responsible for a large percentage of accidents. Under the old method of manufacture in earthenware pots, these injuries were numerous and sometimes serious. But it is marvelous to see an eye clear up that has been so badly burned that the sclera is edematous and lies in folds that protrude between the lids, and has the appearance of the white of a fried egg, the cornea being at the same time obscured by a brownish opacity. There have been 50 acid burns of the eye, varying in severity. In only one case, as far as we have been able to learn, has there been resulting interference with vision. In our first-aid racks we have a bottle of limewater to be used at the time of accident. At the hospital the eye is irrigated with a quart of limewater to make certain that all the acid is neutralized; this is followed with an irrigation of warm boric acid solution and hot boric compresses applied till the inflammation subsides.

DERMATITIS

Dermatitis of the forearms and parts of the body that come in contact with dirty hands is very resistant to treatment. In the summer, when men perspire freely and do not change their clothing frequently enough, a dermatitis is set up, apparently due to acid irritation; failure to keep the hands clean carries this trouble to other parts of the body. Treatment consists in first cleaning the part thoroughly with soap and water, and then going down the list of the conventional lotions, ointments, and powders till the most beneficial one is discovered.

Indigestion, headache, and constipation have been very frequent causes for complaint. Whether these are due to hasty eating, many times to poor lunches, to alcohol, to improper attention to the bowels, is hard to say, but these certainly have been very important factors. I believe we should be reluctant to attribute these complaints to working conditions, till the other contributing causes are ruled out.

ACTUAL PICRIC ACID POISONING

Finally, there have been very few cases of an interesting condition that we have attributed to picric acid poisoning. These have been men who had been engaged in scraping the brick lining of the diluting tanks. Inhalation of the dust made the men light-headed, dizzy, and caused them to say things which they were conscious were silly and absurd, but which they could not control. At the same time they were unsteady on their feet. There was no cough, substernal oppression, or praecordial distress. Benzol was not in any way concerned. After a short period of rest in the fresh air, these symptoms disappeared.

Repeated physical examinations of the older employees and careful inquiry have failed to discover a symptom-complex that could be attributed to chronic picric poisoning. If the digestive disturbances above mentioned are evidences of such poisoning, then we must admit that such a condition is very easily and rapidly acquired, as many of the men with these complaints reported shortly after being employed. The men working with this substance for the longest time show no predisposition.

This is without question a dangerous trade and many accidents occur as a natural result. Even though a company makes every effort to protect its men, trouble will still follow gross carelessness on the part of employees; and it is entirely proper to attribute a very large percentage of accidents to this cause. Also, because it is a dangerous occupation, and the men are working with something that is more or less a mystery to them, they are prone to find in their work a cause for all their bodily ills, regardless of how absurd may be the relation of cause to effect.

WOBURN, MASSACHUSETTS

A NEW DIRECT READING PRECISION REFRACTOMETER WITH UNIFORMLY DIVIDED SCALE

By G. W. MORFITT

Received December 18, 1916

I—INTRODUCTION

It has long been known that the value of the index of refraction frequently serves as a valuable criterion of the qualities of a liquid. That the means for testing thus afforded is not in more general use seems to be due to the lack of satisfactory means for easily determining the index of refraction rather than to any inherent weakness in the method itself. If some dependable instrument combining ease of operation with accuracy of results were at hand it is probable that there are many who would avail themselves of its possibilities. While there are several good refractometers which may be obtained, their use involves a great deal of care and skill if results are to be obtained showing the necessary high degree of accuracy. In some of them the operation is long and the result is not available without more or less calculation and reference to tables.

There seems, therefore, to be a real demand in the field of food and industrial chemistry for a simple, accurate refractometer so simple in operation that one without any special knowledge of optics could obtain accurate results easily and with certainty. Such an instrument has been recently designed by the writer¹ and a brief description of the refractometer and a discussion of its theory are here given for the purpose of placing the instrument before those who have need of it in their work. The good points of the instrument will appear in the discussion, and may be briefly summarized as follows:

1.—A linear scale calibrated directly in terms of the index of refraction of the liquid under examination.

2.—The possibility of so constructing the instrument that white light may be used when it is desired to determine the mean index, the instrument still retaining approximate achromatization in many cases.

3.—Simplicity, and ease of manipulation.

4.—Few adjustments other than those fixed permanently in the construction of the instrument.

5.—Settings obtained by comparing the dimensions of an image with those of an eye-piece scale—an accurate means of determining the proper adjustment.

6.—Adequate means for temperature control whenever required.

7.—Small amount of the liquid required for a determination, a single small drop being sufficient.

8.—Ability to determine the index to one or two points in the third decimal place—a degree of precision equal to, if not better, than that of the total reflection instruments.

The entire operation of determining the index of refraction of a liquid consists in placing a drop of the liquid at the proper place on a convex surface, bringing the nose of the microscope down upon it, and focusing the eye-piece. The value of the index is then read off directly from the uniformly divided scale on the focusing tube of the instrument. In an instrument of convenient size the change in setting for a change of index from 1.000 to 1.500 may be more than 10 cm. With an eye-piece of fairly high power the uncertainty in a setting need not be more than 0.02 cm. In most cases it will be less. The sensitiveness will, therefore, compare favorably with that of the best total reflection instruments.

II—THEORY

CASE 1.—Consider the arrangement shown in Fig. I. Let a point source of light be placed at C, distant R below the surface of the liquid. Its image, due to the refraction at the surface of the liquid, will be at S, so that $ST = R/n$, where n is the index of refraction of the liquid. Let S act as a virtual object at distance $k + R/n$ from a converging lens L of focus f , and let the image of S formed by this lens be at I, distant ρ from the lens. Then

$$k + R/n = \frac{1}{\rho} - \frac{1}{f} \quad (1)$$

Clearing of fractions,

$$n\rho f + knf + Rf = \rho k + R\rho \quad (2)$$

This equation becomes linear in n and ρ when

$$n\rho f = n\rho k, \text{ or when } k = f \quad (3)$$

Equation 2 then becomes

$$n = \frac{R}{\rho} - \frac{R}{f} \quad (4)$$

Thus, if Equation 1 is satisfied, the position of the image depends directly on the index of the liquid.

CASE 2.—Consider the arrangement shown in Fig. II. Let the point source be placed at C, the center of curvature of a spherical, non-reflecting, transparent surface, and let S be the image of C formed by passage of the

¹ *Physical Review*, December, 1916.

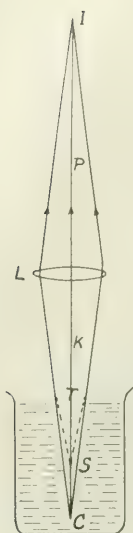


FIG. I



FIG. II

and a plane parallel glass plate placed in contact with the lens. The treatment differs from that of Case I in that the effect of the plane parallel glass plate must be considered. Beginning with C as a point source to locate its image C' by refraction at the surface T we have the following equation:

$$C'T = \frac{Rn'}{n}, \quad (5)$$

where n' is the index of refraction of the plane parallel plate. In the same way the refraction at T' may be expressed.

$$ST' = (CT' + t) \frac{1}{n'} = \frac{R}{n} + \frac{t}{n'} \quad (6)$$

where t is the thickness of the plane parallel glass plate. From the equation of the converging lens,

$$\frac{1}{p} + \frac{1}{\frac{R}{n} + \frac{t}{n'} + k} = \frac{1}{f} \quad (7)$$

The condition that this equation be linear in n and p is

$$\frac{t}{n'} + k = f. \quad (8)$$

Making this substitution and clearing of fractions we have

$$n = \frac{R}{f^2} p - \frac{R}{f}. \quad (9)$$

It will be noticed that Equation 9 is identical with Equation 4, but that the conditions for linearity of scale stated in Equations 3 and 8 are slightly different, owing to the effect of the plane parallel glass plate. It will be seen that in both cases the adjustment for linearity of scale is such that if parallel rays were incident upon the upper face of the lens L they would

be brought to a focus at the plane surface of the liquid.

CASE 3—Consider the case when the source is not at the center of curvature of the concentric lens, or when the lens is of some other form, but at a distance from it such that its apparent distance from the curved liquid surface is u . The image by refraction of the liquid lens into the plane parallel plate is according to the equation for the plano-concave lens bounded on the plane side by a medium of index n' .

$$\frac{n'}{C'T} - \frac{1}{u} = \frac{n-1}{R}, \text{ or, } C'T = \frac{uRn'}{R + u(n-1)} \quad (10)$$

The refraction at T' may be expressed as follows:

$$ST' = \frac{C'T + t}{n'} = \frac{uR}{R + u(n-1)} + \frac{t}{n'} \quad (11)$$

The object distance for lens L is

$$SO = \frac{uR}{R + u(n-1)} + \frac{t}{n'} + k. \quad (12)$$

Applying the equation for the converging lens,

$$\frac{1}{p} + \frac{1}{\frac{uR}{R + u(n-1)} + \frac{t}{n'} + k} = \frac{1}{f} \quad (13)$$

Differentiating with respect to n ,

$$\frac{dp}{dn} = \frac{u^2 R n'^2 f^2}{\{uRn' + (t + n'k - n'f)[R + u(n-1)]\}^2} \quad (14)$$

When the condition expressed in Equation 8 holds

$$t + n'k - n'f = 0, \quad (15)$$

and the slope is a constant, Equation 13 taking the simpler form

$$n = \frac{R}{f^2} p + \left(1 - \frac{R}{u} - \frac{R}{f}\right). \quad (16)$$

When k is too large the second term in the denominator is positive and increases with n . Therefore, the slope decreases as n becomes greater and the curve is concave toward the axis of p . If k is too small the reverse is true and the curve is concave towards the axis of p . If u be set equal to R , Equation 16 becomes identical with Equation 9, that equation being a special case of the general equation just derived.

RELATIONS BETWEEN DIMENSIONS OF OBJECT AND IMAGE—Let C represent the size of the object in Fig. II, and let C' , S and I represent the size of the images formed at these respective points. Then

$$\frac{C'}{C} = \frac{C'T}{u} = \frac{S}{C} \quad (17)$$

since no change in size of image is produced by the refraction at T'. By refraction at the converging lens L,

$$\frac{1}{S} = \frac{p}{SO}. \quad (18)$$

Combining 17 and 18,

$$\frac{I}{C} = \frac{S}{C} \times \frac{I}{S} = \frac{C'T}{u} \times \frac{p}{SO}. \quad (19)$$

Substituting the values of $C'T$, p , and SO from Equations 10, 12 and 16, and simplifying,

$$\frac{I}{C} = \frac{f}{u} \quad (20)$$

The image is of constant size for a fixed value of u , a property of the system utilized in a method for precise focusing to be described in a later paragraph.

III—ABERRATIONS

SPHERICAL ABERRATION AND DISTORTION—With the direct illumination that may be used in this instrument it is possible to use a stop of rather small diameter and still have a well-lighted field of view. Since only a small portion of each lens is used in forming the image of any point in the object the effect of spherical aberration in blurring the image is very small. Therefore, it seems unnecessary to take particular precautions to eliminate spherical aberration.

Curvature of the image, however, may affect the performance of the instrument to a slight extent. The curvature of the virtual image formed by the liquid lens is concave towards the eye-piece. The effect of the converging lens L in forming the image at the eye-piece is to diminish the curvature. The curvatures of the surfaces and the position of the stop should be so chosen that the resulting image will be as nearly plane as possible over the area covered by the image at the eye-piece.

Even if the radius of curvature of the image were so small as 5 cm. in an instrument whose image were 0.5 cm. in extent, the periphery of the image would be out of the plane of the center by

$$h = \frac{d^2}{8R} = \frac{.25}{400} = 0.06 \text{ mm.}$$

This value is less than the error of a setting. And since the focusing is always done on the peripheral portions of the image the effect would be to change slightly the position of the zero point of the scale.

CHROMATIC ABERRATION—In considering the chromatic properties of the system two distinct cases arise. If the converging lens L be strictly achromatic the adjustment for k is correct for all wave-lengths. The instrument will not give an achromatic image at the eye-piece, but the various colored images will be distributed along the axis according to the dispersion of the particular liquid in the apparatus. Such would be the construction of the refractometer if it is desired to measure the value of the index for different wave-lengths in order to determine the dispersion of the liquid. In this case monochromatic illumination is, of course, necessary. Lens L must be thoroughly achromatized in order that the adjustment of k shall be correct for all the values of wave-length with which the instrument is to be used.

The other case arises when the lens L is of the simple uncorrected type. This leads to a construction which may be approximately achromatized for liquids of ordinary dispersion, and which when illuminated with white light will give the index for some particular value of the wave-length for which the instrument has been calculated. Considering the positions of the red and the blue images formed by the liquid alone, we find that the blue image lies nearer the lens L than

does the red image. If the chromatic properties of this lens are such that its images of the images formed by the liquid lens fall at the same point the system will be achromatic in the sense that the different colored images will be at the same point in the eye-piece. This condition can be realized only for liquids whose dispersion bears a certain relation to the index of refraction for some intermediate wave-length. Since no such relation is general it will be seen that it is not possible to achromatize the instrument completely, although an approximation may be realized which will be satisfactory for many liquids. Whenever it is desired to use the instrument with a liquid which gives chromatic effects detrimental to accurate focusing it would be necessary to use the monochromatic light for which the instrument was designed to give accurate readings.

The condition for approximate achromatization may be derived as follows: For the converging lens L , assumed bi-convex,

$$\frac{1}{V_F} - \frac{1}{V_C} = \frac{V'_C - V'_F}{V'_C V'_F} = \frac{V'_C - V'_F}{V'^2_D} = \frac{2d'}{r} \quad (21)$$

where V'_F and V'_C are the virtual object distances for the lens L for the same value of p , and where $d' = n'_F - n'_C$ for the lens, and r is the radius of curvature of the lens faces. For the plano-concave liquid lens,

$$\frac{V_C - V_F}{V_F V_C} = \frac{V_C - V_F}{V_D^2} = \frac{d}{R} \quad (22)$$

where V_C and V_F are the distances from the liquid to the corresponding images for a given value of u . R is the radius of curvature for the curved surface of the liquid and $d = n_F - n_C$. The condition for achromatization is

$$V_C - V_F = V'_C - V'_F \quad (23)$$

Dividing (21) by (22) and substituting (23),

$$\frac{V_D^2}{V'_D^2} = \frac{2Rd'}{rd} \quad (24)$$

This reduces to

$$uR\sqrt{2f_D(n'_D - 1)d} = n_D f_D u \sqrt{2Rd'} + (uR + f_D R - r_D u) \sqrt{2Rd'} \quad (25)$$

which shows that it is possible to achromatize the system for any liquid whose mean index bears a certain relation to the square root of its dispersion. This relation is determined by the constants of the optical system.

IV—THE INSTRUMENT

The refractometer may be set up in a convenient form resembling an ordinary microscope in appearance. Instead of the usual state a heating tank may be provided, through the center of which passes a spring-mounted tube carrying the object scale at the lower end and the lens on which the liquid is placed at the upper end. The spring mounting sets into play so that the lens comes above the top of the heating tank when the microscope is raised. In this position it is easy of access for cleaning and for placing the drop

of liquid in position. At the lower end of the microscope tube is placed the plane parallel plate, and up in the tube at the proper distance is placed the converging lens *L*. The microscope tube is arranged so that it may be lowered into position and the two lenses brought into contact, and in contact with the liquid, and lowered into the heating jacket. The eye-piece should be mounted in the end of a tube telescoping into the microscope tube with rack and pinion adjustment for ease of focusing. The focusing tube should also be provided with a scale, read with a vernier, whose divisions are in accord with Equation 16, if the instrument is to be direct reading. The eye-piece should be of fairly high power and should be mounted in such manner that it and the eye-piece scale may be moved laterally a short distance in order to enable the user to bring the image and the scale into coincidence.

ADJUSTMENTS—The adjustments of the instrument are few and simple. The converging lens and the plane parallel plate must be carefully fixed with respect to each other. On this adjustment depends the linearity of scale. It will be seen that the proper adjustment is such that parallel light incident on the lens from above is brought to a focus on the lower surface of the plate. If the system be lined up with a telescope focused for parallel light by the auto-collimation method, the adjustment may be made by eliminating parallax between the cross wire of the telescope and the images of fine dust particles on the lower surface of the plate. If the lens is not achromatic this adjustment should be made with monochromatic light of the same wave-length for which the instrument is to read correctly.

FOCUSING—In the development of the equations it was shown that the image in the eye-piece is of a fixed size whenever the instrument is in proper focus. The ratio of the image size to the object size is given in Equation 20. Therefore, if two scales be ruled with divisions in the ratio of f to u the one may be used as an eye-piece scale and the other as an object whose image is formed at the eye-piece. When focusing is complete, image and eye-piece scale will be of the same size and coincident.

POSITION OF STOPS: EFFECT ON FOCUSING—The rays usually used when locating the position of an image graphically are seldom those that actually form the image. The position of the stop that limits the aperture of the instrument determines the rays that actually form each part of the image. This would seem to be of small importance here in its effect on spherical aberration and curvature of field but it plays an important part in focusing by comparison of image with eye-piece scale. While the eye-piece is moved outward throughout the range of clear focus we may have the image increasing, decreasing, or remaining of constant size, depending on the position of the stop. And the steeper the slope of the chief image rays with the axis of the instrument the greater will be the accuracy with which the focusing may be done. Several cases arise.

1—When the stop is between the object and the liquid lens the chief image rays are slightly convergent and the image increases in size as the eye-piece is racked in. This convergence is never very great. A rather large aperture for the liquid lens is also required. For these reasons this position of the stop is not good.

2—When the stop is in the plane of the liquid lens it is at the principal focus of the lens *L* and the chief image rays are parallel. No change in the size of the image results on moving the eye-piece toward or away from the lens. Accurate focusing cannot be done with the stop in this position.

3—When the stop is at the converging lens the chief image rays diverge from a point approximately coincident with the optical center of the lens. Their slope decreases with increase of the index of the liquid, thus decreasing the accuracy of a setting for the higher

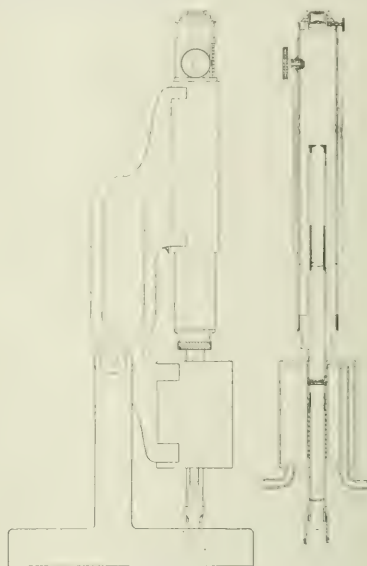


FIG. III

values of the index. It is apparent, however, that the decrease in accuracy is less rapid than the increase in value of the index so that the percentage error decreases with increase of the index. It will be noted that the center of the liquid lens is used to form the center of the image while the peripheral rays form the edge of the image. This arrangement enables one to focus with a good degree of precision.

4—If the stop be placed at a fixed distance above the converging lens, say at its principal focus, the divergence of the chief image rays is increased over that of Case 3, and the accuracy of a setting thereby increased. Between the liquid lens and the converging lens the chief rays are parallel to the principal axis. The effective apertures of both lenses are the same and vary inversely with the index of the liquid. The percentage accuracy of the settings is a constant because the distance from the stop to the image is directly propor-

tional to the index of the liquid. This position of the stop seems most likely to give high precision in the readings. Evidently the most accurate settings can be made when the divergence of the chief image rays is as great as is consistent with a good length of image and reasonably small apertures of the lenses, especially of the liquid lens. Since the aperture of the lenses is increased by bringing the stop nearer the eye-piece it is seen that there is a limit where the increase in aberration effects due to increased aperture of the lenses will counterbalance any gain in accuracy of focusing due to increased divergence of the chief image rays.

A compact instrument with a very open scale, and covering a long range, might be constructed in the following manner: Let the spring-mounted tube carry three object scales instead of one. Let these scales be so ruled and placed that when focusing on the first scale values of index from 1.000 to 1.2+ would cover the range of the engraved scale of the instrument. By focusing on the second scale values from 1.2 to 1.4+ could be read, and by focusing on the third scale values from 1.4 to 1.6+ could be determined. Such an instrument would be of practically the same size as one with single scale covering the same range with one-third the openness of scale. With certain values of index two scales would be in focus in the field of view at the same time. Each scale should be given a distinguishing mark and the three should be placed at different angles across the field of view in order to prevent confusion of the scales.

V—EXPERIMENTAL

After considerable preliminary work a single scale instrument was constructed essentially as described above. The lenses, except the optical flat, were made by a local firm of spectacle lens grinders. The centering was not all that could be desired and for this reason a satisfactory study of the effect of varying the position of the stop was impossible. The stop was placed at the converging lens *L* which had a focal length of about 8.5 cm. The aperture used was somewhat less than a centimeter in diameter. The radius of curvature of the upper face of the concentric lens was 6.0+ cm. Actual openness of scale was found to be 1.282 cm. for a change of 0.1 in the index of the liquid. The value of u was placed equal to that of f , since that adjustment leads to the shortest tube length for the instrument. It also leads to more accurate focusing than when the tube is longer since the chief image rays are more divergent. The length of the object and the image scales was 0.5 cm. The approximate adjustment of k was made by the collimation method already described, using sodium light.

Careful determinations of the index of refraction were then made for several liquids using a spectrometer and a hollow 60° prism. Immediately after the deviation readings were taken with the spectrometer a drop of the liquid was removed from the prism and placed in the refractometer. A number of settings were made and the reading of the centimeter scale on the focusing tube of the instrument recorded each time. The illumination for all readings was furnished by a Bunsen burner whose flame was colored

by a piece of asbestos soaked in a solution of common salt. The procedure was carried out for all the liquids in the table below.

Substance	Spectrometer Value of n	Refractometer Readings cm.			
Air.....	1.000 assumed	1.42	1.41	1.42	1.41+
Water.....	1.3318	5.87	5.59	5.58	
Kerosene.....	1.4478	7.02	7.03	7.04	
Cedar Oil.....	1.4994	7.68	7.66	7.67	
Carbon Bisulfide.....	1.6209	9.12	9.14		

Curve I, Fig. IV, shows the results graphically. It will be noticed that the curve deviates somewhat from a straight line, being concave toward the axis of index of refraction. If we refer to Equation 14, which gives the slope of this graph as n varies, we see

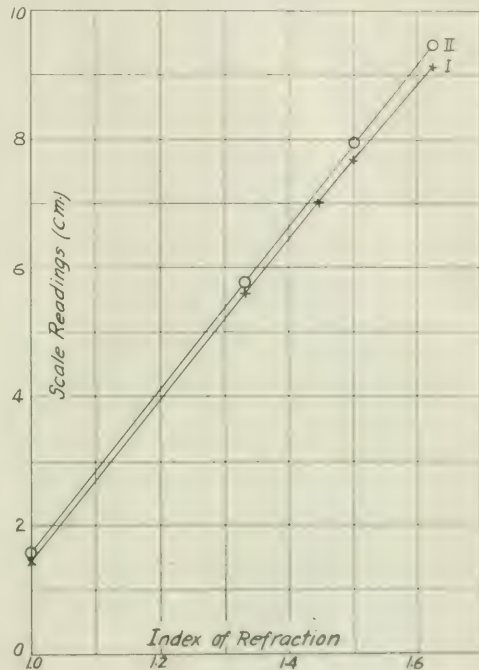


FIG. IV

that the curve would be concave toward the axis of indices when the value of k is too great. The value of k was then decreased by 0.03 cm. and readings again taken. The results are shown in Curve II, Fig. IV. The graph is sensibly a straight line.

It is obvious that if a uniformly divided scale be placed so that the 1.000 mark shall coincide with the 1.55 cm. mark of the centimeter scale on this instrument as well as making the above change, and the 1.600 mark be made to coincide with the 2.42 cm. mark we shall have a direct reading instrument with an openness of scale sufficient to determine the index to the third decimal place.

This refractometer has been made the subject of patent application, and its manufacture will be taken up if sufficient demand arises.

WASHINGTON UNIVERSITY
BY LOUIS MONTAGNA

REPORT OF THE JOINT RUBBER INSULATION COMMITTEE

THE JOINT RUBBER INSULATION COMMITTEE LIST OF MEMBERS—1916

CONSUMERS' CHEMISTS & ENGINEERS, AND CONSULTING CHEMISTS

- W. A. Del Mar, Interborough Rapid Transit Co., New York.
A. E. Ellis, Interborough Rapid Transit Co., New York.
W. B. Geiser, New York Central R. R. Co., Collinwood, Ohio
E. W. Gundy, Pennsylvania R. R. Co., Altoona, Pa.
H. B. Rodman, Binghamton, N. Y.
J. B. Tuttle, Bureau of Standards, Department of Commerce, Washington, D. C.
C. F. Woods, A. D. Little & Co., Boston, Mass.

MANUFACTURERS

- C. R. Boggs, Simplex Wire & Cable Co., Boston, Mass.
W. S. Clark, General Electric Co., Schenectady, N. Y.
G. d'Eustachio, Standard Underground Cable Co., Perth Amboy, N. J.
C. W. Walker, American Steel & Wire Co., Worcester, Mass.
E. L. Willson, Hazard Mfg. Co., New York.

RESIGNED

- P. Poetschke, Lederle Laboratories, New York.
J. P. Millwood, Consulting Chemist.

SECRETARY

- W. A. Del Mar, 621 Broadway, Room 807, New York City.

PART I—GENERAL REPORT

NEED OF SPECIFICATIONS

A demand for specifications which will enable purchasers of rubber insulation for wire or cable to secure good material on the basis of competitive bids has existed for many years.

In recent years, there has been no difficulty in securing insulation having the dielectric strength, specific resistance, elasticity and mechanical strength required in practice. Indeed, with the possible exception of dielectric strength these qualities are usually in excess of actual service requirements. There is another quality, namely, permanence, which although equally essential, has not been so easy to obtain.

While the physical properties of rubber insulation are susceptible of positive determination by tests which can be made before acceptance by the purchaser, the permanence of insulation can be ascertained with certainty only by actual trial, often at great loss, inconvenience and even danger. It should, therefore, be the aim of specifications to overcome this difficulty and by some indirect means, ensure that the manufacturers supply compounds having the required endurance.

This obviously presents a difficult problem, as it requires that some relation be established between permanence and one or more of the properties which are susceptible of test. It has been established by experience that Hevea rubber or the rubber of the *Hevea Brasiliensis* tree, when properly cured, is a superior grade which is entirely satisfactory for electrical insulation of the class under consideration. Hevea rubber may, therefore, be specified with advantage, although certain other rubbers of good quality may be excluded. The rubber has to be Hevea rubber of good quality, the materials associated with it in the compound must be known to be non-deleterious and the compound itself must be well prepared, applied and vulcanized.

TYPES OF SPECIFICATIONS

Two types of specifications have been devised to compass those restrictions. The first type of specification proceeds on the assumption that certain physical characteristics are developed to an unusual degree by the use of Hevea rubber, especially the grade known as fine Para. Among the qualities affected by the

grade of rubber, and alleged to be useful indications of the presence of Para rubber, are the tensile strength, elasticity and specific electrical resistance. Accordingly some specifications have been issued in which one or more of these qualities is specified in an exaggerated degree. Experience has shown that such specifications are ineffective, as the specified physical quality can be obtained either by manipulation of poor compounds or at the expense of permanence in compounds made originally of good materials. In consequence of this, specifications based exclusively on physical tests have fallen into disrepute, but such tests now serve in modified form as adjuncts to other types of specifications.

The second type of specifications to be considered is that in which a more or less rigid formula for the compound is specified and compliance with it exacted either by inspection during manufacture, or by chemical analysis supplemented by other tests of the finished product. Inspection which will really ensure compliance with such specifications is usually impracticable. Reliance must, therefore, be placed principally upon chemical analysis. Three difficulties at once arise. In the first place, chemical analysis cannot directly ascertain the quality of the rubber which has been used in the manufacture of a compound; it can determine quality only by the indirect method of measuring certain characteristic constituents. It is, therefore, necessary to present in the specification a relation between the desired formula and the chemical findings. The second difficulty is that in the past, chemists have employed diverse methods of analysis which give inconsistent results. It is, therefore, necessary to establish a satisfactory and standard procedure for analysis. The method of analysis must not only yield the information desired, but it must also be practical and capable of yielding uniform results when applied to the same compound by different chemists. In order to secure this uniformity it is important to describe the methods of analysis in detail. The third difficulty has been the non-uniform interpretation of analytical results.

The specification hereinafter presented is of the second or chemical type, in which an endeavor has been made to meet the three objections hitherto urged against such specifications. It contains a table showing the range of analytical results that should be obtained from a good compound containing 30 per cent of high class Hevea rubber, and is supplemented by a detailed analytical procedure. The specification is not complete as given, it being necessary to add appropriate electrical and mechanical test requirements. Examples of complete rubber insulation specifications are cited in Part VI of this report.

The specification should always be used in conjunction with the analytical procedure. The latter will, however, serve for the analysis of any compounds of the 30 per cent Para type with mineral fillers, provided the interpretation is made to correspond.

HISTORY OF THE COMMITTEE

The necessity of purchasing insulated wire under conditions of competitive bidding led the various departments of the government, the railroads and other large consumers, to issue specifications for rubber insulation. These specifications were based upon the individual experience or theories of a number of engineers, aided by suggestions from some of the manufacturers. For several years no attempt was made to standardize these specifications, and much trouble was given to the manufacturers by the diversity of requirements contained in them. In 1906, the Rubber Covered Wire Engineers' Association, consisting of representatives of the leading manufacturers, prepared a specification which was offered as a standard. This was followed in 1911 by the revised specification of the National Board of Fire Underwriters, which, however, calls for a comparatively

low grade of compound. The former specification, although the best that could be agreed upon at that date, was so defective as to afford little or no protection to consumers. The latter occupies a field by itself, and makes no pretension to specifying the highest quality of compound. Consumers desiring high-grade insulation of great permanence, therefore, continued to use their own specifications, altering them from time to time, in accordance with the best information available, with a growing tendency to rely upon chemical rather than physical tests. Some difficulty was experienced both in obtaining bids and in enforcing these specifications owing to the inability of chemists to make concordant analyses of rubber compounds. This matter reached an acute stage in 1911, when a number of manufacturers and consumers held a conference in order to discuss the possibility of standardizing specifications and analytical methods for rubber insulation. This conference was held at New York on December 7, 1911, Col. Samuel Reber of the U. S. Signal Corps presiding.¹ The following interests were represented:

Signal Corps, U. S. Army.	General Electric Co.
American Chemical Society.	Hazard Manufacturing Co.
Lederle Laboratories.	Simplex Wire & Cable Co.
New York Central Lines.	Standard Underground Cable
Pennsylvania R. R. Co.	Co.

After a full discussion of the subject, a Committee was appointed to devise a specification and an analytical procedure for rubber insulation, the Committee to report at a future conference. The Chairman, assisted by other members, appointed the following to serve upon this Committee which was named "The Joint Rubber Insulation Committee:—"

C. R. Boggs, Simplex Wire & Cable Co.
W. S. Clark, General Electric Co.
W. A. Del Mar, N. Y. Central R. R. Co. (later Interborough Rapid Transit Co.).
W. B. Geiser, N. Y. Central R. R. Co.
J. P. Millwood, Consulting Chemist.
P. Poetschke, Lederle Laboratories.
H. B. Rodman, Pennsylvania R. R. Co.

Later at the request of the Committee and by unanimous consent of the members of the original Conference, the following were added:

J. B. Tuttle, U. S. Bureau of Standards.
E. L. Willson, Hazard Manufacturing Co.

W. A. Del Mar was elected secretary of both the Conference Committee and of the Joint Rubber Insulation Committee. No permanent chairman was elected, it being left to the Committee to elect a chairman at each meeting.

The Committee immediately upon its formation decided to confine itself to the development of a specification and an analytical procedure for compounds of the 30 per cent Para type. In accordance with this policy it made a study of the chemical characteristics of Hevea rubber and of the available analytical procedures. New procedures were also developed and studied. Samples of different rubber compounds were analyzed by these tentative methods. The results were unsatisfactory and the discrepancies were investigated. Subcommittees were formed to do much of this work. Twelve regular committee meetings, besides numerous subcommittee meetings, were held, many different compounds were distributed to be analyzed by the entire committee, and others were experimented upon by the subcommittees and individual members.

After two years of this work the Committee presented a preliminary report to a Second Conference which was held at New York on October 13, 1913, Col. S. Reber again presiding. The report was unanimously accepted by the Conference and the Committee authorized to continue its existence for another year.

¹ The invitations were issued by Mr. E. B. Rattle, Chief Engineer of Electric Traction of the New York Central Railroad Company.

for the purpose of making any revisions that might appear necessary in its report, as the result of a year of experience with it.

The Committee was also authorized to publish the preliminary report. This was accomplished through the courtesy of the American Chemical Society, the American Institute of Electrical Engineers, and the U. S. Bureau of Standards, the report appearing in their official publications, *THIS JOURNAL* (January, 1914), the *Proceedings of the American Institute of Electrical Engineers* (January, 1914), and Bureau of Standards Circular No. 38, respectively.

Instead of reporting in a year, the Committee found it necessary to devote nearly 3 years to this work, holding 13 additional meetings, or a total of 25 general meetings exclusive of subcommittee meetings.

The Committee was authorized at the second Conference, to increase its personnel without securing the approval of the Conference Committee. It has added the following chemists to its membership:

A. E. Ellis, Interborough Rapid Transit Co., New York.
G. d'Eustachio, Standard Underground Cable Co.
E. W. Gundy, Pennsylvania R. R. Co.
C. W. Walker, American Steel & Wire Co.
C. F. Woods, A. D. Little Co., Inc., Boston.

The following resignations have been accepted since the Second Conference: J. P. Millwood and P. Poetschke. Mr. Geiser also resigned, due to stress of other work, but has been re-elected.

The Joint Rubber Insulation Committee's specification for rubber insulating compound has been adopted by the principal engineering societies which issue standards of the kind. Among these are the American Electric Railway (Engineering) Association, the Association of Railway Electrical Engineers and the American Society for Testing Materials. The specification has also been adopted by a large number of important purchasers of insulated wire, including the U. S. Signal Corps, the Panama Canal, the New York Central R. R. Co., the Interborough Rapid Transit Co., the Public Service Corporation of New Jersey, etc.

The Committee desires to express its thanks to the many gentlemen not members, who have actively participated in the work, especially to Messrs. F. S. Deemer, F. A. Hull, M. M. Kahn, C. B. Martin, G. H. Savage, J. F. Tinsley and D. Whipple.

PART II SPECIFICATION FOR 30 PER CENT HEVEA RUBBER COMPOUND (CHEMICAL CLAUSES)

1—A 30 per cent fine Para or best quality plantation Hevea rubber compound with mineral fillers, shall be furnished. It shall contain only the following ingredients: (1) Rubber; (2) Sulfur; (3) Inorganic mineral matter; (4) Refined solid paraffin or ceresine.

2—The vulcanized compound shall conform to the following requirements, when tested by the procedure of the Joint Rubber Insulation Committee, results being expressed as percentages by weight of the whole sample:

REQUIREMENTS ESSENTIAL TO THE AMOUNT OF RUBBER PRESENT

	Minimum	Maximum
Rubber	25	35
Wax Hydrocarbon	0	5
Free Sulfur	0	1

Real lead carbon or other inert filler, not to exceed:

Requirements for inorganic mineral matter, expressed as percentages by weight of the whole sample:

Requirements for ceresine or paraffin, expressed as percentages by weight of the whole sample:

	Minimum	Maximum
Paraffin	0	5
Ceresine	0	5

Submitted to American Electric Railway Association

Approved by American Electric Railway Association

Approved by American Institute of Electrical Engineers

Approved by Bureau of Standards

Total Sulfur (see note 2) ... 2.10 ... 2.30

- 3—The acetone solution shall not fluoresce.
 - 4—The acetone extract (60 cc.) shall be not darker than a light straw color.
 - 5—Hydrocarbons shall be solid, waxy and not darker than a light brown.
 - 6—Chloroform extract (60 cc.) shall be not darker than a straw color.
 - 7—Failure to meet any requirement of this specification will be considered sufficient cause for rejection.
 - 8—Contamination of the compound, such as by the use of impregnated tapes, will not excuse the manufacturer from conforming to this specification.
- NOTE 1—This specification shall be supplemented by appropriate clauses relating to tensile strength, elasticity, electric insulation resistance and dielectric strength. (See the Wire and Cable Specifications of the American Society for Testing Materials, the Association of Railway Electrical Engineers, etc., for examples of such clauses.)
- NOTE 2—The limit on total sulfur may be omitted at the option of the purchaser. (See Part IV of this Report.)

PART III—ANALYTICAL PROCEDURE

OBJECT OF THE ANALYSIS—The object of this procedure of analysis is to determine whether rubber compounds comply

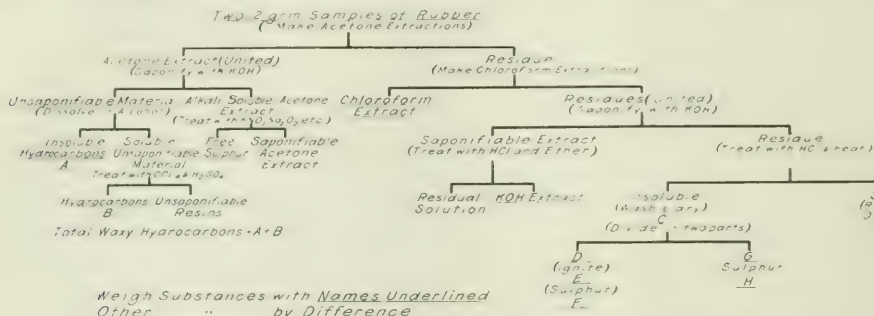


FIG. I—OUTLINE OF METHOD OF RUBBER ANALYSIS (EXCLUSIVE OF TOTAL SULFUR DETERMINATION)

chemically with the accompanying specification which is intended to secure compounds containing 30 per cent of the best Hevea rubber, and mineral fillers.

OUTLINE OF PROCEDURE—The general procedure is shown in Fig. I.

GENERAL—Make the analysis upon the insulation after vulcanization and, whenever possible, before the saturation of the braid. Wipe the insulation thoroughly with a damp cloth to remove any adhering material, but do not remove waxy hydrocarbons from the surface.

If, however, a saturated braided sample must be used, remove the braid and sandpaper the insulation to a depth of at least 0.005 in. and wipe with a damp cloth. The latter procedure, however, is not to be recommended, as it may cause an appreciable error in the acetone extract. In such cases report the condition of the sample.

Perform all determinations in duplicate and take the average value arbitrarily as the true value. Duplicate determinations must check within the limits specified.

Make blanks on all determinations and deduct the results accordingly.

SAMPLE—Remove the insulation entirely from sufficient wire to give a sample weighing about 25 grams. Cut this into small pieces¹ and grind slowly in either a No. O Enterprise coffee mill or a mill such as shown in Fig. II. Adjust the grinder so that

¹ This is most conveniently done with a meat chopper.

not more than 20 per cent will pass through a 40-mesh sieve. Sift all the material through a 20-mesh sieve, regrinding what is retained on the sieve until the entire sample has passed through. The wires of the sieves shall be evenly spaced in both directions and shall be of 0.016 and 0.010 inch diameter in the 20- and 40-mesh sieves, respectively. Remove with a strong magnet any metal that may have come from the grinder and thoroughly mix the sample.

EXTRACTION APPARATUS—The extraction apparatus shall conform with the accompanying Fig. III. It shall be heated so that the period of filling an empty syphon cup with acetone and completely emptying it will be between 2½ and 3½ minutes.

PREPARATION OF REAGENTS: 1—Acetone shall be freshly distilled over anhydrous potassium carbonate, using the fraction 56–57° C.

2—Alcoholic potash solution shall be of normal strength and shall be made freshly by dissolving the proper amount of potassium hydrate (purified by alcohol) in 95 per cent alcohol which has previously been distilled over potassium hydrate. The solution shall be allowed to stand for 24 hours and only the clear liquid used.

3—Ether shall be washed with three successive portions of distilled water and distilled, using the fraction 34–36° C.

4—Chloroform shall be shaken with water, dried by calcium

chloride, decanted, and freshly distilled, only the clear distillate being used.

5—Carbon tetrachloride shall be pure and freshly distilled.

6—The nitric acid bromine reagent shall be prepared by adding a considerable excess of bromine to the concentrated nitric acid, shaking thoroughly and allowing it to stand for some hours before using.

7—The fusion mixture for sulfur determinations shall be made by mixing equal quantities of sodium carbonate and powdered potassium nitrate.

8—The barium chloride solution shall be made by dissolving 100 g. of crystallized barium chloride in one liter of distilled water and adding two or three drops of concentrated hydrochloric acid. If there is any insoluble matter or cloudiness the solution shall be heated on a steam bath over night and filtered through 589 S. & S. Blue Ribbon filter paper.

9—Distilled water only shall be used in preparing solutions and in all washing operations. Reagents not otherwise specified shall be of a "C. P. tested" quality.

ACETONE EXTRACT—Extract continuously with 60 cc. acetone for eight hours, two 2-g. samples that have been prepared within 24 hours. Unite the extracts in a weighed flask, using hot chloroform to rinse the flasks. Distill off the reagents and dry the flask and contents for four hours at 95–100° C. Desiccate until cool and weigh. Continue to dry for two-hour periods until constant weight is obtained. In drying, place the flask on its side but

CHLORFORM-UNTERSACHT—Erfolgt vollständig. Die nachfolgenden
Eigenschaften des untersuchten Substanzen sind charakteristisch für

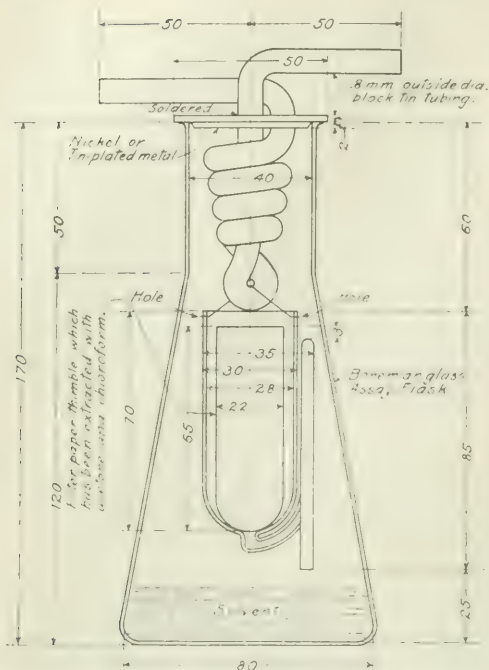


FIG. III—RUBBER ANALYSIS EXTRACTION APPARATUS. ALL DIMENSIONS IN MILLIMETERS

moving the acetone that may be on them) for four hours with 60 cc. chloroform. Unite the extractions in a weighed flask, using hot chloroform to rinse the flasks. Distill off the solvent and dry the flask and contents for two hours at 95–100° C. Cool in desiccator and weigh. Continue to dry for one-hour periods until constant weight is obtained. In drying, place the flask on its side but at a sufficient angle from the horizontal so that the extract does not appreciably run down the side of the flask. (If it is needful to wait after the acetone extraction, before starting the chloroform extraction, the sample must be kept in a vacuum of at least 50 mm. of mercury.)

ALCOHOLIC POTASH EXTRACT—Dry the residues from the chloroform extractions at 50–60° C. until the odor of chloroform can no longer be detected; unite the residues from the two 2-g. samples in a 200 cc. Erlenmeyer flask. Add 100 cc. alcoholic potash solution and boil for four hours under a reflux condenser. Filter the solution by decantation through an 11-cm. hardened filter paper into a beaker and wash twice, using each time 25 cc. hot absolute alcohol and then wash thoroughly with hot water. Wash any rubber on the filter paper back into the original flask and reserve this for the determination of Rubber Hydrocarbons. Evaporate the solution to approximate dryness, take up in warm water and transfer to a separatory funnel. Acidify with 30 cc. of 5*N* hydrochloric acid, using this to rinse the beaker. Add sufficient water to make the bulk of the solution 100 cc. When cool add 40 cc. ether, using it to rinse the beaker in 20 cc. portions. Shake the aqueous and ethereal solutions thoroughly. After complete separation, draw off the aqueous solution and treat in another separatory funnel, with a fresh 20-cc. portion of ether. Continue to shake the aqueous solution with fresh portions of ether until a colorless portion has been obtained, then shake out twice more. Unite the ethereal solutions and wash with successive additions of water, continuing twice after the

water shows no acid reaction. Filter through a plug of extracted cotton into a tared flask, wash the filter and funnel with ether, evaporate the ether without boiling and dry the residue at 95–100° C.; cool in a desiccator and weigh. Continue to dry until constant weight is obtained.

RUBBER HYDROCARBONS—Add to the flask containing the rubber residue from the alcoholic potash extraction, sufficient water to make the total volume of the solution 125 cc. and then add 25 cc. concentrated hydrochloric acid. Heat for an hour at 97–100° C. Decant the supernatant liquid through a hardened filter paper on a Büchner funnel, 7 cm. diameter, using suction; wash the residue with 25 cc. hot water and decant. (While a Büchner funnel is recommended, it is permissible to use an 11-cm. hardened filter paper with platinum cone, in a 60° funnel.) Perform this entire treatment with water and hydrochloric acid, three times and save the first and second decantations for the "organic matter" test described in ORGANIC FILLERS below. The rubber at this stage should be white and practically free from black specks of undissolved fillers; if not, continue the acid treatment until the black specks disappear. (If carbon is present, all the particles of rubber will be grayish, bluish, or black, depending on the form and quantity of carbon used. Black specks in light particles of rubber usually indicate the presence of lead sulfide which must be removed to prevent the formation of lead sulfate on igniting the residue C.) Add 150 cc. hot water to the flask and let stand on a steam bath or hot plate for half an hour and decant through the filter paper. Return to the flask any rubber that goes on the filter paper. Repeat until the washings are free from chlorides (see ORGANIC FILLERS). Transfer all the rubber in the flask to the filter paper and dry as much as possible by suction. Wash the rubber with 50 cc. of 95 per cent alcohol, using suction. Transfer the entire residue to a weighing bottle. Dry at 95–100° C. for an hour, cool in a vacuum desiccator under reduced pressure and weigh. Dry for a half hour, cool and weigh, repeating this process until either constant weight is reached or the weight starts to increase. Let this weight be represented by *C*. On a portion (*D*) of this residue (*C*) determine the ash (*E*) according to the paragraph immediately following this and the sulfur (*F*) in the ash (*E*). Determine the sulfur (*H*) in another portion (*G*) of residue (*C*). Make all sulfur determinations as described under TOTAL SULFUR.

Place about 0.5 g. of residue *C* into a weighed porcelain crucible. Let the weight of residue be represented by *D*. Heat gently gradually driving off the volatile matter. When the crucible has ceased to smoke, raise the temperature gradually to between 450 and 500° C. until all organic matter has been burned away, which is usually indicated by the ash becoming white. (An electric muffle furnace with pyrometer is recommended for this purpose.) Cool in a desiccator and weigh, the weight of ash being represented by *E* in the formula for rubber hydrocarbons. Make sulfur test on ash by the method described under TOTAL SULFUR. If, however, $50 \times C \times E$ is not over unity, the determination of sulfur in the ash may be omitted and *F* assumed to be zero. Then,

$$\text{Rubber Hydrocarbons} = 100 \frac{C}{4} \left[1 - \frac{E - F}{D} - \frac{H}{G} \right]$$

expressed as a percentage of the total sample.

TOTAL SULFUR—Place a 0.5-g. sample of rubber in a porcelain crucible of about 100 cc. capacity. Add 20 cc. nitric acid bromine reagent, cover the crucible with a watch glass, and allow to stand for one hour. Heat very carefully for an hour, remove the cover, rinsing it with a little water, and evaporate to dryness. Add 5 g. of the $\text{KNO}_3\text{-Na}_2\text{CO}_3$ fusion mixture, and 3 to 4 cc. of distilled water. Digest for a few minutes, and then spread the mixture half way up the side of the crucible to facilitate drying. Dry on a steam bath or hot plate. Fuse the mixture, using a sulfur-free flame until all the organic matter has been destroyed and the melt is quite soft. Allow to cool, place the crucible in a

600 cc. beaker, and cover with water. Digest three or four hours on the steam bath. Filter into an 800 cc. beaker, washing thoroughly with hot water. The total volume should be about 500 cc. Allow to cool, add 7 to 8 cc. concentrated hydrochloric acid to the filtrate, and heat on the steam bath. Test the solution for acidity with congo paper and add 10 cc. of hot barium chloride solution. Allow to stand over night, filter, wash, weigh the barium sulfate, and calculate to sulfur.

SPECIFIC GRAVITY—The specific gravity shall be the ratio of the weight of a given volume of the compound to the weight of an equal volume of water, both at 20° C. Cut strips of the largest practicable size from the conductor and use about 5 g. for the sample. Determine the specific gravity in the usual manner by means of a specific gravity bottle. Care must be taken that no air bubbles adhere to the sample.

CHECKS—Specific gravity determinations shall check within 0.01. The other duplicate determinations shall check within the following limits expressed as percentages of the original sample:

DETERMINATION	Check
Acetone Extract.....	0.10
Saponifiable Acetone Extract.....	0.10
Unsaponifiable Resins.....	0.10
Waxy Hydrocarbons.....	0.10
Free Sulfur.....	0.05
Chloroform Extract.....	0.10
Alcoholic Potash Extract.....	0.10
Rubber Hydrocarbons.....	0.20
Total Sulfur.....	0.10

INTERPRETATION—The percentage of rubber shall be considered to be the sum of the rubber hydrocarbons, saponifiable acetone extract, unsaponifiable resins, chloroform and alcoholic potash extracts, expressed as percentages. If the chloroform extract is over 3.0 per cent of the rubber so calculated, subtract the excess from the rubber. If the alcoholic potash extract is over 1.8 per cent of the rubber, as first calculated, subtract this excess also from the rubber.

RED LEAD—Dissolve 1 g. of the sample in 75 cc. xylol at a temperature of about 100° C. When the rubber is dissolved, the absence of any red particles indicates the absence of red lead. If red particles are present, filter the solution into a Gooch crucible and wash thoroughly with benzol, acetone and alcohol successively. Remove the felt and residue to a distilling flask, add 25 cc. 10 per cent hydrochloric acid, and distil over the chlorine liberated by the lead peroxide, absorbing the gas in a solution of potassium iodide and starch. Not more than 0.1 cc. of 0.1 *N* thiosulfate shall be required to titrate the iodine liberated.

ORGANIC FILLERS—Transfer the first and second decantations of the hydrochloric acid solutions to a carefully cleaned porcelain dish and add 20 cc. concentrated sulfuric acid. Place dish on steam bath or hot plate to drive off water and hydrochloric acid. A pronounced charring of the residue indicates the presence of organic matter soluble in water or hydrolyzed by hydrochloric acid.

Examine filter paper and rubber while decanting acid solution and again while washing free of chlorides. Some types of organic filler, not removed by water and hydrochloric acid, would be plainly visible at this point.

Place a small portion of residue (C) under a microscope and examine for fibrous and other characteristic organic material. If organic fillers are indicated and not clearly proven by this test, place a g. of the organic sample in a beaker, add 75 cc. xylol and heat on hot plate until the rubber is dissolved. Decant xylol solution and wash residue with ether several times by decantation. Dry residue and examine under the microscope.

STATEMENT OF RESULTS

The results of the analysis shall be stated in the following form:

	Per cent
Acetone Extract.....
Saponifiable Acetone Extract.....
Unsaponifiable Resins.....
Waxy Hydrocarbons.....
Free Sulfur.....
Chloroform Extract.....
Alcoholic Potash Extract.....
Total Sulfur.....
Rubber.....
Color of Acetone Extract (50 cc. vol.).....
Fluorescence in Acetone Extract Solution (present or absent).....
Hydrocarbons A (consistency and color).....
Hydrocarbons B (solid or liquid).....
Color of Chloroform Extract (50 cc. vol.).....
Carbon (present or absent).....
Organic Fillers (present or absent).....
Red Lead (present or absent).....
Specific Gravity.....
Sample braided or not.....

PART IV—EXPLANATION OF SPECIFICATION

Experience has shown that compounds of the grade which contains only good Hevea rubber, may be relied upon to be more permanent than those made of rubber of other grades. It is not affirmed by the Committee that a compound which conforms with this specification, is necessarily permanent, or that a better compound cannot be made, but it is believed that enforcement of the specification will limit the use of inferior materials and that it will put the manufacturers more nearly upon an equality of endeavor, where they can use their experience to obtain the best results. Used in connection with the analytical procedure, the specification will enable purchasers to obtain a good compound and to ascertain, with a greater certainty than heretofore, whether the material received represents the compound specified.

The term Hevea applied to rubber means rubber from the *Hevea Brasiliensis* tree whether wild or cultivated and regardless of the locality in which it has been grown. Para rubber is Hevea rubber of the kind originally shipped from the port of Para, Brazil, and comes in several grades. The rubber required by this specification should be Hevea rubber of good quality, such as fine Para or best quality plantation rubber.

Carbon is excluded not only because it is considered, by some purchasers, to be deleterious, but because it interferes with the determination of rubber hydrocarbons.

Red lead is excluded because of the possibilities of its deleterious effects on the rubber.

Ozokerite is prohibited because the acetone extract obtainable from it interferes with the separation of the acetone extract obtainable from the rubber, thereby vitiating the assay of the rubber extract. This prohibition is unimportant to the manufacturers, as ceresine, which is permitted, is the essential constituent of ozokerite.

An upper limit is placed upon the rubber in order to prevent the attainment of electrical and mechanical strength by the use of an extra quantity of inferior rubber whose lasting qualities might not be satisfactory.

The hydrocarbons are limited, owing to their tendency to separate from the compound and thus possibly cause porosity.

The free sulfur is limited because an excessive amount may be deleterious.

The maximum limit on the saponifiable acetone extract is to prevent the use of raw or reclaimed rubber with high saponifiable extract. The medium limit is to prevent the use of Hevea rubber, since it is characteristic of the acetone extract from Hevea rubber to be largely saponifiable.

The maximum limit on the color is to prevent a low percentage of unsaponifiable resins in chloroform and Hevea rubber. A high result might be due to the presence of oxidized rubber.

The alcoholic potash extract is limited, first to prevent the use of inferior materials and second, to prevent the use of materials which are not of the quality specified.

The alcoholic potash extract is limited to prevent the use of saponifiable rubber substitutes.

The specific gravity is limited to reconcile the specification of ingredients by weight with the practice of purchasing material by volume.

Fluorescence of the acetone solution is prohibited as it indicates the presence of bituminous substances, rosin oil or mineral oils.

The color of the acetone extracts is specified to conform with the normal color of the extract from Hevea rubber. A darker color indicates adulteration or an inferior grade of rubber.

The hydrocarbons are required to be solid in order to prevent the use of oils and paraffin of low melting point. The shade required is that obtained from paraffin wax or ceresine. If hydrocarbons *B* are liquid this would indicate reclaimed rubber softened with mineral oil, or paraffin of low melting point.

The color of the chloroform extract is specified to conform with the color of dissolved gum in minute quantities. The presence of bituminous substances would be indicated by a brown or black color.

It would be desirable that the sulfur of vulcanization be limited to exclude reclaimed rubber, which contains the sulfur of its previous vulcanization, but the Committee has not yet developed an acceptable method for determining this quantity. It is, therefore, confronted with the choice of either placing a limit on the total sulfur or giving up the attempt to exclude shoddy by sulfur limitation. Option is, therefore, given to the purchaser to insert or omit the limit on total sulfur. Such insertion will at times exclude reclaimed rubber and the Committee believes it possible to make a suitable compound with this limitation. The Committee thinks that a sulfur limit positively excluding reclaimed rubber, would place too great a hardship, in other ways, on the manufacturers. Where the specification is used with no total sulfur limit, the use of many kinds of, or much, reclaimed rubber, will be guarded against by the limits of the various components of the acetone extract. When the limitation on total sulfur is omitted, sulfur-bearing fillers, which possess certain advantages, may be used.

This specification should be supplemented by appropriate elasticity and tensile strength tests, in order to add to the assurance that good rubber has been used and that the vulcanization process has been properly carried out; also by appropriate electric stress and resistance tests, to assure proper insulating qualities and homogeneity of structure. The exact value of the limits for these tests will depend upon the use to which the material is to be put.

PART V—EXPLANATION OF PROCEDURE

GENERAL—The tentative report of the Committee, presented in October, 1913, provided for the determination of the percentage of rubber present by the method of difference. The mineral fillers were determined by the terebene solution method. Results obtained in the use of this method showed that it gave inaccurate results on some compounds. The Committee, therefore, determined to abandon it and to find a suitable substitute. It is believed that the method now recommended will satisfactorily solve the problem.

The most feasible means of limiting the kind of rubber was considered to be the determination of the saponifiable and unsaponifiable resins. These are fairly constant characteristics of the resins of Hevea rubber, and of compounds made from the same. Other methods, such as the determination of the saponification number and the optical activity of the resins, were thought to be unpractical.

The method as developed is applicable to the analysis of any

pure rubber compound containing only mineral matter with or without ceresine or paraffin wax, regardless of the kind or amount of rubber, and can be used in conjunction with other specifications provided the limits are changed to correspond with the amount and kind of rubber desired, and due consideration is given to interfering mineral matter. When applied to a compound without ceresine or paraffin wax the unsaponifiable acetone extract is the unsaponifiable resins.

The method has been definitely described, to make it certain that experienced chemists may obtain concordant results. The interpretation has been rigidly defined, obviating any ambiguity as to the meaning that will be assumed, even though this sometimes appears to be arbitrary.

SAMPLE—In order to obtain uniform results, the Committee has established by experiment that a definite method of sampling has to be adopted and that for all extractions the sample must be reduced in a prescribed manner to at least an approximately similar degree of fineness. For this reason the procedure specifies a definite type of grinder obtainable in two forms, and also specifies definite sieves.

EXTRACTION APPARATUS—The Committee has proved that the extraction apparatus used by different chemists must be of exactly the same form and the same size. It was also proven that small samples in the apparatus give the maximum results and that the rate of extraction is dependent upon the amount of solvent and its temperature as it passes through the sample. The apparatus finally adopted combines the advantages of several forms that were studied, and, together with simplicity of operation and adjustment to uniform conditions, gives practically complete extraction when used as specified. A number of other variations that might have a possible effect upon the amount of extract, were tried but found to be inappreciable.

ACETONE EXTRACTION—The extraction is made within 24 hours of the preparation of the sample, so obviating any appreciable oxidation. Two samples are extracted and united, so that a larger amount of extract may be obtained for the subsequent separations, and the extraction apparatus kept within a convenient size. Hot chloroform is used to facilitate the complete transference of the extract. The flasks are placed on their sides when drying, to hasten the emission of the solvent and thus reduce the chance of volatilizing, through longer heating, some of the more volatile constituents of the extract. Drying *in vacuo* at room temperature, does not remove all the moisture if paraffin is present and such drying with heat or at 100° C. in an inert gas presents no practical advantage over the method given.

SEPARATION OF THE ACETONE EXTRACT—The method given was developed so that all the desired constituents could be determined on one sample.

Emphasis is laid on thorough extraction of the unsaponifiable material and the retention of the flocculent material with the ethereal solution. This latter material is not soluble in either ether or water, but it was proven that if such as was chloroform-soluble was included in the unsaponifiable material, the subsequent determination of the hydrocarbons would be more exact. A portion of this flocculent material is insoluble in chloroform.

The hydrocarbons are determined in two places, making an approximate separation between the solid and the liquid ones, if both are present. The first hydrocarbons (*A*) are those insoluble in the solvent at a low temperature. The presence of unsaponifiable resins in the solution prevents the more complete freezing out of the hydrocarbons, but the remainder is obtained after treatment of the resins with sulfuric acid. In this way, chance of loss through the action of the acid has been largely eliminated.

The method for free sulfur gives all the sulfur in the acetone extract with the exception of negligible amounts which may be in the unsaponifiable material. It was proven that the results agree with determinations made directly on other acetone extracts.

The saponifiable and unsaponifiable resins are obtained by difference.

CHLOROFORM EXTRACTION—The chloroform extraction should be made at once after the acetone extraction, or the sample put in a vacuum, so as to avoid the danger of an abnormally high extract. When the extract is dried as specified, constant weight is obtained before any appreciable oxidation occurs. If bituminous substances are present, that portion which has not been extracted by the acetone will be largely soluble in chloroform and can be readily distinguished by its color. The amount of extract is also affected by the presence of uncured and inferior rubber. A properly cured Hevea compound will always give a little extract with chloroform, which varies somewhat with the method and conditions of cure.

ALCOHOLIC POTASH EXTRACTION—The alcoholic potash extraction is the usual saponification process for obtaining the fatty acids of rubber substitutes. The total amount of such substitutes is not obtained, but if any appreciable amount is present, the value will exceed that of the limit allowed. When no substitutes are present, this determination always yields a small amount of extract from Hevea rubber.

RUBBER HYDROCARBONS—Methods for the determination of the percentage of rubber are of two kinds, the direct and the difference methods. The Committee adopted a difference method after trial of various methods, both direct and indirect.

The difference methods are those in which the rubber is removed and the residue weighed. This may be done in either of two ways: by the use of solvents, or by ignition. The early work of the Committee was largely along the line of removing the rubber by means of solvents. Many kinds and probably every class of rubber solvents were tried. Some did not completely dissolve the rubber at low temperatures and ordinary atmospheric pressure; others appeared to dissolve the rubber, but formed a colloidal solution holding some of the fillers, which could neither be filtered nor centrifuged clear of mineral matter. Many of them were so time-consuming as to render them worthless, even if accurate results could be obtained. The solvent method given in the Preliminary Report was found to give inaccurate results with compounds containing much litharge or zinc oxide, but gave very good results on most classes of compounds if xylol, instead of terebene, is used as the solvent. It has since been demonstrated, however, that it is practically impossible to obtain correct results on an important class of compounds and that method was, therefore, abandoned.

Asking the compound gives fairly accurate results provided no volatile or decomposable fillers are included. This, however, cannot be assumed to be the case. In the method which the Committee recommends, these objectionable fillers are largely removed before the compound is ignited, and provision is made for testing those few materials which are volatile, but not removed. This method is a modification of an unpublished one devised some years ago by G. H. Savage.

In the testing of this method, compounds containing most of the known commercial inorganic fillers were analyzed. Whiting, talc, magnesium, and lead compounds and barium carbonate which are objectionable in direct asking do not in any way interfere with the determination of rubber by this method. A number of organic fillers were used, but these, too, did not cause any great error.

The securing of accurate results by the method given depends largely on two things: the complete solution of decomposable fillers, and the removal of all chlorides. With these precautions, the analyst is almost certain to obtain reasonably accurate

results. The formula for calculating the rubber hydrocarbons presents no difficulty if the exact quantities called for in the method are used.

The rubber as it is weighed under (C) contains sulfur in combination with the rubber. On ignition sulfur is driven off with the rubber. By determining the sulfur before and after ignition, the amount so lost can readily be calculated, and the proper correction made.

TOTAL SULFUR—The sodium peroxide method, specified in the Committee's Preliminary Report, is widely used in the analysis of wire insulation, and is known to yield accurate results on such compounds. The liability of explosion with that method, however, renders it somewhat objectionable.

It will be noted that the bromine nitric acid method which is now specified does not require the dehydration and separation of silica. If the filtrate, after the fusion and extraction with water, is acidified in the cold, and after the precipitation of the barium sulfate the solution is not permitted to concentrate to a relatively small volume, any silica which is in solution will remain dissolved. The elimination of this step by proper precautions saves considerable time without in any way interfering with the accuracy of the determination.

INTERPRETATION OF RESULTS—Emphasis is laid on the method of calculating the results. The saponifiable acetone extract and the unsaponifiable resins are considered to be parts of the rubber. The chloroform and alcoholic potash extracts, when within the limits specified, are also so considered. Any quantity in excess of these limits is assumed to be due to foreign substances or in case of chloroform extract, to undervulcanized rubber. No allowance is made for the ash in the raw rubber, as it is considered to be negligible. This method of calculation has to be adopted if the rubber found is to agree with that originally put into the compound.

MOISTURE—A determination of moisture is not given, as electrical tests will detect its presence if in excess. If electrical tests are required, the error introduced by the omission of this determination is very small.

NOTE—With a procedure of this length it is impossible to explain every detail without undue elaboration, and the Committee wishes to point out that while to experienced chemists the procedure may seem overburdened by detail, yet every specified detail was found necessary in order that the conditions essential to accurate and consistent work might be reproduced by all chemists using the procedure. For this reason it is extremely important that all instructions be observed, even if their significance is not perceived by the individual chemist. It will probably be found that even with the instructions properly observed, some experience will be needed to apply the method successfully.

PART VI—LIST OF IMPORTANT SPECIFICATIONS CONTAINING THE JOINT RUBBER INSULATION COMMITTEE'S CHEMICAL CLAUSES OR ANALYTICAL PROCEDURE

AMERICAN ELECTRIC RAILWAY (ENGINEERING) ASSOCIATION Standard Specification for Rubber Insulated Wire and Cable

AMERICAN SOCIETY FOR TESTING MATERIALS Proposed specifications for Insulated Wire and Cable Covered with Heavy Rubber

ASSOCIATION OF RAILWAY ELECTRICAL ENGINEERS Standard Specifications for Wire and Cable

INTERNATIONAL RAINBOW INSULATED CABLE WORKS INSULMENT, NEW YORK Specification No. 1

NEW YORK CITY PUBLIC UTILITIES COMMISSION Proposed Specification No. 100

PARANA CABLE Company of General Insulating Agency (London, New York)

RESEARCH CABLE WORKS (London) Proposed Specification No. 100

CURRENT INDUSTRIAL NEWS

CORROSION AND ELECTRICAL PROPERTIES OF STEELS

At a meeting of the Royal Society, held on November 23rd in London, an interesting paper on the above subject was submitted by Sir Robert Hadfield, F.R.S., and Dr. E. Newbery. The condition that a metal shall dissolve in an acid with evolution of hydrogen is: single potential of metal plus overvoltage less than single potential of hydrogen electrode, all measurements being, of course, made in the given acid. If, therefore, it is assumed that the atmospheric corrosion of a metal is a process similar to that of dissolution in an acid, it should be possible to predict the corrosion-resisting power of a given metal by determining its single potential referred to a hydrogen electrode together with its overvoltage in a suitable electrolyte. Experiments on a number of special steels have been carried out to test the validity of the above assumption. The overvoltage, single potential and loss of weight in acid of each specimen were determined and compared with the atmospheric corrosion after exposing clean surfaces for ten weeks. The results show that the electrical methods give decidedly better estimates of the corrosion-resisting powers of steels than the acid methods and, although neither method gives reliable estimates in all cases, yet the electrical method appears to rest upon a sound theoretical basis and is probably capable of further developments which may result in the formation of reliable corrosion data.—A. McMILLAN.

CRACKING OF PETROLEUM

Papers dealing with the "Pyrogenesis of Petroleum" were read before the Institution of Petroleum Technologists, London, at a recent meeting. In the first, Mr. E. Lawson Lomax presented a mass of historical and bibliographical matter illustrating the development since the beginning of the last century. It was pointed out that the products obtained, when petroleum is heated, may be placed in four classes—permanent gas, illuminating oils, aromatic hydrocarbons and volatile fuels for internal combustion engines—and these classes may be taken to represent the lines along which development has taken place. The second paper, by Messrs. A. E. Dunstan and F. B. Thole, dealt with some general considerations regarding the chemical reactions involved in the decomposition and synthesis of hydrocarbons with heat. They remarked that, starting with acetylene at a moderate temperature and using reduced nickel, Sabatier has synthesized fair imitations of American, Caucasian and Galician oils, while, by using higher temperatures and the same gas as starting point, some chemists have obtained compounds identical with those occurring in coal tar and of the highest complexity, and, as an inference, it was suggested that the nature of the material to be cracked has little influence on the final products.—M.

NEW PROOFING MATERIAL

According to *India Rubber Journal*, 52 (1916), 5, a new process of proofing materials with cork has been introduced in France and has brought orders from the French government for hospital sheetings, etc. It has also been used for featherweight waterproofs and is said to be quite waterproof, a non-conductor of heat and unbreakable. By using a special machine, thin slices of cork of an even thickness are obtained from a block of cork. The slices are placed in chemical baths in order to remove the resinous parts which make cork a more or less brittle substance. Upon their removal, the cork sheets become flexible and may be compared in this respect with thin leather.

In fact, the sheets can be folded and bent without breaking. By combining the cork sheets with a suitable cloth, preferably a thin and strong cloth of good color, an excellent waterproof material is obtained. An adhesive preparation is used to cement the cork to the cloth or, if a stronger garment is desired, the cork sheets are placed between two layers of cloth. The cork fabric is said to have a decided advantage over ordinary waterproof materials because, being porous, it permits of ventilation whereas ordinary waterproof prevents it, and, in addition, the cork is very light. A coat made of it is said to be the lightest in the market.—M.

SEARCHLIGHT PROJECTORS

Messrs. Crompton & Co., of London and Chelmsford, have issued a catalogue which gives an account of searchlight projectors manufactured by them. The smaller ones are controlled by hand with or without gearing for the elevating and training mechanisms but the larger ones, with mirrors 24 in. in diameter and upwards, are often arranged to be operated electrically, the motors being housed within the cone base. Different forms of distant mechanical control can be fitted, whereby the projectors may be operated from the bridge or charthouse of a ship by means of rods or wire ropes. The mirrors, which may range up to a diameter of 60 in., are usually of plate glass ground to true parabolic form and silvered to give maximum reflection; the lamps are of the horizontal carbon type. The catalogue points out that statements regarding the candle-power of a projector are of no value since the factor which has most effect on the beam, *viz.*, atmospheric conditions, is quite beyond the control of the manufacturer. In addition to a description of commercial types of projector, a few details are given of a portable apparatus, for use in fortresses, which includes a petrol-driven air-cooled generating plant, mounted on wheels, a 60 in. projector with remote control and carts for horse and manual haulage to carry a sufficient length of main and control cable to permit the projector to be worked at a distance of 600 yards from the generating plant.—M.

COKE INDUSTRY OF NEW SOUTH WALES

Messrs. L. F. Harper and J. C. H. Minguye, in Paper No. 23 of the New South Wales Department of Mines and Mineral Resources, give a general survey of the coke industry of the province. The paper contains chemical analysis and physical properties of all types of coal found in New South Wales and also gives complete analysis of the ashes. It would seem that coke-burning, which has been carried on for a half century, is a growing industry, the production having risen from 304,800 tons in 1914 to 417,753 tons in 1915. The report suggests, however, that the methods of the industry have not been entirely in accordance with modern coke-oven practice. The sulfur in the coals and cokes is remarkably low while the coking properties of the coals are good. The most commonly used oven is the beehive oven, rectangular in form but with arched roof. The coke is discharged with a ram and quenched outside the ovens. Only one modern by-product plant is in full operation, a battery of regenerative Semet-Solvay ovens at Newcastle, N. S. W., with semi-direct ammonia recovery and a benzol plant. It would seem that coking for by-products should give good prospects, the yields being given as 30 lbs. of ammonium sulfate, 3 gals. of benzol, 8 gals. of tar and 12,600 cu. ft. of gas (585 B. t. u.) per ton of coal. These results, the report says, should do something to destroy the prejudices evidenced by the older and cruder types of plant.—M.

IRON INDUSTRY IN NORMANDY

The British Consul at Havre reports that the iron mines and blast furnaces of Caen are at present being worked by the Government, and that the industry, which was languishing for many years, is now in a most flourishing condition. A large new plant of the most modern type is being installed and the railway authorities are doing their utmost to develop the industry. The output of iron ore in the district has now reached over 1,000,000 metric tons per annum.—M.

VULCANIZATION

In an investigation on the problem of accelerating vulcanization and, in the course of numerous experiments with various types of organic compounds, Professor S. J. Peachey, according to a report in *Engineer*, 123 (1916), 37, has discovered that the nitroso-derivatives of certain bases, such as dimethylaniline, methylaniline, diphenylamine and so on, are capable of acting as powerful accelerators of the vulcanizing process. A mixing of 100 parts rubber and 10 parts sulfur, which normally requires to be heated to 138° C. at 40 lbs. steam pressure for 1½ hours, may be completely vulcanized in from 20 to 25 min. by incorporating 0.5 per cent of paranitrosodimethylaniline with the mixing prior to heating. Similarly, a vulcanite mixing containing 25 per cent sulfur, which, under ordinary circumstances requires to be heated for 6 hrs. at 140° C., may be vulcanized in 2 hrs. by the addition of 0.75 per cent nitrosobase.—M.

NATIVE AND ARTIFICIAL ASPHALT

According to Graefe, who writes in the *Zeitschrift für angewandte Chemie*, native asphalt can be distinguished from the artificial preparation by the black coloration (due to H₂S) imparted to lead acetate paper by fumes given off, when a sample is heated to 200–205° C. for a few minutes. All samples of native asphalt examined by him gave a powerful reaction but not the artificial varieties, except that Californian asphalts and the residue from crude Trinidad oil reacted faintly. All the extracts with the exception of that from Val de Travers rock gave a fairly strong reaction.—M.

ELECTRO-METALLURGY OF ZINC

In a recent article on the French outlook, *L'Information* makes some observations on the electro-thermic reduction of ores. Attention is called to the fact that not only is there ordinarily a loss of from 20 to 25 per cent of metal in the ores, but there is a consumption of 6 to 8 tons of coal per ton of spelter. In view of these facts, the possibilities of the electric furnace demand consideration. Electric smelting of zinc has long been the subject of experimental working in France. The Arudy works in the Pyrenees, which have been in operation since 1904, claim to be able to smelt a ton of raw blende containing 35 per cent metal with a loss of not more than 2 per cent. The Uginé works are now using the Cote and Pierron furnace. An electro-metallurgical company is being formed in Lyons to operate works at Iperre, in Savoie, as well as in the Pyrenees.—M.

SHIPBUILDING RETURNS

According to the *Glasgow Herald Supplement* for 1916, there are two principal features in the statistics representing the work done in the shipyards and engineering shops of the world during 1916. The first is the decreased production in the United Kingdom and the second the increase in the aggregate tonnage produced in foreign countries. This latter increase is accounted for almost wholly by the work done in America and Japan. In the United States the production was more than double that of 1915, while in Japan the total was almost three

times that of 1915, the increase being accounted for principally by the construction of a good many large cargo steamers. It is not remarkable that there should be a decrease in the Dutch production owing to the difficulty of obtaining materials. The comparative tonnages of all the foreign countries are shown in the following table:

	1916			1915		
	Ves.	Tons	H. P.	Ves.	Tons	H. P.
U. S. A.....	178	554,810	306,895	127	270,124	322,168
Japan.....	230	246,134	327,776	157	98,213	182,039
Holland.....	300	211,693	159,765	390	217,592	114,510
Germany.....	20	81,950	168,700	46	179,804	188,156
Italy.....	30	60,472	41,691	4	20,230	20,000
Norway.....	70	44,902	32,948	89	61,477	41,925
Sweden.....	35	40,090	27,433	33	25,927	32,530
France.....	10	39,457	52,400	32	41,438	20,950
Denmark.....	30	37,150	21,780	40	51,361	32,042
Spain.....	10	11,171	28,400	14	14,306	13,750
China.....	38	7,862	6,356	50	8,073	6,400
Russia.....	13	792	540
TOTAL.....	971	1,335,791	1,172,440	985	989,337	975,010

With regard to the German figures, these are taken to represent the launches, of which information has been received but cannot account for the total work done in the country.—M.

ECONOMIC UTILIZATION OF COAL

In the course of a series of lectures delivered at the Royal Society of Arts, London, on the economic utilization of coal, Professor Brame spoke of the composition of coal, and of coal as a source of heat and power, and also dealt with the by-product side of coal in general. It was mentioned that no great addition to our knowledge of coal constituents has developed, various important points at the present time existing where results were contradictory. The results of low-temperature carbonization as obtained in McLaurin's plant where the gases were non-luminous and the tar was of a drying character and completely soluble in caustic soda were specially interesting. The lecturer suggested a promising line of attacking this problem by applying the methods which have been found so useful in the case of alloys—the use of solvents in conjunction with the micro-structure. In dealing with the prospects for the more economical use of coal, reference was made to the use of powdered coal and to the advantage of briquetting coke dust. In this connection mention was made of the work being done at the Smethwick gas works. As regards prepared fuels, it was shown that the high price of coal is bringing gas-works coke into favor as an agent for steam-rising and that, by its use at Deptford, a saving of 16 per cent in fuel costs was effected.—M.

COKE-FUEL FOR ELECTRIC-POWER STATIONS

It is reported that the London County Council have placed an order for eight coke burning mechanical stokers for use under the steam boilers at their Greenwich generating station. It is calculated that the first set of stokers now contemplated will, if worked to their full capacity, consume 100 tons of coke per 24 hrs., and, having regard to the relatively high cost of coal as well as the relatively greater degree of efficiency attainable by the use of coke, every effort will, no doubt, be made to use the new stokers to their fullest capacity.—M.

GLASS WORK DEVELOPMENTS IN ENGLAND

A new national center of glass technology has been established at the University of Sheffield, England, and a special exhibition of chemical glass, laboratory glass and optical glass was recently held in the university buildings. The exhibits were declined by experts in glass manufacturing to be good, and consisted mainly of articles which had not been made in England prior to the war. Dr. Heath, of the Advisory Council of Scientific and Research Research, in an address, declared himself convinced that, in ten years' time, the glass industry of England would be in the first rank.—M.

NEW PAPER-MAKING MATERIAL

According to a report in the *Chemical Trade Journal*, 59 (1916), 572, the Trade and Industry Committee of the Royal Colonial Institute have been investigating the qualities of the grass known as *alang* as a possible paper-making material. It is found in large quantities close to the coasts of Malaya and, as it is a waste product, it can be got for the mere cost of collection. A chemical analysis shows that the grass is capable of yielding a good quantity of cellulose suitable in every way for the manufacture of paper. It is very susceptible to the action of dilute alkalis but the final product is exceptionally pure and readily resolved. The pulp obtained after washing is of good quality and color. By using a mixture of half-pulp obtained from the *alang* grass and half-cotton beaten together, the paper obtained would prove useful as a high-class wrapping paper as it is strong and possesses a comparatively high resistance to folding. The paper made from all-grass pulp, it is added, would, with judicious treatment for improvement of color, be very suitable for writing purposes.—M.

MINERAL PRODUCTION OF SPAIN

The Spanish mineral production for last year, according to official returns, is as follows:

	No. Tons	Mines
Iron ore.....	5,617,839	367
Iron pyrites.....	740,968	20
Copper pyrites.....	1,464,349	45
Copper.....	23,067	10
Lead ores.....	285,265	8
Zinc ores.....	81,921	50
Stibnite.....	20,717	17
Manganese.....	14,328	11
Wolfram.....	511	13
Antimony.....	300	4
Tin.....	102	4
Sulfur.....	28,937	6
Phosphorite.....	9,080	3
Steatite.....	963	5

M.

ARTICLES DECLARED CONTRABAND

By a Proclamation published in the *London Gazette*, December 29, the following articles are declared absolute contraband: Oxalic acid and oxalates, formic acid and formates, phenates, metallic sulfites and thiosulfates, soda lime and bleaching powder, platinum, osmium, ruthenium, rhodium, palladium, iridium and the alloys of the metals, strontium salts and compounds thereof, sulfate of barium (barites), bone-black. The following amendments are made in Proclamation of October 14: For "ethyl alcohol, methyl alcohol" are substituted "alcohols including oil and wood spirit and their derivatives and preparations;" for "aluminum, alumina and salts of aluminum" read "aluminum and its alloys, alumina and salts of aluminum;" for "wolframite, scheelite" read "tungsten ores;" for "fuel other than mineral oils" is substituted "fuel including charcoal other than mineral oils."—M.

INDUSTRIAL COMBINE IN SWEDEN

According to *Engineering*, several amalgamations have lately taken place in Sweden and an important move has just been recorded. The large and ably managed General Swedish Electric Company in Vesterås has purchased a controlling interest in the shares of the Swedish Turbine Co., Ljungström, and in the Surahammar works. The Surahammar works hold a leading position in Sweden as regards railway material, and this specialty as well as others will be pushed with all energy and, at the same time, other lines particularly adapted for the General Swedish Electric Co. will be taken in hand and extended. The Ljungström Turbine Co. controls the Ljung-

ström patents for Sweden, Norway, Denmark, Finland and Russia. A branch factory will probably soon be erected in Russia to meet the great demands of that country. The other Ljungström patents are owned by a separate company with which the General Swedish Electric Co. has arranged an intimate coöperation so far, however, without buying any shares in it, and has in consequence increased its capital from \$5,616,000 to \$7,200,000. The Ljungström Turbine Co. has a share capital of \$1,620,000, of which the General Swedish Electric Co. has purchased \$1,065,600, having likewise acquired two-thirds of the Surahammar Co.'s share capital of \$1,176,000. The General Swedish Electric Co. has done exceedingly well during the war increasing its turnover for the first half of 1916 by some 60 per cent and the share capital has been increased from \$3,216,000 to \$5,616,000 during the period of war.—M.

CELLULOSE FROM SPINACH

As reported in *Paper-Maker*, 52 (1916), 538, a French horticulturist, Mons. R. de Noyer, indicates a very simple and remunerative means of remedying, in a measure, the shortage of paper. In his opinion, it is a question merely of cultivating spinach, which is an excellent vegetable and the stems of which contain 46 per cent of cellulose, while wheat straw contains only 4.1 per cent. Now cellulose forms a considerable factor in the composition of paper, and M. Noyer says that he has experimented with this commodity and, by following the method of the Grenoble paper-making school, has been able to produce a product of remarkable consistency equal to any Japanese product. He concludes by remarking that, with spinach stems after four or five months' culture, an economy of 50 per cent may be realized on the wood-pulp which is ordinarily employed alone, and a paper of good quality is obtained, samples of which M. Noyer possesses. Now is an opportune time to experiment on a large scale and M. Noyer offers to do all in his power to advance this desirable study both by advice as to methods of culture and supply of seeds of which he has an ample provision. —M.

BRITISH BOARD OF TRADE

During the month, December 15 to January 15, the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding the articles are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.

Bakelite	MACHINERY AND PLANT FOR:
Cabot cloth, for Sudan	Molding galalith into rods and
Carbon blocks, for making carbon	slabs
brushes	Making photograph and picture
Carbon brushes	frames
Carbons, cinema	Making horseshoes
CHEMICALS:	Making eyelets for boots and
Ferric chromate	shoes
Ferric oxide	Making matches
Phenolphthalein	Manufacture of saccharine
Saccharin	Making hempen cables for ships
Sodium peroxide	Briquetting bituminous schists
Sulfocyanides	Metal edging for cardboard boxes
Tin oxide, light	Metal name tabs
Zinc chloride, solid	Needles, sewing
Zinc oxide	PAINTS:
Zinc dust (blue powder)	Luminous paint
Dental Plate shears	Red lead
IVORY:	White lead
Acid yellow	"Carbolineum" wood preservative
Naphthol yellow	Pliers, small, 5-in., American make
Rhodamine	Pulleys, pressed steel, American
Tartrazine and other dyes	make
Aniline	Phosphorus compound for match
Elastic cord or cable of 40, 50 or 60	manufacture
elastic threads	Stoves, spirit and "réchaude"
Gabardine cloth, waterproof and	Steel hoops, 3 in. by 26 G.
rubberized	5/16 in. by 26 G.
Gum Thus	Thimbles, nickel-plated

—M

OBITUARIES

CHARLES MARCHAND

Charles Marchand, chemical engineer, was born in la Loupe, Eure et Loire, France, on March 7, 1848, and died at his residence Sea Gate, Long Island, N. Y., January 16, 1917. Soon after his arrival in this country he was elected to Membership in the American Chemical Society, on February 6, 1879. He belonged to a group of French chemists who did much for the Society in those early days—Tessié du Motay, P. Casamajor, A. Bourgougnon, Auguste J. Rossi, and Charles Marchand.

Marchand was a graduate of the "École Centrale des Arts et Manufactures," Paris, France. To enter he had to be a Bachelor of Arts, and on graduating he became "Ingénieur des Arts et Manufactures." While attending lectures there by Prof. Berthelot he was inspired to endeavor to prepare a food ration containing a large amount of protein. He further hoped to provide a large amount of nourishment in tablet or powder form to be taken by invalids who could not tolerate large amounts of heavy foods.

Marchand realized that a large amount of money and time would be required before such a food could be perfected. America seemed to offer a fertile field wherein his goal might be achieved.

Marchand's work in scientific fields probably will be best known by his success with the preparation and preservation of peroxide of hydrogen which was known only as a curiosity and unstable product before Marchand's work. It remained for him to discover the means for producing it in quantities and in such a condition that it could be marketed and used by the consumer when and as desired. When he had perfected his methods of manufacturing a stable and reliable peroxide of hydrogen solution in water, he proudly and joyfully wrote of it to his former colleagues in France. His chagrin may be imagined when they wrote urging him not to speak seriously of his plans because they believed that people would consider him mentally unbalanced. This rebuff from his friends in his native country wounded him beyond his powers to express himself. Later he sent full details to France and when his scientific friends had studied the process, they sent him a large gold medal and their sincere wishes for the successful introduction of the process and product to humanity. After hydrogen peroxide came hydrozone and glycozone, the essential constituent of each being oxygen which is to be liberated in the nascent state.

Marchand gave his personal attention to the manufacturing and marketing of his peroxide of hydrogen, developing the business to a very large and profitable one, finally disposing of his interests in the company to engage in the manufacture of a condensed food product, called "Meatox," which he prepared from beef. However, it developed that the launching successfully of a business of the magnitude he had conceived, required a larger sum than he had available and he was, therefore, compelled to suspend his efforts for the time being.

Later he moved to Portland, Oregon, and became interested in mining and land properties and although these ventures did not prove successful, he was able to live happily and keep up his enthusiasm despite his reverses. While living in Portland, he became acquainted with some paper pulp manufacturers on the Willamette River and from them learned of the serious problem confronting paper pulp manufacturers, the disposal of the waste liquor from sulfite mills. He investigated the problem and then undertook some research work in the laboratory which resulted in his discovering how to purify the liquor so as to produce ethyl alcohol. Marchand then erected a demonstration plant at Kimberly, Wisconsin, which would show the commercial value of his process. This plant has been in operation for some months now, producing pure ethyl alcohol from the waste sulfite liquor at an expense that

would leave a considerable margin of profit. Marchand was engaged in making a few modifications and improvements in his process when he was suddenly stricken with apoplexy.

Marchand was made very happy by the results of his latest invention and while he expected it would make handsome profits, his first desire was to use the large part of these for altruistic purposes. One of his plans was to create a fund to be devoted to improving the welfare of inventors in general, but especially those who are without adequate funds to commercialize their discoveries. He also wanted to offer prizes for research along certain lines, especially looking to the solution of chemical problems having national and even international scope.

Marchand's genial nature endeared him to his friends and scientific associates. His introduction of peroxide of hydrogen to the world entitles him to lasting credit both from his co-scientists and from humanity.

CHARLES A. DOREMUS

RICHARD BRYANT DOLE

Richard Bryant Dole, chemist, Water Resources Branch, U. S. Geological Survey, died in Washington on January 21, after a brief illness. He was born in Portland, Maine, May 8, 1880; graduated with honors from Bowdoin College in 1902; was a graduate student in chemistry and sanitation at Massachusetts Institute of Technology in 1903; and from 1903 until his death served in positions of increasing importance and responsibility with the U. S. Geological Survey.

Mr. Dole's principal activities were related to the chemical and sanitary quality of surface and ground waters of the United States. He conducted a number of surveys of hydrologic basins, determining and reporting on quality of water, source and nature of pollution, methods of purification, and value for industrial use. One of the larger investigations he supervised was a general survey of stream waters of the United States and the published results of this work stand as the most comprehensive compendium of information as to quality of stream waters that has been produced for any country in the world. At the time of his death he was engaged in preparing for publication a compilation of all available information on the quality of surface and ground waters of the United States with interpretations and suggestions for their use in industrial processes. His research into methods of water analysis led to his appointment as a member of the Committee on Standard Methods of Water Analysis of the American Public Health Association and as chairman of the Division of Water, Sewage, and Sanitation of the American Chemical Society. He was a member of these societies for many years and was active in the work of several other associations of chemists, engineers, and sanitarians. He was a member of the Cosmos Club, Washington, D. C., and of the Phi Beta Kappa Society.

Mr. Dole was the author of many articles in technical journals and of several important publications of the Geological Survey. His chapter on Water for Industrial Purposes in *Mineral and Animal Matter in Natural and Chemical Waters* is one of his notable contributions. He represented the United States Government as a member in charge of studies at the National Chemical Conference in 1909 and assisted in the organization of the committee of the Department of the Interior to study international regulations.

Mr. Dole's position for the Government and for the limited technical circles with which he was connected were somewhat restricted by a knowledge of a number of literary expressions in English and French, and by his very high standard of moral and intellectual values in connection with his scientific work.

N. A. COOK

NOTES AND CORRESPONDENCE

COÖPERATION IN INDUSTRIAL RESEARCH WORK

Editor of the Journal of Industrial and Engineering Chemistry:

One of the most important measures of our industrial progress is the ability of American chemists to carry out successful research work. The conditions for such work were never better than now nor have we ever brought out results under greater pressure than in these times of violent activity in chemical industries.

Duplication in research is often an unconscious crime and a needless waste of time with many of us; for when we are forced to develop processes, in absence of information in literature, etc., and produce results at any cost, we often find, at some later day, our work already done by others. Would not an abstract registry of researches permit of greater speed in investigating problems with better results and at the same time largely prevent duplication? Again, in establishing patent rights, would not such a registry open to the public minimize priority claims litigation as well as such antagonistic controversies as the Redmanol-Bakelite?

The writer has reviewed these ideas elsewhere¹ and reads with interest the report² of the Subcommittee of the Committee of One Hundred on Scientific Research of the A. A. S. That there is need for a broader coöperation, a more liberal attitude of industrial heads and a complete publication of researches requires no comment.

In the hands of the members of the American Chemical Society the economic fabric of American industry rests and it is now time to break away from those old retrogressive traditions and from the secrecy of research work to establish that broad coöperation which spells success for our Society. Invested interests have held the situation iron-bound up to the present time with the result that not more than fifty per cent of the data of research work done has been published, while many important results are still withheld—an injustice to the chemist and a serious bar to industrial progress. The reasons for non-publication may be due to a desire for secrecy of unsuccessful results, but in any event if we are to emerge from a superstitious chemical era, narrow-minded secrecy must be replaced by the fullest of coöperation quickly and if such is not the case, are we to suspect that there is no honor among us, or to be driven to look only for selfish advantages?

It often happens that in unsuccessful researches or in those partly completed, there lies an idea of immense value to others—an idea that the original observer overlooks or which does not bear potentially upon results desired. Should not these investigations too be published for the benefit of all? Any answer to these questions largely depends upon our trust in fellow chemists, upon our ability to promote real progress and upon our desire to gain high ethical standards of success.

For final consideration I would suggest that clear abstracts of researches: (1) Complete, (2) In process, (3) Unsuccessful—be published in a special section in *THIS JOURNAL* but preferably in *Chemical Abstracts*. Abstracts so published should be numbered or keyed (so that those interested could learn the source) after some predetermined plan developed perhaps by the Council of the Society. The form used could well pattern after patent abstracts in *Chemical Abstracts*, *vis.*

Purification crude resorcin. No. —, Dec. 20, 1916. 95% U. S. P. product commercially recovered at cost, 70 cents per pound.

Citric acid from acetone. No. —, Dec. 30, 1916. Citric acid and other compounds formed with acetone and dil. H_2SO_4 about 270–280° in 16–18 atmospheres CO_2 .

ROCHESTER, N. Y., January 24, 1917

R. T. WILL

¹ *THIS JOURNAL*, 8 (1916), 78, et seq.

² *Science*, N. S., 35, 1150.

ASSISTANTSHIPS AND FELLOWSHIPS IN CHEMISTRY PRINCETON UNIVERSITY

The Department of Chemistry of Princeton University announces that there are a number of laboratory assistantships in the Department filled by yearly appointment. The holders are ordinarily required to devote about twelve hours per week to assisting in the conduct of the various undergraduate courses. These assistantships afford the holders ample opportunity to pursue graduate studies and investigations leading to one of the higher degrees. At present, the salary is \$500 in case of first-year men, while in case of those re-appointed it is \$550. No tuition or laboratory fees are required and all assistants are allowed \$15 per term (\$30 per year) to cover necessary supplies and breakage of apparatus.

Recommendations for these assistantships must be made on special application blanks, which, with any further information regarding these positions, may be obtained from the Secretary of the Department of Chemistry.

The Department also calls attention to the University Fellowships open to graduate students in Chemistry. These fellowships are divided into two classes, the advanced and the ordinary. The advanced fellowships have an annual stipend of \$1000, exempt from charge for tuition, and are assigned only to graduate students of at least one year's standing who have given evidence of unusual ability in their graduate work and of capacity to engage successfully in research. The ordinary fellowships regularly have a stipend of \$600 on first appointment, and of \$700 on re-appointment, subject to the charge of \$100 for tuition. Candidates for fellowships should write for application blanks to the Dean of the Graduate School, Princeton University.

INDUSTRIAL FELLOWSHIPS IN RUBBER CHEMISTRY MUNICIPAL UNIVERSITY OF AKRON, OHIO

Two industrial fellowships in the study of the chemistry of India rubber have been established at the Municipal University of Akron, one by the Goodyear Tire and Rubber Company and the other by the Firestone Tire and Rubber Company. These fellowships will yield \$300 per year each and will be open to graduates of standard American colleges who have completed a thorough college course in chemistry and are recognized as students of excellent ability. By action of the directors of the university the holder will be exempt from all fees and will render certain services in instruction and laboratory supervision. At the end of the year of work at the Municipal University the holder of the fellowship will enter the employ of the company which has provided the fellowship.

OUR NITROGEN DEMAND AND SUPPLY IN THE EVENT OF WAR—CORRECTION

In the letter by Prof. M. C. Whitaker in *THIS JOURNAL*, 9 (1917), 204, he quotes the estimate in my Iron and Steel Institute paper, of the probable coke-oven ammonia capacity at the end of 1917, as given out under date of July 1st. This is an error, as the paper was in print on May 26th, and the data used were actually of May 1st. The estimate was made from a conservative point of view, and included only plants actually agreed upon at that time. Since then there has been a decided increase in the figures.

THE BARRETT COMPANY

W. H. CHILDS

THE SAMPLING OF FERTILIZERS—A CORRECTION

The address given at the end of the above article, which appeared in *THIS JOURNAL*, 9 (1917), 167, should read "Laboratory of Armour Fertilizer Works, Chicago," instead of Laboratory of Armour & Company, Chicago.

F. S. LODGE

PERSONAL NOTES

The Franklin Institute has recently awarded its Elliott Cresson Gold Medal to Dr. Edwin Fitch Northrup, Research Physicist, of Princeton, N. J. This award was made in recognition of a special type of electric furnace developed by Dr. Northrup, in which a temperature of more than 3000° C. can be developed, and of his pyrometric methods and new pyrometric apparatus for the direct and accurate reading of high temperatures up to 1600 or 1700° C.

Mr. Alex. L. Feild has left the Bureau of Mines and accepted the position of metallurgist and physical chemist with the Gulf Pipe Line Company. His address after March 15 will be Gulf Pipe Line Company, Gulf Building, Houston, Texas.

Mr. James M. Wadsworth of California has been appointed assistant petroleum technologist of the Bureau of Mines.

Mr. K. L. Kithil, formerly connected with the Bureau of Mines, is now general manager of the Schlesinger Radium Company, Denver, Colo.

Mr. George M. Berry, chairman of the Syracuse Section of the A. C. S., and chief chemist of the Halcomb Steel Company, Syracuse, N. Y., has been engaged to give a special course of lectures on metallurgy in the College of Applied Science, of Syracuse University.

Dr. Herbert H. Dow, founder of the Dow Chemical Company, Midland, Mich., spoke on "The Evolution of the American Manufacturing Industries and Their Probable Trend in the Future," at the February 15th meeting of the Detroit Section of the A. C. S. Dr. Bernhard C. Hesse, of New York, will talk on "The American Chemical Society and the Nation," at the March 15th meeting of the Detroit Section Dr. C. E. K. Mees, of the Eastman Kodak Company, has chosen for his illustrated lecture of April 19, the title, "Photographic Research: An Example of the Work of a Specialized Research Laboratory."

A Committee on Analyzed Reagents consisting of W. F. Hillebrand; *Chairman*, Chas. Baskerville, and W. D. Bigelow, has been appointed by President Steiglitz of the American Chemical Society. [See THIS JOURNAL, 9 (1917), 109.]

Mr. William James Mullins, of Franklin, Pa., died on January 20, at the Hotel Schenley, Pittsburgh. Mr. Mullins was born in Steubenville, O., on August 21, 1860. He was reared in Pittsburgh and received his later education in the Massachusetts Institute of Technology, Boston. He went to Franklin as chemist for the Standard Oil Company, which position he held until 1893, when he resigned from active work and devoted himself to art and church work. He is survived by a wife and three daughters.

The next annual convention of the National Fertilizer Association will be held in White Sulphur Springs, W. Va., on July 9.

The United States Civil Service Commission announces an open competitive examination for *metallurgist* (male), salary \$2400-\$3300, on March 6, 1917.

The Burdett Oxygen Company began operation of its Oklahoma plant, located at the Stock Yards Station at Oklahoma City, on February 15th, and will be in a position to furnish oxygen to users in that territory. This is the twelfth plant installed by the Burdett Company in the various industrial centers of the country.

Mr. G. L. F. Philips, technical director of Philips' Glow-lampworks, Limited, Emmlooven, Holland, has been nominated *Doctor honoris causa* by the senate of the Technical University at Delft, Holland.

The department of chemistry of the College of the City of New York offers during the Spring Semester, 1917, the following remaining lectures, open to the public:

March 2—"New Method for Nitrogen Fixation" (experimental, showing utilization of home-made apparatus), by Dr. J. E. Bucher, professor of chemistry, Brown University, Providence, R. I.

March 16—"Chemical Structure and the Biological Function of Tissue Elements," by Dr. P. A. Levene, chief chemist, Rockefeller Institute, New York City.

March 23—"The Conservation of Pine Forests through the Methods of Chemical Research" (illustrated by specimens and stereopticon), by Chas. H. Herty, Editor, *Journal of Industrial & Engineering Chemistry*.
March 30—"The Getting of Wisdom," by Dr. C. E. K. Mees, director of research department, Eastman Kodak Co., Rochester, N. Y.

April 13—"Colloids in Pharmacy" (illustrated and experimental), by Dr. John Uri Lloyd, Cincinnati, O.

April 27—"Some Chemistry of the Tropics" (illustrated from recent observation), by Dr. L. H. Friedburg, professor emeritus, College of the City of New York.

Dr. Chas. H. Herty addressed the Pittsburgh Section of the A. C. S., on "Chemistry in a National Crisis," at their 133rd Regular Meeting on February 15.

Mr. C. D. McCourt, of London, who was prominently identified with Prof. William A. Bone in surface combustion matters, was killed on October 8, 1916, at Eaucourt l'Abbaye, France. This information was received in a letter from Mr. Henry Edmunds, Brighton, England, to Mr. Carleton Ellis, Montclair, N. J. Mr. McCourt spent some time in this country several years ago in the development of the applications of surface combustion and his charming personality made for him many friends.

The Mont Color & Chemical Company, Monticello, N. Y., has been formed to produce chemicals, intermediates and dyes from coal tar.

Prof. F. P. Venable, of Chapel Hill, N. C., an ex-president of the University of North Carolina, and an ex-president of the American Chemical Society, was appointed by President Steiglitz to represent the American Chemical Society at the inauguration of Wallace Carl Riddick as president of the North Carolina College of Agriculture and Mechanic Arts, on February 22, 1917.

The First National Bank of Boston is opening a South American Branch at Buenos Aires, Argentina, under the managership of Mr. Noel F. Tribe, a banker of experience, who has resided in the Argentine for the past 20 years.

Dr. Benjamin T. Brooks, of the Mellon Institute, has accepted the position of Research Chemist for the Bayway Chemical Company, of New York, and will take up his new duties on April 1st.

Mr. Edgar B. Carter, director of scientific work at Swan-Myers Company, addressed the Indiana Section of the A. C. S. on "Immunity and Immuno-Chemistry," at their February 9th meeting. Dr. Wilder D. Bancroft's address on March 9th will be "Contact Catalysis."

Mr. Earl B. Smith has been transferred to the U. S. Bureau of Soils as mechanical engineer in the design and construction of the new government potash plant at Sumnerland, Cal., where he and Dr. Turrentine, of the Department of Agriculture will investigate the commercial possibilities at extracting potash iodine, tar products, acetone, etc. from Pacific coast kelps.

John Woods Beckman and Herbert Emil Linden announce the formation of the Beckman and Linden Engineering Corporation for the purpose of undertaking the development and management of chemical metallurgical, petrochemical and electrochemical industries, as well as hydroelectric enterprises. Office: Edison Building, San Francisco.

GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

SMITHSONIAN INSTITUTION

International Catalogue of Scientific Literature. Separate from Report, 1916. 5 pp. This is a report of the United States Regional Bureau of International Catalogue of Scientific Literature, fiscal year 1916.

SUPERINTENDENT OF DOCUMENTS

Forestry. Government publications relating to tree planting, wood tests, and lumber and timber industries, for sale by the Superintendent of Documents, are given in Price List 43, 10th Edition, 21 pp. Issued December, 1916.

Soils and Fertilizers. Government publications relating to these subjects and for sale by the Superintendent of Documents are given in Price List 46, 10th Edition, 20 pp. Issued December, 1916.

CONGRESSIONAL COMMITTEES

Paper Mills. House Report 1244, 19 pp. This is a report to accompany House Bill 17699 which authorizes the Public Printer to provide pulp and paper mill or mills for manufacture of print paper for the Government.

Coal and Other Mineral Lands. Senate Report 882, from Committee on Indian Affairs. 3 pp. December 19, 1916. This report relates to the disposal of coal and mineral deposits in Indian lands and is intended to accompany Senate Bill 583.

Coal Lands. Senate Report 889, from the Committee on Indian Affairs. 3 pp. December 20, 1916. This report, to accompany House Joint Resolution 306, relates to the authorization of the Secretary of the Interior to extend the time for payment of deferred installments due on purchases of tracts of surface of segregated coal and asphalt lands of Choctaw and Chickasaw tribes in Oklahoma. See also House Report 1219 intended to accompany the same bill, dated December 15, 1916.

Mines and Mineral Resources. Senate Report 880, from the Committee on Indian Affairs. 3 pp. December 16, 1916. This report relates to House Bill 12426 to authorize mining for metalliferous minerals on Indian reservations.

DEPARTMENT OF AGRICULTURE

The following four articles in the December issues of the *Journal of Agricultural Research* contain material of chemical interest. Page references and dates refer to Volume 7.

(1) **Nitrification in Semiarid Soils.** W. P. KELLEY. (Pp. 417-438; December 4.)

(2) **Factors Affecting the Evaporation of Moisture from the Soil.** F. S. HARRIS AND J. S. ROBINSON. (Pp. 439-460; December 4.)

(3) **Assimilation of Iron by Rice from Certain Nutrient Solutions.** P. L. GILE AND J. O. CARRERO. (Pp. 503-528; December 18.)

(4) **Influence of Bordeaux Mixture on the Rates of Transpiration from Abscised Leaves and from Potted Plants.** WILLIAM H. MARTIN. (Pp. 529-547; December 18.)

Important Soils of the United States. Unnumbered publication of Bureau of Soils. 28 pp. and map. This report is issued

to accompany the collection of soils and sub-soils for use of schools and colleges teaching agriculture and physical geography.

Sea Island Cotton. W. A. ORTON. *Farmers' Bulletin* 787, from the Bureau of Plant Industry, issued December 30, 1916. 40 pp.

The Production of Sweet-Orange Oil and a New Machine for Peeling Citrus Fruits. S. C. HOOD AND G. A. RUSSELL. Department Bulletin 399, contribution from the Bureau of Plant Industry. 45 pp. Paper, 40 cents. Possibility is suggested of the commercial production of sweet-orange oil from waste oranges, and there are given detailed descriptions and illustrations of a machine for peeling oranges, grape fruit, and lemons.

The Soy Bean, with Special Reference to its Utilization for Oil, Cake, and Other Products. C. V. PIPER AND W. J. MORSE. Department Bulletin 439, contribution from the Bureau of Plant Industry, issued December 22nd. 20 pp. Paper, 5 cents. This reports on the cultivation of soy beans in various countries of the world, their use as food for man and beast and as a fertilizer, methods of oil extraction, uses of the oil, etc.

The Chemical Composition of Lime-Sulfur Animal Dips. ROBERT M. CHAPIN. Department Bulletin 451, contribution from the Bureau of Animal Industry, issued December 14. 20 pp. Paper, 5 cents. Experiments are described in the preparation of a solution for dipping cattle and sheep, and the "8-18-10" formula prescribed by the Animal Industry Bureau.

The Chemical Composition of American Grapes Grown in the Central and Eastern States. W. B. ALWOOD, B. G. HARTMANN, J. R. EOFF, S. F. SHERWOOD, J. O. CARRERO AND T. S. HARDING. Department Bulletin 452, contribution from the Bureau of Chemistry, issued December 18. 20 pp. Paper, 5 cents. Statistical data are given of grapes examined, discussion of analytical results, and summary of sugar and acid for five years.

The Effect of Cultural and Climatic Conditions on the Yield and Quality of Peppermint Oil. FRANK RABAK. Department Bulletin 454, contribution from the Bureau of Plant Industry, issued December 9. 16 pp. Paper, 5 cents. Proof is presented that conditions of soil and climate are influential factors in the formation of oil and its constituents in the peppermint plant.

The Drying for Milling Purposes of Damp and Garlicky Wheat. J. H. COX. Department Bulletin 455, contribution from the Bureau of Plant Industry, issued December 15. 11 pp. Paper, 5 cents. This article indicates the proper temperature and the best methods for artificial drying, cleaning, and handling.

The Use of Energy Values in the Computation of Rations for Farm Animals. HENRY PRENTISS ARMSBY. Department Bulletin 459, contribution from the Bureau of Animal Industry, issued December 15. 31 pp. Paper, 5 cents. This is a revision of *Farmers' Bulletin* showing 346, the feed requirements of various cattle, relative value of feed, and methods of compounding rations.

Fats and Their Economical Use in the Home. A. D. HOLMES AND H. L. LANG. Department Bulletin 469, contribution from the States Relations Service, issued December 15. 27 pp. Paper, 5 cents. This report discusses character, selection, and use of edible fats, of interest to teachers and students of domestic science, housekeepers, and others concerned with the problems of food selection and preparation.

Studies on the Digestibility of the Grain Sorghums. C. F. LANGWORTHY AND A. D. HOLMES. Department Bulletin 470,

contribution from the States Relations Service, issued December 22. 31 pp. Paper, 5 cents.

Table for Converting Weights of Mechanical Separations into Percentages of the Sample Analyzed. E. G. BOERNER. Department Bulletin 516, contribution from the Bureau of Plant Industry and the Office of Markets and Rural Organization, issued December 28. 21 pp. Paper, 5 cents. A table is given which enables the grain analyst to obtain the equivalent percentage of a sample of grain when the weight of the sample analyzed and the weight of the mechanical separation are given.

Phosphate Fertilizers for Hawaiian Soils, and Their Availability. WILLIAM T. MCGEORGE. Bulletin 41, Hawaii Agricultural Experiment Station, issued December 2. 45 pp., 4 plates. Paper, 10 cents. Results are presented of scientific and practical investigations in which it is found that phosphate fertilizers should be applied to Hawaiian soils in a soluble form to produce the best results.

Improved Apparatus for Use in Making Acidity Determinations of Corn. H. J. BESLEY AND G. H. BASTON. Circular No. 68, Office of the Secretary, issued December 30. 4 pp. Paper, 5 cents.

Pulp and Paper and Other Products from Waste Resinous Woods. Reprint from the Bureau of Chemistry Bulletin 159. Paper, 5 cents. This gives results of experimental work in the making of pulp, paper, turpentine, resin oil, and methyl alcohol.

Technical Paper Studies. Reprint from the Bureau of Chemistry Bulletin 150. Paper, 10 cents. Methods are described with analysis and investigations of the quality of commercial hydrogen dioxide, glycerin, beeswax and cocaine.

Peanut Butter. Circular 98, Reprint of the Bureau of Plant Industry. Paper, 5 cents. This is a description of the varieties of peanuts and factory and equipment necessary for the manufacture of peanut butter.

BUREAU OF MINES

Prospecting and Mining of Copper Ore at Santa Rita, New Mexico. DONALD F. MACDONALD AND CHARLES ENZIAN. Bulletin 107. 115 pp. Paper, 25 cents.

Molybdenum: Its Ores and Their Concentration with a Discussion of Markets, Prices and Uses. FREDERICK W. HORTON. Bulletin 111. "The direct purpose of this bulletin is, on the one hand, to prove to possible consumers of molybdenum that the element is not as rare as commonly supposed, and that this country possesses many deposits of low-grade ore from which large supplies may be derived, and on the other hand, to prove to present and prospective producers of molybdenum that there is a latent market for their product in the alloy-steel trade, which needs only the assurance of steady supplies for a considerable development. It is also intended to assist the miner of molybdenum by giving him information regarding various methods of concentration that have proven applicable to the different types of molybdenum ore, and by acquainting him with market conditions, uses, prices, etc. The various molybdenum minerals are described in detail, and tests for their determination are given to aid the prospector in recognizing them. In addition to the most applicable and reliable qualitative tests for molybdenum, the quantitative determination of the element is described in some detail, as the methods of analyses recommended in the ordinary textbooks will not in general give correct results, particularly on low grade ores."

"The unprecedented demand for steel hardening metals occasioned by the European war is slowly drawing the attention both of prospective consumers and of producers to possibilities in regard to molybdenum. Several mining operations looking toward a considerable production of both molybdenite and wolframite have already been commenced, and manufacturers are investigating the possibilities of using molybdenum in a large way. The fact that molybdenum is now (April 1, 1916)

selling at \$3 to \$4 a pound, as compared with \$8 to \$10 a pound for tungsten, and the further fact that 1 pound of molybdenum will produce approximately the same results as 2 or 3 pounds of tungsten, are serving to quicken this interest.

"Under the influence of the high prices being paid for the metal and the unusual demand, the whole molybdenum industry is developing as never before, not only in the United States, but also in Queensland, New South Wales, and Norway, the three countries that have previously supplied practically the entire world's production."

The Principles and Practice of Sampling Metallic Metallurgical Materials with Special Reference to the Sampling of Copper Bullion. EDWARD KELLER. Bulletin 122, 94 pp. Paper, 20 cents. A large number of methods are discussed in considerable detail with elaborate illustrations and a considerable number of experimental results showing the relative value of different procedures.

"Considerable space has been devoted to the general and theoretical principles on the ground that under modern conditions the best results in any field of activity can be attained only with the aid of an adequate knowledge of the best theories underlying the practice. . . . No attempt has been made to advocate any one method, but it is hoped that the analyses of all of the methods in use will show where each may be correctly and safely applied. The fact that it is possible to demonstrate the theoretical correctness of several methods indicates the invalidity of the claim that any single one of them is the standard."

The Analytical Distillation of Petroleum. W. F. RITTMAN AND E. W. DEAN. Bulletin 125, 68 pp. Paper, 15 cents. "This report presents the results of an investigation conducted by the Bureau of Mines for the purpose of assisting in the establishment of a satisfactory standard method for the analytical distillation of petroleum, a problem of great importance to the petroleum industry. Experiments were performed for the purpose of studying the characteristics of methods typical of those in use; comparative studies were made of the efficiencies of the principal types of fractionation apparatus available to the petroleum chemist; and the characteristics of a type of apparatus that the results of the experiments seemed to indicate was best adapted to the purpose, were investigated in detail. Also, some experiments were made to determine the effect of cracking as a factor in the analytical distillation of petroleum in still-heads."

This report is substantially an extension of the articles published by the same authors, *THIS JOURNAL*, 7 (1915), 185-95 and 754-60.

Bibliography of Recent Literature on Flotation of Ores, January to June, 1916. D. A. LYON, O. C. RALSTON, F. B. JANNEY AND R. S. LEWIS. Technical Paper 135, 18 pp. Paper, 8 cents.

Physical and Chemical Properties of Gasolines Sold Throughout the United States during the Calendar Year 1915. W. F. RITTMAN, W. A. JACOBS AND E. W. DEAN. Technical Paper 163, 35 pp. Paper, 10 cents. "The Bureau of Mines, in the course of its petroleum investigations, has noted the dearth of published information regarding the physical and chemical properties of different varieties of gasoline generally marketed. Such information is of great importance both to producers and consumers, and for this reason it was deemed advisable to conduct an investigation to determine the properties of gasolines sold throughout the United States during 1915. The results of this investigation are reported in this paper."

GEOLOGICAL SURVEY

Gypsum in Southern Part of Bighorn Mountains, Wyoming. CHARLES F. LEITCH AND J. D. DALL COOPER. Bulletin 404, 11 pp.

Placer Deposits of the Manhattan District Nevada. HENRY G. FERGUSON. Bulletin 640-J, from Contributions to Economic Geology, 1916, Part I, pp. 163-193. Published January 20, 1917.

The Garrison and Philipsburg Phosphate Fields, Montana. J. T. PARDEE. Bulletin 640-K, from Contributions to Economic Geology, 1916, Part I, pp. 195-228. Published January 20, 1917. "Workable deposits of high-grade rock phosphate (containing 60 per cent or more tricalcium phosphate) occur in both the Garrison and Philipsburg fields. That in the Garrison field lies from 6 to 10 miles north of the town of Garrison and is easily accessible, and the portion considered as available to mining contains by estimate 97,000,000 long tons (equivalent to 108,640,000 short tons of 2,000 pounds), an amount about twice as great as the total production of the United States to date. About one-third of the amount lies above the natural drainage levels, and much of this portion can be very readily extracted by means of adits driven along the phosphate bed.

"In the Philipsburg field too little work has been done to justify a tonnage estimate, but the deposits are believed to be extensive, and are known to be in two places at least of workable size and readily available to mining."

Anticlines in the Blackfeet Indian Reservation, Montana. EUGENE STEBINGER. Bulletin 641-J, from Contributions to Economic Geology, 1916, Part II, pp. 281-305. Published January 22, 1917. "The purpose of this paper is to give a brief account of the geologic formations in the reservation and of their lay or geologic structure, and a more detailed description of the anticlines and of the formations that appear to contain oil or gas in Southern Alberta and Northern Montana.

"The discovery of small quantities of oil and gas in several anticlines along the eastern front of the Rocky Mountains west of Calgary, Alberta, has aroused interest in the possible oil and gas resources of the formations in this general region, especially of the southern extensions of the folded and faulted beds that were productive in Canada.

"The general conditions in this region suggest that drilling in the Blackfeet Indian Reservation would have about the same chance of success as in the adjacent region in Southern Alberta, extending from the international boundary northward to Calgary—a region in which drilling by over 40 companies during the last three years has been slightly successful."

Coals in the Area between Bon Air and Clifty, Tennessee. CHARLES BUTTS. Bulletin 641-K, from Contributions to Economic Geology, 1916, Part II, pp. 307-310. Published January 19, 1917. "Present knowledge, therefore, seems to justify the conclusion that two coal beds lie beneath the area represented by the unshaded space on the economic-geology map in the Pikeville folio but that the areas in which these coals are workable are patchy in distribution, so that any investment or mining in this area should be preceded by careful and thorough prospecting."

Petroleum Withdrawals and Restorations Affecting Public Domain. Bulletin 623, Appendix A, 15 pp. Paper, 5 cents.

Nickel in 1915. FRANK L. HESS. Mineral Resources of the United States, 1915, Part I, pp. 743-766. Published January 12, 1917. "No nickel ores are known to have been mined in the United States in recent years, but an equivalent of 822 short tons of nickel was saved in 1915 as a by-product in the electrolytic refining of copper. Of this output the larger part was marketed as metallic nickel and the smaller part was contained in hydrous nickel sulfate.

"What part of this nickel came from American pig or blister copper and what part from foreign copper is uncertain, but it is roughly estimated that American ores produced between one-half and two-thirds of the whole.

"The great bulk of the nickel supply of the United States has been drawn for years from Canada. During 1915 smaller quanti-

ties were imported from New Caledonia, Australia, and Norway.

"During the general stock-taking which has been going on in the United States during the last year many questions as to the country's resources in nickel have been asked, and in order to answer these questions and to show what nickel and nickel ore would be available in case of urgent need and shortage of supplies from other countries, the information available on the deposits of the United States has been epitomized in this paper.

"The nickel deposits of the United States are small compared with the unrivaled deposits at Sudbury, Canada, but they have in the past made some production and will probably do so again.

"The United States refines much more nickel than it can use, so that though not a large producer it is a large exporter."

This report also discusses the forms of occurrence of nickel, nickel minerals, market for nickel ores, laboratory tests for nickel, and the uses of this metal. A long table is presented giving the analyses reported by various authors of a large number of nickel alloys.

Coke in 1915. C. E. LESHER. Mineral Resources of the United States, 1915, Part II, pp. 515-558. Published December 14, 1916. "The quantity of coke produced in the United States in 1915 was 41,581,150 net tons, valued at \$105,503,868, an increase, compared with 1914, of 7,025,236 tons, or 20 per cent, in quantity, and of \$17,169,651, or 19 per cent, in value. By-product coke showed the larger gain, the total quantity, 14,072,895 tons in 1915, being an increase of 2,852,952 tons, or 25 per cent over 1914. Beehive coke output in 1915 was 27,508,255 tons, a gain of 18 per cent, compared with 1914. By far the greater part of the coke manufactured (about 90 per cent in 1915) is used in the iron furnaces of the country, and the quantity of coke made annually depends to a large extent upon the demand from the iron and steel trade. It follows, then, that the rate of production of coke should correspond closely to the rate of pig-iron output, and that this is true is indicated by the graphic record shown.

AVERAGE YIELD OF BY-PRODUCTS PER TON OF COAL (2,000 POUNDS) FROM ALL OPERATIONS IN 1915

Coke.....	1,440	pounds
Tar.....	7.1	gallons
Ammonium sulfate.....	20.1	pounds
Light oil.....	1.54	gallons
Total.....	10,950	cu. ft.
Surplus sold or used.....	4,325	cu. ft.
Burned in coking process.....	6,270	cu. ft.
Wasted.....	355	cu. ft.

BY-PRODUCTS OBTAINED FROM COKE-OVEN OPERATIONS IN 1915

PRODUCT	QUANTITY	VALUE	Average value
Tar obtained and sold.....	138,414,601 gallons	\$ 3,568,384	\$0.026
Ammonia obtained and sold.....			
Sulfate.....	199,900,487 pounds	5,648,958	0.028
Liquor.....	10,626,612 gallons	1,240,473	0.117
Anhydrous or free ammonia(g).....			
30,002,196 pounds		2,978,044	0.099
Gas produced.....	213,667,614 M cu. ft.
Surplus gas sold or used:			
Illuminating.....	17,196,426 M cu. ft.	3,083,311	0.179
Domestic fuel.....	27,590,624 M cu. ft.	3,158,129	0.114
Industrial fuel.....	39,568,864 M cu. ft.	2,383,459	0.060
Benzol products:			
Crude light oils.....	13,082,678 gallons	4,304,281	0.33
Secondary light oils.....	182,039 gallons	28,731	0.16
Benzol.....	2,516,483 gallons	1,428,323	0.568
Toluol.....	623,506 gallons	1,529,803	2.45
Solvent naphtha.....	196,151 gallons	46,233	0.24
Naphthalene.....	465,865 pounds	46,959	0.10
Other products(b).....	379,491
Coke.....	14,072,895 net tons	\$29,824,579 48,558,325	3.45
		\$78,382,904	

(a) Includes liquor and sulfate sold on pound basis of NH₃.

(b) Includes breeze, retort carbon, domestic coke and coke dust, and aniline oil.

"The average value per ton at the ovens of the coke manufactured in 1915 was \$2.54, a slight decrease from \$2.56 in 1914. Alabama, Colorado, Illinois, Indiana, and Tennessee were the only states recording increase in value per ton.

"The recovery of the valuable by-products from American coke manufacture made big advances in 1915 and has now at-

tained the proportions of an important industry. The value of these by-products was nearly \$30,000,000, a large increase over the previous high-water mark of \$17,500,000 in 1914. Although there were material increases in the output and value of gas, tar, and ammonia, which was to be expected with a greater output of by-product coke, the increase in benzol products was remarkable and presented the most interesting feature of the year in the coke industry. The value of these products rose from less than \$1,000,000 in 1914 to more than \$7,760,000 in 1915. Benzol has been recovered in this country from coke-oven gas for a number of years, but prior to 1915 the market was small and the price low.

"In 1914 there were 14 benzol plants in the United States, but they were all controlled by one company, and, therefore, it is not feasible to publish the statistics of their production for that or previous years. Sixteen additional coke plants were equipped with benzol apparatus in 1915, and the output was very greatly increased.

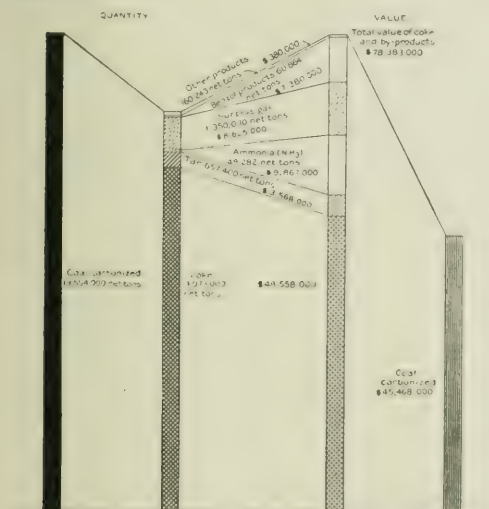


DIAGRAM SHOWING QUANTITY AND VALUE OF COAL CARBONIZED IN BY-PRODUCT COKE OVENS IN THE UNITED STATES IN 1915, AND QUANTITY AND VALUE OF THE PRODUCTS OBTAINED

"The accompanying diagram shows graphically the quantity of coal carbonized or treated in by-product ovens and the quantities of by-products obtained; also the value at the ovens of the coke and the resultant products. The by-products shown in preceding tables in various units, as gallons and cubic feet, have been reduced to net tons for comparison. The weight of gas used, 32 pounds per 1000 cubic feet, was calculated from an average analysis of debenzolized gas. Tar was considered to have a specific gravity of 1.14, and light oil a specific gravity of 0.88. All ammonia was reduced to tons of NH_3 . Surplus gas only is shown, as no value is attached to gas consumed in the process or wasted."

Petroleum in 1915. JOHN D. NORTHRUP. Mineral Resources of the United States, 1915, Part II, pp. 559-760. Published December 12, 1916. "Measured by marketed production, the year 1915 was the greatest in the history of the crude petroleum industry in this country, the quantity involved being 780,304,304 barrels, as compared with the previously established record of 365,760,535 barrels, attained in 1914."

The data presented in this report are given in great detail by districts and for different periods.

Clay-Working Industries and Building Operations in the Larger Cities in 1915. JEFFERSON MIDDLETON. Mineral Resources of the United States, 1915, Part II, pp. 859-926. Published December 22, 1916. "Of the two great divisions of the industry—(1) brick and tile and (2) pottery—the former showed a decrease and the latter showed an increase in value. The decrease in value of brick and tile was \$3,793,978 or nearly 3 per cent; the increase in pottery was \$1,927,227, or more than 5 per cent.

CLAY PRODUCTS OF THE UNITED STATES IN 1915

PRODUCT	VALUE	Percentage Increase or decrease in 1915
Common brick.....	\$ 42,145,292	+ 3.71
Vitrified brick or block.....	12,230,899	+ 2.16
Front brick.....	9,535,536	+ 2.65
Fancy or ornamental brick.....	109,425	+12.08
Enameled brick.....	835,808	+22.25
Drain tile.....	8,879,264	+ 4.19
Sewer pipe.....	11,259,349	+19.66
Architectural terra cotta.....	4,796,062	+21.22
Fireproofing.....	7,800,928	+ 6.97
Tile (not drain).....	5,186,055	+ 9.11
Stove lining.....	459,111	+11.76
Fire-brick.....	18,839,931	+14.68
Miscellaneous.....	3,716,944	+17.41
Total brick and tile.....	125,794,844	+ 2.93
Total pottery.....	37,325,388	+ 5.44
GRAND TOTAL.....	\$163,120,232	+ 1.13

"A study of the tables shows that the pottery industry has made much progress, that the value of the domestic output has nearly doubled in the last 15 years, that from an industry of minor importance, both as to quality and value, pottery has risen to great importance, supplying large quantities of wares of ever-increasing excellence, and that this country has reached a state where it is practically independent of the Old World in the manufacture of pottery, more than four-fifths of the wares now sold being domestic. The imports of pottery, which have always been a large factor in consumption, reached their maximum value in 1907, and have declined since that date, the acceleration of the decline in the last two years being doubtless due to the European war. In 1915 they were valued at less than half as much as in 1907.

"Production of porcelain electrical supplies, in which there was the largest decrease in 1914, showed the largest increase in 1915—\$540,932, or more than 13 per cent. White ware and stoneware also increased considerably in value. The value of china showed a small decrease—\$54,530, or about 2 per cent.

"The value of white ware, including china, but excluding sanitary ware and porcelain electrical supplies, was \$17,654,398. In 1915, an increase of \$301,633 over 1914. If the value of sanitary ware and porcelain electrical supplies be added, the total for 1915 would be \$30,318,816, or more than 81 per cent of the value of all pottery products, and an increase of \$961,512."

Natural Gas in 1915. JOHN D. NORTHRUP. Mineral Resources of the United States, 1915, Part II, pp. 927-1015. Published December 29, 1916. "The steady annual increase in gasoline production that has characterized the growth of the casing-head gasoline industry in the United States during the last five years was fully maintained in 1915. In that year the quantity of raw gasoline extracted from natural gas and sold in this country amounted to 65,364,665 gallons, a quantity greater by 22,712,043 gallons, or 53 per cent, than the record output in 1914 and greater by 31,303,848 gallons, or 103 per cent, than the output in 1913.

"As a factor in the total production of gasoline in the United States the contribution of the casing-head gasoline industry is of relatively slight though increasing importance. According to statistics compiled by the Bureau of the Census the total quantity of gasoline produced in the United States during 1915 was 1,278,712,043 gallons, of which 65,364,665 gallons, or about 5 per cent, was extracted from natural gas.

"At the end of 1915 there were 244 plants for the production of gasoline from natural gas in operation in the United States, as compared with 1914 when there were 200. The total capacity of these plants was 1,278,712,043 gallons per year."

capacity of all gasoline plants increased from 179,353 gallons at the end of 1915, a gain of 30 per cent that is accounted for in part by a 7 per cent increase in the number of new plants and in part by the fact that many of the plants in operation at the end of 1914 operated during only a part of that year. On the basis of 300 working days, the actual average output of casing-head gasoline in 1915 was 217,882 gallons a day."

SANITARY LEGISLATION

Transportation of Living Cultures of Pathogenic Bacteria. Regulation of the Public Health Council of New York State, February 4, 1916. Reported *Public Health Reports*, 32, p. 96

Milk and Milk Products. The following three regulations reported in *Public Health Reports* in the volume and page indicated relate to "Milk and Milk Products, Their Production, Care and Sale" and include standards for purity or composition of certain of these materials:

- (1) Winston-Salem, North Carolina, Ordinance of June 9, 1916. (Vol. 31, pp. 3440-2.)
- (2) San Antonio, Texas, Ordinance of November 20, 1916. (Vol. 31, p. 3483.)
- (3) San Francisco, California, Ordinance 3961 N. S. adopted November 9, 1916. (Vol. 32, pp. 25-39.)

COMMERCE REPORTS—JANUARY, 1917

The mineral output of India in general shows a decided increase, particularly of petroleum, magnesite, copper and ochre. (P. 4.)

The Argentine and Paraguayan producers of quebracho extract, used for tanning, have arranged to limit the production in order to maintain the price. (P. 12.)

The production of cement in Japan is now in excess of the demand. (P. 23.)

Ferro-tungsten is now being produced near Liverpool, the supply being now greater than the demand. (P. 23.)

A large plant for creosoting lumber, especially for marine construction, has been erected at Vancouver. (P. 30.)

A new process for the recovery of sucrose from the final molasses has been devised in Hawaii. It depends upon evaporation to 99 per cent Brix, and the use of special high-speed centrifugals. (P. 31.)

The dyestuff industry in Switzerland has been greatly hampered by the lack of coal tar and sulfuric acid. (P. 82.)

Experiments in Germany upon the use of **nettle fiber** as a substitute for cotton are very promising. It is estimated that in Austria there is sufficient uncultivated land to produce sufficient nettle fiber to replace the normal cotton imports of Germany and Austria. (Pp. 89, 114.)

There is a marked increase in the demand in the United States for Spanish oxide of iron used as a red pigment. (P. 94.)

A process has been devised in England for the manufacture of artificial milk from water, sugar, phosphates, and ground peanuts and soya beans. Lactic bacteria culture is used to produce a slight acidity and after pasteurization, a small amount of citric acid is added. (P. 130.)

Pig iron production of Canada in 1916 exceeds that of 1915 by 28 per cent; and the production of steel exceeds that of 1915 by 42 per cent. In 1916, 43,790 tons of steel were made in electric furnaces, as compared with 61 tons in 1915. (P. 135.)

A large factory is to be erected at Messina, Sicily, for the manufacture of tartaric, citric, and sulfuric acids. (P. 146.)

Efforts are being made to increase the use in France of "alfa" for paper stock. Alfa is a variety of esparto, grown extensively in Algiers and Tunis. (Pp. 158-9.)

Special efforts are being made to increase the cultivation of flax in Silesia, Germany. (P. 172.)

Cultivation of coconuts for the production of copra is being increased in the Bahamas. (P. 200.)

With favorable weather conditions the Cuban sugar crop for

this year, will exceed the record crop of last year. (P. 209.)

Detailed statistics of the seed-oil industry of the United Kingdom are given, including the following seeds and oils, *viz.*, castor, cotton, linseed, rape, soya bean, oil nuts, copra, and palm kernels. (Pp. 218-21.)

Efforts are being made by Scandinavian capitalists to obtain concessions in Argentina for the cultivation of native fibers and manufacture of twine, bagging, etc. (P. 223.)

The supply of certain dyes in Japan is now in excess of the demand, so that efforts are being made to cancel the embargo on exports. (P. 223.)

Experiments are being made upon the cultivation of sugar beets in China. (P. 227.)

The sugar crop of Java and the Philippines is larger than in previous years. (P. 227.)

The output of leather in Japan is now twice as great as in 1914. (P. 236.)

The production of manganese ore in the United States in 1916 was three times that of 1915, the leading producer being California. Imports of manganese ore were nearly double those of 1915. (P. 260.)

At present paper pulp is more expensive in England than rags, so that the latter are being used in many cases instead of pulp. (P. 290.)

The use of kapok, the silky fiber from the West Indies, for upholstery, life preservers, etc., is increasing in England. (P. 295.)

Large numbers of American experts are employed in Australia in the glass, rubber, copper, lead and steel industries. (P. 306.)

Manganese ore is now being exported from Costa Rica. (P. 309.)

The Chilean Government is about to sell some of its nitrate lands. (P. 310.)

A large beet sugar factory is to be erected in Chosen (Korea) by Japanese capital. Large amounts of paper, made from mulberry bark, are being exported from Chosen. (P. 317.)

New cinnabar deposits are reported from New Zealand. (P. 327.)

Large deposits of monazite have been discovered in Ceylon. (P. 354.)

The Japanese output of zinc has increased over 250 per cent. (P. 375.)

The British Empire produces 75 per cent of the world's supply of rubber but consumes not more than 12 per cent of it, the United States taking approximately 62.5 per cent. (P. 393.)

The United States imports 88 per cent of the paper and pulp exported from Canada. (P. 407.)

SPECIAL SUPPLEMENTS ISSUED IN JANUARY

BARBADOS—22d	CHOSEN (KOREA)—55c
VENEZUELA—48b	STRAITS SETTLEMENTS—56b
DUTCH EAST INDIES—53a	SOCIETY ISLANDS—62a

STATISTICS OF EXPORTS TO THE UNITED STATES

CARTAGENA—370	COLOM.—409	NIAGARA FALLS, CAN.—409	BRUSSELS—241
Gold	Abrasive		Photographic glass
Hides	Aloxite		Window glass
Ipecac	Calcium carbide		Glue
Platinum	Cobalt oxide		Artificial silk
Rubber	Calcium cyanamid		
Tannic acid	Lime nitrogen		ECUADOR—293
Mangrove	Ferrosilicon		Gold
	Pig iron		Hides
	Newsprint paper		Rubber
DUTCH EAST INDIES—Sup. 53a	Silver		
Potassium chloride	Paper pulp		CHOSEN, KOREA—Sup. 55c
Damar			Gold
Gambier	BARBADOS—Sup. 22d		Copper
Peanuts	Bakata		Graphite
Hides	Manjak		Hides
Jelutong	Molasses		
Kapok	SKHS—Sugar		STRAITS SETTLEMENTS—Sup. 56b
Oil of citronella			Gambier
Paraffin	VENEZUELA—Sup. 48b		Gum copal
Quinine	Bones		Gutta percha
Rubber	Copaiba		Hides
Tin	Divi-divi		Jelutong
Gutta percha	Hides		Coconut oil
Gum benzoin	Fustic		Rubber
Gum copal			Tin

NEW PUBLICATIONS

By IRVING DE MATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- Arithmetic for Engineers. C. B. CLAPHAM. 8vo. 436 pp. Price, \$3.00. E. P. Dutton & Co., New York.
- Chemistry for Experimentation. W. F. HOYT. 12mo. 160 pp. Price, \$0.70. D. Van Nostrand Co., New York.
- Chemistry: General Chemistry. H. P. Cady. 8vo. 522 pp. Price, \$2.25. McGraw-Hill Book Co., New York.
- Chemistry: Résumé aide-mémoire Chimie. R. LESPIEAU. 16mo. 152 pp. Price, 1 fr. 50. Hachette et Cie., Paris.
- Concrete, Plain and Reinforced. F. W. TAYLOR and S. E. THOMPSON. 3rd Ed. 8vo. 885 pp. Price, \$5.00. John Wiley & Sons, New York.
- Copper: Sulfate et Acétate de cuivre. P. TEILLARD. 8vo. 164 pp. Charité Pierre Rouge, Montpellier.
- Electrotechnics: Leçons d'électrotechnique général. P. JANET. 8vo. 426 pp. Price, 13 fr. Gauthier-Villars et Cie., Paris.
- Engineering: Notes et Formules de l'ingénieur. de LAHARPE. 2 Vols. 18th Ed. 2956 pp. L. Geisler, Paris.
- Engineering Mathematics. W. E. WYNN and W. SPRAGGON. 220 pp. Price, \$2.00. D. Van Nostrand Co., New York.
- Explosives: Mécanique des explosifs. Etude de dynamique chimique. E. JOUGUET. 18mo. 516 pp. Octave Doin et fils, Paris.
- Heating and Ventilation. C. L. HUBBARD. New Ed. 12mo. 213 pp. Price, \$1.50. American Technical Society, Chicago.
- Hydraulics: Elements of Hydraulics. S. E. SUDGEN. 2nd Ed. 8vo. 329 pp. Price, \$2.50. McGraw-Hill Book Co., New York.
- Internal Combustion Engines: Description et Pratique des moteurs à explosion et à combustion interne. J. M. LE GUILCHER. 8vo. 131 pp. Augustin Challamel, Paris.
- Machine Design: Handbook for Machine Designers. F. A. HALSEY. 2nd Ed. 4to. 561 pp. Price, \$5.00. McGraw-Hill Book Co., New York.
- Oil: Practical Oil Geology. DORSEY HAGER. 2nd Ed. 16mo. 187 pp. Price, \$2.00. McGraw-Hill Book Co., New York.
- Oil-Field Development and Petroleum Mining. A. B. THOMPSON. 648 pp. Price, \$7.50. D. Van Nostrand Co., New York.
- Paint: The Industrial and Artistic Technology of Paint and Varnish. A. H. SAMIN. 2nd Ed. 8vo. 473 pp. Price, \$3.50. John Wiley & Sons, New York.
- Paper: Its History, Sources and Manufacture. H. A. MADDOX. 12mo. 159 pp. Price, \$0.85. Sir Isaac Pitman & Sons, New York.
- Petroleum: List of Books on Petroleum. 8vo. 16 pp. Library of the Mechanics' Institute, San Francisco.
- River Discharge: Prepared for the Use of Engineers and Students. J. C. HOYT and N. C. GROVER. 4th Ed. 8vo. 210 pp. Price, \$2.00. John Wiley & Sons, New York.
- Steam Piping: Its Economical Design and Correct Layout. A. L. JOHNSON, JR. 12mo. 62 pp. Price, \$2.00. Engineering Magazine Co., New York.
- Steel: Elliott's Weights of Steel for Engineers. T. J. ELLIOTT. 8vo. 662 pp. Price, \$30.00. Penton Publishing Co., Cleveland.
- Steel: The Story of Bethlehem Steel. ARUNDEL COYTER. 12mo. 65 pp. Price, \$0.75. Moody Magazine Book Co., New York.
- Synthetic Inorganic Chemistry. A. A. BLANCHARD. 12mo. 214 pp. Price, \$1.00. John Wiley & Sons, New York.
- Textiles: American Textile Report and Directory. 25th Ed. 8vo. 829 pp. Dockham Publishing Co., Boston.
- RECENT JOURNAL ARTICLES**
- Abrasive Paper and Cloth. F. B. JACOBS. *Iron Tradesman*, Vol. 76 (1917), No. 6, pp. 35-39.
- Air Delivery Factors of Blowing Engines. W. TRINKS. *Compressed Air Magazine*, Vol. 22 (1917), No. 1, pp. 8291-8232.
- Assaying: A Handy Method for Assaying Tin Ores. C. M. HENDERSON. *Engineering and Mining Journal*, Vol. 103 (1917), No. 6, p. 267.
- Benzol: Recovering Benzol from Coal Gas. F. W. SPIER, JR. *Iron Trade Review*, Vol. 60 (1917), No. 4, pp. 266-269.
- Brick Sewers. L. F. SPRINGER. *Municipal Engineering*, Vol. 52 (1917), No. 2, pp. 47-52.
- Bronze Powder: The Manufacture of Bronze Powder, an Illustrated Description of Its Production in Germany and Its Industrial Uses. OTTO VON ZIEGLER. *The Metal Industry*, Vol. 15 (1917), No. 2, pp. 77-78.
- Caffeine the Alkaloid. *Tea and Coffee Trade Journal*, Vol. 42 (1917), No. 1, pp. 16-17.
- Carbon: Calculations Covering Carbon in Furnaces. T. W. RICHARDSON. *Blast Furnace and Steel Plant*, Vol. 5 (1917), No. 4, pp. 67-69.
- Ceramics: The Development of the Ceramic Industries in the United States. A. V. BLEININGER. *Journal of the Franklin Institute*, Vol. 183 (1917), No. 2, p. 127-166.
- Chemistry of Manganese. M. I. HARMON. *Metallurgical Engineering Press*, Vol. 114 (1917), No. 3, pp. 91-92.
- Construction: Problems in the Theory of Construction. E. S. ANDREWS. *Concrete and Constructional Engineering*, Vol. 12 (1917), No. 1, pp. 13-17.
- Copying-Ink Pencils and the Examination of Their Pigments in Writing. C. A. MITCHELL. *The Analyst*, Vol. 42 (1917), No. 490, pp. 3-11.
- Cupro-Nickel: Its Microstructure. JAMES SCOTT. *Metallurgical Engineering Press*, Vol. 15 (1917), No. 2, pp. 72-73.
- Draiser for Oil Separator. M. A. SALLER. *Ice and Refrigeration*, Vol. 52 (1917), No. 2, p. 76.
- Flotation of Molybdenite. S. H. INGRAM. *Mining and Scientific Press*, Vol. 114 (1917), No. 6, p. 196.
- Flotation of Sulfate Ores. J. DANIELS and C. R. CORRY. *Engineering and Mining Journal*, Vol. 103 (1917), No. 4, pp. 185-187.
- Formulae for Finding Large Gas Volumes. H. G. CREISSINGER. *Blast Furnace and Steel Plant*, Vol. 5 (1917), No. 2, pp. 55-56.
- Gasoline Tiller. F. C. PERKINS. *The Gas Engine*, Vol. 19 (1917), No. 2, pp. 61-65.
- Grain Growth Phenomena in Metals. ZAY JEFFRIES. *Iron Trade Review*, Vol. 60 (1917), No. 4, pp. 249-253.
- Grinding Wheels and Grinding Machines. C. V. BARNETT. *Engineering Magazine*, Vol. 52 (1917), No. 5, pp. 697-710.
- Heat Density. G. P. PHARCE. *Machinery*, Vol. 23 (1917), No. 6, pp. 471-472.
- Heat-Treatment of Steel. MARTIN SYTS. *Machinery*, Vol. 23 (1917), No. 6, pp. 500-505.
- Industrial Controllers. H. D. JAMES. *The Electric Journal*, Vol. 14 (1917), No. 7, pp. 83-89.
- Internal Combustion Turbine. A. W. H. GRIEPE. *The Gas Engine*, Vol. 19 (1917), No. 2, pp. 68-71.
- Lubrication of Cutting Tools. E. K. HAMMOND. *Machinery*, Vol. 23 (1917), No. 6, pp. 490-499.
- Manganese: Geological Occurrence of Manganese. J. J. RUNNER. *Metallurgical Engineering Press*, Vol. 114 (1917), No. 4, pp. 128-129.
- Mechanical Plating. D. W. ROBINSON. *The Metal Industry*, Vol. 15 (1917), No. 2, pp. 61-64.
- Metalloid Removal from Metal Washing. E. L. FORD. *Blast Furnace and Steel Plant*, Vol. 5 (1917), No. 2, pp. 56-57.
- Nickel Ores: Origin of the Sudbury Nickel Ores. C. F. TOLMAN, JR., and A. F. ROGERS. *Engineering and Mining Journal*, Vol. 103 (1917), No. 5, pp. 206-220.
- Nickel Plate Mine and Mill. T. A. RICKARD. *Mining and Scientific Press*, Vol. 114 (1917), No. 3, pp. 80-86.
- Nitrate: The Chilean Nitrate Industry. A. W. ALLEN. *Engineering and Mining Journal*, Vol. 103 (1917), No. 5, pp. 230-233.
- Nitrogen: Literature of the Nitrogen Industries, 1912-1916. H. R. HOMER. *General Electric Review*, Vol. 22 (1917), No. 2, pp. 156-164.
- Oxy-Acetylene Cutting in England. D. RICHARDSON. *Acetylene Journal*, Vol. 18 (1917), No. 8, pp. 133-134.
- Potash as a Blast Furnace By-Product. R. I. WYNN. *Blast Furnace and Steel Plant*, Vol. 5 (1917), No. 2, pp. 72-73.
- Recorders: CO₂ Recorders and Their Value. A. I. ANDERSON. *Vol. 45 (1917), No. 4, pp. 117-118.*
- Rubber Situation. A. H. KING. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 2, pp. 99-103.
- Steam-Plant: New High-Pressure Central Steam Plant. CLAUDE HARTFORD. *Power*, Vol. 45 (1917), No. 6, pp. 168-170.
- Steel: Some Relations between the Magnetic and the Mechanical Properties of Steel and of Nickel. S. R. WILLIAMS. *Transactions of the American Engineering Society*, Vol. 9 (1917), No. 4, pp. 183-202.
- Stokers and Condensers. R. L. STEETTER. *Engineering Magazine*, Vol. 52 (1917), No. 5, pp. 660-683.
- Sulfuric Acid Industry of Polk Co., Tennessee. A. M. FAIRLIE. *Manufacturers Record*, Vol. 71 (1917), No. 4, p. 31.
- Testing House Heating Boilers. L. P. BROOKINGS and E. B. PROCTOR. *Power*, Vol. 45 (1917), No. 4, p. 80.
- Titanium: How to Use Titanium in Making Steel Castings. A. A. JACOBSON. *The Engineer*, Vol. 45 (1917), No. 1, pp. 15-17.
- Tungsten: Electrolytic Behavior of Tungsten. W. V. KENNEDY. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 1, pp. 40-43.
- Utilization of Lumber Mill Waste. R. L. WATSON. *Power*, Vol. 45 (1917), No. 4, pp. 104-105.
- Valuation of Roasted Mineral Land. T. A. GARDNER. *Engineering and Mining Journal*, Vol. 103 (1917), No. 4, pp. 180-181.
- Vaporization of Metallic Copper in Wireless Furnaces. M. I. HARMON. *Metallurgical Engineering Press*, Vol. 16 (1917), No. 4, pp. 80-82.

MARKET REPORT—FEBRUARY, 1917

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON FEBRUARY 15

INORGANIC CHEMICALS

Acetate of Lime.....	100 Lbs.	3.25	@	3.50
Alum. lump ammonia.....	100 Lbs.	4	@	4 1/4
Aluminum Sulfate, high-grade.....	Ton	60.00	@	70.00
Ammonium Carbonate, domestic.....	Lb.	10	@	10 1/2
Ammonium Chloride, white.....	Lb.	17 1/2	@	18
Aqua Ammonium, 26°, drums.....	Lb.	5 1/4	@	6
Arsenic, white.....	Lb.	10	@	11
Barium Chloride.....	Ton	85.00	@	90.00
Barium Nitrate.....	Lb.	11	@	11 1/4
Barytes, prime white, foreign.....	Ton	35.00	@	40.00
Bleaching Powder, 35 per cent.....	100 Lbs.	3.80	@	4
Blue Vitriol.....	Lb.	9 1/4	@	10
Borax, crystals, in bags.....	Lb.	6 1/4	@	7 1/2
Boric Acid, powdered crystals.....	Lb.	12 1/4	@	13
Brimstone, crude, domestic.....	Long Ton	35.00	@	35.00
Bromine, technical, bulk.....	Lb.	1.30	@	1.40
Calcium Chloride, lump, 70 to 75% fused.....	Lb.	23.00	@	24.00
Calcium Chloride, granulated.....	Ton	39.00	@	—
Caustic Soda, 76 per cent.....	Lb.	4.10	@	4.15
Chalk, light precipitated.....	Lb.	4 1/4	@	—
China Clay, imported.....	Ton	18.00	@	30.00
Feldspar.....	Ton	8.00	@	15.00
Fuller's Earth, foreign, powdered.....	Ton	35.00	@	35.00
Glauber's Salt, in bbls.....	100 Lbs.	60	@	65
Green Vitriol, bulk.....	100 Lbs.	1.15	@	1.20
Hydrochloric Acid, commercial, 18°.....	Lb.	1 1/4	@	1 1/4
Hydrochloric Acid, C. P., conc., 22°.....	Lb.	1 1/4	@	1 1/4
Iodine, resublimed.....	Lb.	3.50	@	3.55
Lead Acetate, white crystals.....	Lb.	13	@	13 1/2
Lead Nitrate.....	Lb.	15 1/2	@	15 1/2
Litharge, American.....	Lb.	9 1/4	@	9 1/4
Lithium Carbonate.....	Lb.	1.02	@	1.05
Magnesium Carbonate, U. S. P.....	Lb.	24	@	26
Magnesite, "Calcedined".....	Ton	6.50	@	7.00
Nitric Acid, 36°.....	Lb.	5	@	5 1/4
Nitric Acid 42°.....	Lb.	5 1/4	@	6
Phosphoric Acid, sp. gr. 1.750.....	Lb.	30	@	32
Phosphorus yellow.....	Lb.	75	@	80
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, casks.....	Lb.	39 1/4	@	40
Potassium Bromide (granular).....	100 Lbs.	1.25	@	1.35
Potassium Carbonate, calcined, 88 @ 92%.....	Lb.	32	@	34
Potassium Chlorate, crystals, spot.....	Lb.	63	@	64
Potassium Cyanide, bulk, 98-99 per cent.....	Mixture	1.70	@	1.75
Potassium Hydroxide, 88 @ 92%.....	Lb.	84	@	86
Potassium Iodide, bulk.....	Lb.	2.90	@	—
Potassium Nitrate.....	Lb.	28	@	33
Potassium Permanganate, bulk.....	Lb.	3.80	@	4.00
Quicksilver, flask, 75 lbs.....	Lb.	\$130.00	@	150.00
Red Lead, American, dry.....	Lb.	10	@	10 1/4
Salt Cake, glass makers'.....	Ton	15.00	@	15.50
Silver Nitrate.....	Oz.	48 1/4	@	—
Soapstone in bags.....	Ton	8.00	@	12.00
Soda Ash, 58%.....	100 Lbs.	2.70	@	2.80
Sodium Acetate.....	Lb.	9 1/2	@	10 1/2
Sodium Bicarbonate, domestic.....	100 Lbs.	1.90	@	2.00
Sodium Bicarbonate, English.....	Lb.	3 1/4	@	4
Sodium Bichromate.....	Lb.	17	@	17 1/2
Sodium Chlorate.....	Lb.	25	@	26
Sodium Fluoride, commercial.....	Lb.	—	@	—
Sodium Hyposulfite.....	100 Lbs.	1.70	@	1.75
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	3.70	@	3.90
Sodium Silicate, liquid, 40° Bé.....	100 Lbs.	1.05	@	1.25
Sodium Sulfide, 30%, crystals, in bbls.....	Lb.	2	@	2 1/2
Sodium Bisulfite, liquid, 32 s. g.....	Lb.	.01	@	.01 1/4
Strontium Nitrate.....	Lb.	30	@	35
Sulfur, flowers, sublimed.....	100 Lbs.	2.30	@	2.70
Sulfur, roll.....	100 Lbs.	1.95	@	2.05
Sulfuric Acid, chamber, 66° Bé.....	Ton	29.00	@	30.00
Sulfuric Acid, oleum (fuming).....	Ton	38.00	@	40.00
Talc, American white.....	Ton	10.00	@	11.00
Terra Alba, American, No. 1.....	100 Lbs.	85	@	90
Tin Bichloride, 50°.....	100 Lbs.	13.50	@	—
Tin Oxide.....	Lb.	53	@	54
White Lead, American, dry.....	Lb.	9	@	9 1/4
Zinc Carbonate.....	Lb.	24	@	26
Zinc Chloride, commercial.....	Lb.	15	@	15 1/4
Zinc Oxide, American process XX.....	Lb.	12	@	12 1/4
Zinc Sulfate.....	Lb.	6 1/4	@	6 1/4

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	45	@	50
Acetic Acid, 56 per cent, in bbls.....	Lb.	7	@	7 1/2
Acetic Acid, glacial, 99 1/2% in carboys.....	Lb.	22	@	23
Acetone, drums.....	Lb.	22	@	23

Alcohol, denatured, 180 proof.....	Gal.	64	@	64
Alcohol, grain, 188 proof.....	Gal.	2.70	@	2.72
Alcohol, wood, 95 per cent, refined.....	Gal.	1.00	@	1.02
Amyl Acetate.....	Gal.	3.75	@	4.00
Aniline Oil.....	Lb.	26	@	28
Benzoic Acid, ex-toluol.....	Lb.	7.50	@	8.00
Benzol, 90 per cent.....	Gal.	57	@	60
Camphor, refined in bulk, bbls.....	Lb.	86 1/4	@	86 1/4
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	45	@	48
Carbon Bisulfide.....	Lb.	51 1/4	@	61 1/4
Carbon Tetrachloride, drums, 100 gals.....	Lb.	15 1/2	@	16
Chloroform.....	Lb.	60	@	61
Citric Acid, domestic, crystals.....	Lb.	74	@	75
Cresosote beechwood.....	Lb.	2.00	@	2.25
Cresol, U. S. P.....	Gal.	1.25	@	1.30
Dextrine, corn (carlows, bags).....	100 Lbs.	3.90	@	3.95
Dextrine, imported potato.....	Lb.	12	@	13
Ether, U. S. P., 1900.....	Lb.	15	@	20
Formaldehyde, 40 per cent.....	Lb.	11 1/4	@	12
Glycerine, dynamite, drums included.....	Lb.	54	@	54 1/2
Oxalic Acid, in casks.....	Lb.	46	@	48
Pyrogallic Acid, resublimed bulk.....	Lb.	—	@	3.50
Salicylic Acid.....	Lb.	0.85	@	0.90
Starch, cassava.....	Lb.	—	@	—
Starch, corn (carlows, bags) pearl.....	100 Lbs.	2.85	@	2.90
Starch, potato.....	Lb.	12 1/2	@	12 1/2
Starch, rice.....	Lb.	8	@	8 1/4
Flour, sago.....	Lb.	4 1/4	@	5
Starch, wheat.....	Lb.	5	@	6
Tannic Acid, commercial.....	Lb.	65	@	70
Tartaric Acid, crystals.....	Lb.	85	@	86

OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	52	@	54
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil No. 3.....	Lb.	17	@	17 1/2
Ceresin, yellow.....	Lb.	14	@	18
Corn Oil, crude.....	100 Lbs.	11.50	@	11.75
Cottonseed Oil, crude, f. o. b. mill.....	Gal.	82	@	83
Cottonseed Oil, p. s. y.....	Lb.	12 1/2	@	12 1/4
Menhaden Oil, crude (southern).....	Gal.	70	@	75
Neat's-foot Oil, 20°.....	Gal.	1.20	@	1.30
Paraffine, crude, 120 m. p.....	Lb.	6 1/4	@	6 1/4
Paraffine Oil, high viscosity.....	Gal.	29 1/2	@	30
Rosin, "F" Grade, 280 lbs.....	Bbl.	6.55	@	—
Rosin Oil, first run.....	Gal.	38	@	—
Shellac, T. N.....	Lb.	45	@	46
Spermaceti, cake.....	Lb.	23	@	25
Sperm Oil, bleached winter, 38°.....	Gal.	1.05	@	1.06
Spindle Oil, No. 200.....	Gal.	24	@	25
Stearic Acid, double-pressed.....	Lb.	14 1/2	@	15
Tallow, acidless.....	Gal.	1.04	@	1.05
Tar Oil, distilled.....	Gal.	30	@	32
Turpentine, spirits of.....	Gal.	52	@	—

METALS

Aluminum, No. 1, ingots.....	Lb.	58	@	60
Antimony, ordinary.....	Lb.	30	@	31
Bismuth, N. Y.....	Lb.	3.05	@	3.10
Copper, electrolytic.....	Lb.	35	@	—
Copper, lake.....	Lb.	35	@	—
Lead, N. Y.....	100 Lbs.	9.50	@	—
Nickel, electrolytic.....	Lb.	50	@	55
Platinum, refined, soft.....	Oz.	105.00	@	—
Silver.....	Oz.	78 1/4	@	—
Tin.....	Lb.	54 1/4	@	—
Tungsten (WOs).....	Per Unit.	16.00	@	—
Zinc, N. Y.....	100 Lbs.	10.87	@	—

FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	5.00	@	5.03
Blood, dried F O B Chicago.....	Unit	4.20	@	—
Bone, 4 and 50, ground, raw.....	Ton	32.00	@	33.00
Calcium Cyanamid.....	Unit of Ammonia	2.75	@	—
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	4.40	@	10
Phosphate, acid 16%.....	Ton	11.30	@	11.75
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.00	@	2.10
Tennessee, 78-80 per cent.....	Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent.....	Ton	425.00	@	430.00
Pyrites, furnace size, imported.....	Unit	nominal	@	—
Tankage, high-grade; f. o. b. Chicago.....	Unit	4.15	@	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

AT EASTON, PA.

Volume IX

APRIL 1, 1917

No. 4

Editor: CHARLES H. HERTY

Assistant Editor: LEOLA E. MARRS

Advertising Manager: M. A. WILLIAMSON

ADVISORY BOARD

H. E. BARNARD, H. K. BENSON, F. K. CAMERON, B. C. HESSE, A. D. LITTLE, A. V. H. MORY, M. C. WHITAKER

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly

Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879

All communications should be sent to The Journal of Industrial and Engineering Chemistry,

Telephone: Vanderbilt 1930

35 East 41st Street, New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

Chemists and Preparedness	332
Again I Say "America for Americans."	332
No Tariff Commissioner for Chemistry	336
A Timely Proposal	336
Plant Precautions	337

THE AMERICAN CHEMICAL SOCIETY AND THE NATION

337

ORIGINAL PAPERS:

Ferro-Uranium. H. W. Gillett and E. L. Mack	342
Inflammability of Carbonaceous Dusts in Atmospheres of Low Oxygen Content. H. H. Brown and J. K. Clement	347
The Thermal Decomposition of Benzene. J. E. Zanetti and G. Egloff	350
Rubber Hose for Use on Aeroplanes. Percy A. Houseman	350
Glue for Use on Aeroplanes. Percy A. Houseman	359
A Study of Certain Ferments with a View to Determining a Method for the Differentiation of Pasteurized Milk from Raw Milk. I. Reductases. Richard Edwin Lee and Melvin Guy Mellon	360
A Study of the Volumetric or Permanganate Method for Determining Phosphoric Acid, with Some Experiments Showing the Influence of Temperature and the Sulfuric Acid Radical on Results. Philip McG. Shuey	367
Thermocline Studies at Kensico Reservoir. Frank E. Hale and John E. Dowd	370
Is the Recovery of the Nitrogen in Sewage Sludge Practicable? William R. Copeland	374
Storage Reservoirs as a Factor in the Purification of Surface Waters. S. T. Powell	377

LABORATORY AND PLANT

An Experiment in the Education of Chemical Engineers The Twenty-fifth Anniversary of the Audubon Sugar School. Charles E. Coats	379
The Concentration of Sulfuric Acid. F. H. Auld	386
Printing Plates from Phenol Resin Compound. L. A. Redman, A. I. Worth, F. P. Brock	388
The Setting of Litharge-Glycerine Cement. H. E. McIlwain	390

The Use of a Condenser to Prevent Arcing in Bomb Calorimeters. Fred F. Flanders	390
---	-----

ADDRESSES:

Development of Chemical Industries in Southern California since January 1, 1916. Arthur W. Kinney	391
Initiation of Explosions. Walter Arthur	392
Water-Meters in Their Sanitary Relations. Henry Leffmann	395
Advantages of Softened Water in Laundry Work. J. H. Ryan	397
Stream Inspection in Connection with the Operation of Sewage Treatment Works. C. B. Hoover	398
Some Remarks on the Biochemical Treatment of Sewage, with Especial Reference to the Activated Sludge Method. George T. Hammond	399
Regeneration as a Factor in the Self Purification of Streams. Earle B. Phelps	403

CURRENT INDUSTRIAL NEWS

405

SCIENTIFIC SOCIETIES:

Calendar of Meetings. Nineteenth Annual Meeting, American Ceramic Society, New York City, March 8 to 8, 1917. Spring Meeting, American Chemical Society, Kansas City, April 10 to 14, 1917. Obituary. Frederick Rowland Hazard	409
--	-----

NOTES AND CORRESPONDENCE

Dutch Balmum Plant Burned. Two Letters on Corrosion of Liquid Iron Containing Cobalt, Nickel, or Copper. Two Letters on Relation of Fat as Mark to the Solvent not Fat. The Fixation of Nitrogen. Correction. The German Alarm Clock. Correction.	414
--	-----

PERSONAL NOTES

417

GOVERNMENT PUBLICATIONS

419

BOOK REVIEWS

A General Guide to the Literature of Chemistry. How to Build up a Library. Library. The Chemistry and Technology of Paper. Engineering Chemistry. Volume of the Transactions of the American Chemical Society. The Chemistry of the World	427
LITERATURE OF THE NINETEENTH CENTURY	444
NEW PUBLICATIONS	449
MARKET PRICES	451

EDITORIALS

CHEMISTS AND PREPAREDNESS

The following letter is now being sent to every chemist in America whose name could be secured:

By request of the Council of National Defense, the Bureau of Mines, in cooperation with the American Chemical Society, will procure a Roster of Chemists of the United States. Data covering the qualifications, experience and skill of each chemist are desired to determine the line of duty in which he could best serve the country in time of need.

European experience has shown that nothing is more important in time of war or other national emergency than a knowledge of the qualifications and experience of the country's expert technical men. Men whose knowledge was invaluable to the production of munitions ordnance, and supplies were killed in the trenches during the first months of the European war. This was due to lack of early information regarding individuals and has now been remedied in every European country. It is therefore important, especially at present, that this information be available in the United States.

You are accordingly requested, as a patriotic duty not only to fill out the card which you will receive herewith, but to see that every chemist within your acquaintance receives one and does likewise. Additional cards will be furnished upon request. You will please check only those subjects in which you are expert, especially where you have had actual manufacturing experience. Please return the card promptly, using the enclosed franked envelope. The information received will be carefully classified, carded and indexed. Your prompt response to this matter will be very much appreciated.

VAN H. MANNING, *Director, Bureau of Mines*

JULIUS STIEGLITZ, *President, American Chemical Society*

The letter is accompanied by blank forms on which is requested information as to personality, experience and special qualifications. This information will be carefully classified, indexed, and carded for future use. It is the hope of the Bureau of Mines to keep this work up-to-date in future years.

For the purpose of mobilizing chemical investigators the following letter is also being mailed:

To assist the Chemistry Committee of the National Research Council in its efforts to prepare for the use of the Government a classification of our chemical investigators, it is requested that you fill out the reverse side of this card. As the matter is urgent, it is hoped that you will give it your careful attention.

MARSTON TAYLOR BOBERT, *Chairman,*

Chemistry Committee, National Research Council

The information requested includes lines of work, willingness to aid the Government in the solution of problems affecting the security and defense of our country, preference in research and available time for such work.

No word of appeal is needed for this patriotic duty. Through President Stieglitz we have already offered our services to our country. This is the first request made of us. The answers to these questionnaires should be immediate and unanimous.

The subject matter is so timely, and the experience of England is so vitally interesting that we reproduce elsewhere an article on "Chemistry in Wartime" from the English Journal, *The Chemical Trade Journal and Chemical Engineer*.

AGAIN I SAY "AMERICA FOR AMERICANS"

In our last issue we announced the policy of always being willing to publish criticisms of matter appearing in *THIS JOURNAL*, with the further statement that those so criticized would be given opportunity to reply. With complete willingness we include ourselves among those subject to criticism, at the same time reserving to ourselves the same privilege of reply.

On the evening of March 9th I was handed the following communication in person by Professor Alexander Smith, Head of the Department of Chemistry in Columbia University and a Past-President of the American Chemical Society, with the request that it be published in *THIS JOURNAL*.

CRITICISMS OF CHEMICAL LEGISLATION WHICH ARE NOT WISE, BUT OTHERWISE

By ALEXANDER SMITH

The editorials in *THIS JOURNAL*, and the reports of addresses by the Editor, Dr. Herty, have called the attention of chemists, and all interested in chemistry, to the wording of one paragraph of the tariff bill of September 1916, in which the dyes relieved from the 5 per cent per pound tax are specified. The classes mentioned include ".....natural and synthetic indigo and all indigoids whether or not obtained from indigo....." My purpose is not to discuss the matters of public policy involved in these exemptions, but simply to call attention to a serious error in the arguments used by the critics of the section in question.

Dr. Herty refers to Nietzsche's *Chemie der Organischen Farbstoffe*, and says "that if our chemists did not know what 'indigoids' were, Professor Nietzsche did know." "In the fifth edition (1906) I found the group of dyes known as 'indigoids' completely specified. The list included all forms of sulfur dyes."

Now no argument is really supported by a misrepresentation of the facts, although in this instance the misrepresentation was entirely unconscious and unintentional. In 1906 Nietzsche did not know what "indigoids" were, because the word does not occur in the book, and was in fact first introduced to the science two years later by Friedländer¹ in a paper entitled "On Indigoid Dyestuffs." In 1896, aside from some halogen derivatives of indigo, and one or two dyes related to indigo and found in natural indigo, practically no dyes closely related to indigo were known, and there was no need for a class-name. The invention of thio-indigo red in 1905 was followed by the production of a large number of substituted indigoes, all of which contained the chromogenic group $\text{—CO—C}=\text{C—CO—}$ and so in 1908 the term "indigoid" was suggested to cover the members of this group. Authoritative works² now all mention indigoids, and define them as indicated above, and the definition in every one of these books absolutely excludes the possibility that any chemist could even think of sulfur colors in the same connection. Numerous other references could be given to show that the word "indigoid" is always used with the meaning stated above. It is sufficient to quote Thorpe:

"Indigoids.—The congeners of indigo may be divided into two different classes. One of them contains the true derivatives of

¹ *Ber.*, **41** (1908), 752.

² Cain Thorpe, "The Synthetic Dyestuffs," **1913**, 174.

Green, "Analysis of Dyestuffs," **1915**, 123 and 38.

Thorpe, "Dictionary of Applied Chemistry," **1912**, **3**, 130.

Wahl, "L'Industrie des Matières Colorantes Organiques," **1912**, 317, 346.

indigo, in which one or more of the 8 hydrogen atoms of the two phenylene groups are replaced by other substituents; the other embraces substances which are strictly analogous to indigo in their constitution, but different from it in the construction of the complex connecting the two phenylene groups, which in this case as well as in that of indigo may have their hydrogen atoms replaced by other substituents. An enormous variety of new dyestuffs may thus be synthesized, all of which contain the characteristic chromophoric group of indigo:— $\text{CO}—\text{C}=\text{C}—\text{CO}—$."

An examination of Nietzsche's book shows clearly that he distinguishes between sulfur dyes and indigo dyes, for he divides dyes into thirteen classes, and places the former in Class X and the latter in Class XII, and uses this classification consistently. Dr. Herty's misunderstanding seems to have arisen from a superficial examination of a more condensed classification occurring in Nietzsche's volume. In one place he mentions five classes determined solely by the properties used in dyeing, namely (1) basic colors, (2) acid dyestuffs, (3) mordant dyestuffs, (4) neutral or salt dyestuffs, and (5) an unnamed group which includes insoluble dyestuffs, such as indigo, certain azo-dyestuffs, and the sulfur dyestuffs. But he does not say, or even imply that these dyes—mostly vat dyes—are similar to indigo, but only that the sulfur dyes do not belong to the other four classes, and he does not use the term indigoids, because that term did not then exist. These are simply a somewhat heterogeneous collection of dyes, which do not belong to the first four classes. Furthermore, an examination of Nietzsche's book shows that he would have felt grossly insulted if anyone had stated that he classed sulfur dyes with indigo dyes. He not only puts them in separate classes, but on page 291 he defines sulfur colors on the basis of the method of manufacture and on page 295 gives their general properties. On page 325 he says "indigo dyestuffs are all derivatives of indol $\text{C}_8\text{H}_7\text{N}$," and not one of the sulfur colors he mentions in Class X, thiazol and sulfur dyestuffs (p. 288, *et seq.*) is derived from indol. There is, therefore, no possibility that anyone would include a sulfur brown as an "indigoid," either on the basis of anything Nietzsche says, or on the definition of indigoids now found in many recent authoritative works, for these definitions absolutely exclude any such interpretation.

Dr. Herty seems to think that Mr. Caesar Cone, who died on March 1, 1917, and cannot now make any reply, caused the introduction of the word "indigoids," and did so with the deliberate intention of widening the exempted group, so as to make it include sulfur dyes. Since the word "indigoid" is a purely scientific term, and is not used as a trade classification, there is no reason to suppose Mr. Cone ever heard of the word before it appeared in the act. All who knew Mr. Cone personally are well aware that he would never have been guilty of using a subterfuge of this description. The introduction of the word indigoids is easily explicable in an entirely different way. In a case¹ tried before the General Appraisers, and reversed by the Court of Appeals, the word indigoids made its first appearance in connection with the chemical trade. Its introduction into the act was undoubtedly based on this case.

A reading of the two reports shows that the act of 1913, § 514, places "indigo and dyes obtained from indigo" on the free list. The Lower Court decided that dyes, chemically similar to indigo (such as thio-indigos) and made from the same fundamental substances, but not made from finished indigo itself, were covered by this exemption. The Higher Court reversed this decision, claiming that the act applied only to dyes made with indigo as one stage in the actual manufacture.

Incidentally, the indigoid group is also defined in the report by references to Thorpe's Dictionary, in a way that excludes

all dyes not containing the characteristic indigo chromogenic group. The new act differs from the old, therefore, in the fact that chemical cousins of indigo, now known as indigoids, even if not made from indigo itself, are included in the exemption. But there is not the slightest possibility of the word indigoid being interpreted so as to cover any dyes not actually containing the indigo chromogenic group.

When Professor Smith handed me this communication in an envelope bearing the printed inscription "Columbia University in the City of New York, Department of Chemistry" I confess I was surprised, for, as far as I could remember he had never published an article before in the field of industrial chemistry. This surprise was largely increased when I learned that the communication was on the subject of dyestuffs.

I have been pretty closely associated with every stage of the fight for an American dyestuff industry, have followed the discussions in all available journals, and, through the aid of clipping bureaus, have followed closely the discussions in the daily press. Never before had I seen or heard of anything written or spoken by Prof. Smith on this subject. This surprise, however, was increased to amazement when I first read the above communication. Let me explain.

The title of Prof. Smith's article is a paraphrase of an article which I wrote for the *Annual Review* of the *New York Journal of Commerce*, published on February 5, 1917, which article was reproduced in the March, 1917, issue of THIS JOURNAL as a part of my editorial "America for Americans." In his opening sentence above Prof. Smith states, "The editorials in THIS JOURNAL, etc." I have written only two on this subject, so it is evident that Prof. Smith has seen the one containing the *Journal of Commerce* article.

In his second paragraph he quotes me, and strange to say, in a contribution to a scientific journal, he gives no reference as to the source of the quoted matter. This is a curious oversight for one so accustomed to publication as he is. As a matter of fact he quoted sentences written by Mr. Isaac Russell, a reporter of the *New York Evening Mail*, who, after a 15-minute interview with me one day in my office and having no knowledge of chemistry or German and with only a few rough notes written on a piece of paper not larger than an ordinary envelope, wrote a three-quarter column story about indigoids and tariff legislation which was printed in the *Evening Mail* of January 3, 1917.

Reading the story I felt that Mr. Russell had done a pretty good piece of reportorial work for so technical a subject and was gratified to note that in recording my discussion of the subject he did not use quotation marks, for there were a number of errors in his article. Knowing that the evening newspaper public would not be interested in a correction of such inaccuracies of chemistry and of German translation, I determined to put the matter straight before those who would be

¹ Treasury Decisions, 16489, 30, No. 23, 11-15 (June 8, 1916), and 16665, 32, No. 5, 64-67 (February 1, 1917).

interested in such matters and so tore up the partly written article on "Chemical Legislation: Wise and Otherwise" which I had been requested to write for the *Journal of Commerce* and wrote instead the article referring only to dyestuff legislation under the modified title "Chemical Legislation: Not Wise but Otherwise." Thus I gave over my own signature my views, for which I would therefore be solely and entirely responsible.

Among the inaccuracies of the reportorial statements were those quoted by Prof. Smith. I did not make such statements. Prof. Smith's unctuous sentence, "Although in this instance the misrepresentation was entirely unconscious and unintentional" smacks of insincerity for the merest tyro in chemistry could not have made such statements if they were "unintentional."

What I did say over my own signature was, "If a poll were taken of the dyestuff consumers in the United States as to what is an 'indigoid' which is 'not derived from indigo' how many could answer the question definitely?" and further that I had failed to receive an answer from "five of the most prominent American dyestuff chemists." I further stated that from information received there was good ground to believe that effort would be made to bring in sulfur dyes without payment of the special duty and that the basis of the effort would be the classification in the 5th edition of Nietzsche's book. I did not seek to justify any such contention. I did refer to the misfortune that would befall the American dyestuff industry if such a contention should be sustained by the Board of Appraisers. I certainly hope that it would not be so sustained but that does not affect the intention of the importer who had determined to test the matter.

It was a public duty to call attention to this intended move against the revenue of the country and the American dyestuff industry. Regardless, however, of anybody's views as to "indigoids not obtained from indigo," one thing is certain—if Congress would repeal that excepting clause, no test cases of sulfur dyes could ever arise and that is the point for which all who are interested in the American industry should struggle. "Safety First" fits this case.

From the mere reading of Prof. Smith's communication I fail to see its purpose. Many things suggest that the natural thing for Prof. Smith to have done would have been to tell me frankly of his researches in the meaning of indigoids and to advise that I publish a correction. This would have enabled me to clear up his misunderstanding of the situation. Instead he hands me a paper fully prepared with the request that it be published in *THIS JOURNAL* of which I am the Editor.

Does he seek to safeguard the American industry? If so he should reserve his ammunition for the Board of Appraisers and aid the government attorneys should the case arise. Was it to exhibit great learning in this popular field? If so he seeks notoriety in a way which is extremely unusual, to say the least. Does he seek to bolster up the cause of the importers by allaying discussion of a matter which might sweep away with it indigo, alizarin and the

other excepted dyes, or by lulling us into a false sense of security?

I regret to harbor the last thought but am impelled to it by the unexpected defense which he makes of the late Mr. Caesar Cone's motives. Mr. Cone made no secret of his position in this matter. In the brief of the Proximity Manufacturing Company (Mr. Cone's Company) to the Senate Committee on Finance, filed last July, these words occur: "and we respectfully submit that the second paragraph of Section 401 should be amended by adding:

and natural and synthetic alizarin, and dyes obtained from alizarin, anthracene and carbazol: and natural and synthetic indigo and all indigoids, whether or not obtained from indigo, shall be returned to the free list and shall be exempt from duty."

Again, in an address by Mr. Cone before the National Association of Garment Manufacturers at St. Louis, Mo., on November 16, 1916 (a printed copy of which is before me bearing the imprint of Harrison Printing Company, Greensboro, N. C.), Mr. Cone said (page 10 of this address): "Now while we are on this dyestuff question—I don't know whether you gentlemen know it or not, but I have been personally villified somewhat by some of my friends because I was the only man, the only manufacturer in the United States that attempted to oppose the duty that they have put upon certain dyestuffs, and particularly on indigo. . . . On the 8th or 9th of September a bill was passed putting a duty of 30 per cent on indigo, and any indigo that comes to this country now bears that duty, and I dare say that it would have been 30 per cent plus 5 cents a pound but for the efforts made by my attorney and myself in Washington. And I thought at one time that I was going to be successful in keeping that 30 per cent off." Engaging frankness, amounting even to a boast. His own words confirm completely every statement I have ever made concerning Mr. Cone and this legislation.

No, if there is a joker in this tariff bill I have never thought that Mr. Cone was primarily responsible for it: he was not a chemist. There is good ground, however, for a reasonable inference at this date that if this discussion continues a little longer we shall know who is responsible for it.

Meanwhile, more light is thrown on Prof. Smith's remarkable contribution by a chain of interesting events which have happened recently. On February 7, a card was mailed to me from E. D. Lee, Librarian of the Chemistry Reading Room of Columbia University, requesting me to return the volume of Nietzsche which I had taken out on Prof. Metzger's card. Returning from Washington, D. C., on the 10th the volume was immediately returned. Then arose the following correspondence:

671 James Street
Pelham Manor, N. Y.
February 23, 1917

MR. CHARLES H. HERTY, Editor,
Journal of Industrial & Engineering Chemistry,
41st St. and Madison Ave., New York.

DEAR SIR:

In the *Textile Record* of February 2nd, I read the article mentioning that in the 5th edition of Nietzsche, the group

of dyes known as Indigoids is completely specified and that the list includes all forms of Sulphur dyes.

This classification of Sulphur dyes being quite new to me, I tried to find the information about Indigoids, but after getting hold finally of the above mentioned book and looking all over it, I cannot find it.

I would appreciate very much if you would write me the exact page of Nietzsche dealing with this matter.

It may interest you to know that I have, however, found an exact definition of Indigoids in the following text books:

The Synthetic Dyestuffs, etc. by Cain Thorpe
The Manufacture of Organic Dyestuffs by Wahl
Analysis of Dyestuffs by Green
and also in Dictionary of Applied Chemistry by Thorpe.

Sincerely yours,
(Signed) DR. H. MEYER

35 East 41st Street
New York City
February 26, 1917

DR. H. MEYER,
671 James Street,
Pelham Manor, N. Y.

DEAR SIR:

Replying to your letter of February 23rd, I beg to refer you to the two concluding paragraphs of the introductory chapter, fifth edition, of Nietzsche's "Chemie der Organischen Farbstoffe," page 27.

Very truly yours,
(Signed) CHAS. H. HERTY, *Editor*

671 James St.
Pelham Manor, N. Y.
March 2, 1917

MR. CHARLES H. HERTY, Editor,
Journal of Industrial & Engineering Chemistry,
41st St. and Madison Ave.,
New York

DEAR SIR:

I am in receipt of your letter of February 26th, and wish to thank you for your information.

In going over the two paragraphs on page 27 of Nietzsche's "Chemie der Organischen Farbstoffe," fifth edition, I can, however, not find anything about sulphur dyes being "Indigoids." Nietzsche after giving the 4 groups of dyestuffs, namely, I Basic—II Acid—III Mordant and IV Neutral or Salt dyestuffs, puts in a fifth group all the colors which do not belong to any of these four groups and on account of their unsolubility have to be produced direct on the fiber, and mentions as examples, Indigo, insoluble Azo dyestuffs and also Sulphur dyestuffs, but I do not think it says that Sulphur dyestuffs belong to the Indigo class; it would then be not as correct to call Indigo a Sulphur dyestuff.

Sincerely yours,
(Signed) DR. H. MEYER

As the two letters from Dr. H. Meyer were written on paper without letterhead and as I had never even heard of anyone in Pelham Manor, I did not care to continue such a discussion and so simply filed the letters. A few days later, however, I was somewhat interested to learn that a Dr. H. Meyer was a chemist at the

Badische Company at 128 Duane St., New York City.

On the 9th of March Prof. Smith handed me his communication. I was at once struck by the similarity of literature references to definitions of indigoids given by him and by Dr. Meyer in his letter of February 23 and a somewhat similar treatment by both of Nietzsche's "condensed classification," as Prof. Smith alliteratively describes it.

A few days later I was interested to learn that on June 30, 1913, an application for a patent on "Producing Hydrogen" (U. S. Patent 1,115,776, issued November 3, 1914) was filed by Carl Bosch and Wilhelm Wild of Ludwigshafen-on-the-Rhine, Germany, assignors to Badische Anilin & Soda Fabrik, of Ludwigshafen-on-the-Rhine, Germany, a corporation of Baden. The assignment was executed June 12, 1913, and recorded June 30, 1913. On July 3, 1914, the U. S. Patent Office, Division 31, received a communication labelled Paper No. 3 (a certified copy of which is before me) in which was recorded certain amendments to the patent and the substitution of new claims for the original claims. The paper further gives what the attorneys of these applicants assert to be a report "of Prof. Alexander Smith of Columbia University, a leading authority and who has reported as follows:" Here follows what purports to be from a report by Prof. Smith. I shall not take the space in THIS JOURNAL to publish it unless these statements are questioned. This was the first definite knowledge I had of a direct connection of Prof. Smith with the Badische Anilin und Soda Fabrik.

With some light gained yet still puzzling over the meaning of all of this, I finally referred to Mr. Isaac Russell, the *Evening Mail* reporter who had written the first interview on this subject, the letters of inquiry sent to me by Dr. H. Meyer. I told Mr. Russell he would probably find Dr. Meyer with the Badische Company at 128 Duane St. Mr. Russell thanked me and said he would seek an interview with him and bring out the fact that there appeared to be definitions of indigoids not made from indigo which made the tariff revision, as drawn, perfectly safe. On March 21, Mr. Russell informed me that he visited the offices of the Badische Company at 128 Duane Street, and found that Dr. H. Meyer was out; he was informed, however, that Dr. Meyer lived at Pelham Manor and could be reached by telephone at the number given in the Westchester Section of the telephone directory. This number shows the address 671 James Street, thus agreeing with the address given on Dr. Meyer's letters to me. On March 22, Mr. Russell appeared at my office. He reported that he had been to the Badische Company, and saw Dr. Meyer.

Instead of giving him an interview, Dr. Meyer said, "Mr. Russell proposed to me, 'If you had better not take this up in the newspaper. It is a technical chemical subject and it had better be settled by the chemists and not by the newspapermen.'"

said that Dr. Meyer had referred him to me as Editor of the paper in which the article was to appear. Mr. Russell asked me for a copy of this article out of which to make an article for the *Evening Mail* as a follow-up to the first *Mail* article. He said he had told Dr. Meyer he would go to me for a copy of the article and use it in lieu of the interview which Dr. Meyer had declined. He said Dr. Meyer approved this idea. I declined to give Mr. Russell a copy of this article as the galley proof of Prof. Smith's article had not yet been sent to him.

This article by Prof. Smith, about which Dr. Meyer was so well posted, is the only communication I have received on this subject. To my mind all of this establishes with reasonable certainty a Smith-Meyer-Badische connection and all that goes with it.

Only one thing more—all of the rest of us have been fighting to build up an American dyestuff industry, not simply as an economic necessity, but because we know how closely related this industry is to the production of high explosives for our army and navy.

Meanwhile, during the progress of the details recorded in this reply, our country has been drawn daily nearer and nearer into war with Germany, and even to-day when most of us hold strongly the conviction that we are already at war with Germany, Prof. Smith telephoned at noon to the office of THIS JOURNAL to learn whether his communication would be published in the April issue and was seemingly gratified to be assured that it would.

Again I say, **AMERICA FOR AMERICANS!**

CHAS. H. HERTY

March 22, 1917

NO TARIFF COMMISSIONER FOR CHEMISTRY

The announcement of the personnel of the Tariff Commission brought with it keen regret that President Wilson had not been sufficiently impressed by the many recommendations and arguments forwarded him to lead him to appoint Mr. Ellwood Hendrick as a member of that body.

It must be gratifying, however, to Mr. Hendrick to know that while he had from the outset declined to enter into any active canvass for appointment, nevertheless he received the unanimous endorsement of all the organizations of chemists and of those allied organizations whose needs could be thoroughly understood and comprehended only by one having a thorough grasp also of the chemical situation and the interlacing character of all of these industries.

A TIMELY PROPOSAL

We are very glad to feature in this issue the address delivered by Dr. B. C. Hesse before the Detroit Section on the subject of "The American Chemical Society and the Nation." In this address Dr. Hesse has put forward a constructive suggestion which deserves the

serious consideration of every member of the Society and especially of the members of the Council who will assemble soon at Kansas City for the Spring Meeting.

The remarkable growth in membership in recent years has enabled the Society to do things which have excited the admiration of the chemical world. Its continuous and its present accelerated growth offer marked possibilities of still greater achievements in the future. This great numerical strength, however, contains within itself grave possibilities of danger through discord and consequent disruption, unless statesman-like provision be made for the logical and orderly expression of the convictions of members on matters in which they, as experts, have the right and the duty to be heard.

Things have moved rapidly in this world during the past three years, necessitating new viewpoints and new adjustments. The nation has suddenly awakened to the fundamental importance of the work of its chemists and now holds them in higher regard than ever before. In return for this national recognition we must assume a national obligation, namely, a national viewpoint. For the formulation and expression of opinions on national problems, the membership is too bulky; even the Council has grown too large, while the Directors are charged rather with the financial administration of the Society.

Furthermore, quick decision is often demanded. For these reasons a small group of experienced men is required whose judgment can be promptly gathered—a group somewhat continuous yet changing in its personnel and thoroughly representative of the Society. In its efforts such a group should have the hearty indorsement of the members or be abolished. Dr. Hesse seems to have had all such points in mind in working out the proposal which he has submitted.

So often during the past two eventful years, in the capacity of President of the Society, we have felt the need of such a body as the proposed Board of Control of National Policies. Without it we did the best we could in the many exigencies which arose, sometimes assuming authority to speak when we really doubted the possession of such authority. Many times, when occasion demanded action, we took the risk of rebuke, trusting solely to the good-will of fellow members and their confidence in our honesty of purpose. Fortunately we met with no rebukes, but such situations are dangerous for the Society, as well as somewhat embarrassing to its executive head.

There is also the constant danger of the action of a Local Section being misinterpreted as the action of the parent organization. On two occasions last year it was necessary for us officially to call attention to the fact that the recommendations regarding tariffs on dyestuffs were not those of the American Chemical Society, but were those of the New York Section of the Society, and that consequently such use of the name of the Society was not authorized.

It is not at all difficult to conceive a case where two Local Sections in different parts of the

country might have opposite views on a question of public policy. The confusion which might arise incident to the publication of those opposing views and their misconception as views of the Society, might easily lead to a popular discrediting of the organization as a national influence. Such possibilities suggest that Local Sections could well forego their present privilege of unlimited public expression, confining themselves in this public capacity to local matters and privately presenting their views on national matters to a National Board.

As we see the matter now, Dr. Hesse's suggestion involves a change in the constitution, and it is possible that discussion of the proposal by the Council may lead to some changes in the details of the plan, but the fundamentals are essentially sound. We are all indebted to him for this thoughtful address.

Following the reading of Dr. Hesse's paper the Detroit Section passed a Resolution favoring the adoption by the Society of a policy along the lines suggested. Later the Board of the Detroit Section unanimously voted to propose at the Kansas City Meeting of the Council an amendment to the Constitution of the Society creating a Board of Control of National Policies.

PLANT PRECAUTIONS

At the outbreak of the European war this country was threatened with a serious shortage of barium salts. With fine energy and courage the Toch brothers immediately began the erection of a plant at Sweetwater, Tenn., to utilize the ores in that vicinity. This plant had been continuously enlarged and methods improved, thus constituting an important factor in our program of national self-containedness.

In spite of full provision of facilities for fighting fire, including the thorough training of both the day and the night forces, this plant was gutted by fire on the night of March 8th, although the time clock of the watchman showed that just ten minutes previously he had been at the place where the fire originated.

In view of such an occurrence it cannot be too strongly urged that no steps be left untaken which will insure the safety of our chemical industrial plants against incendiary fires.

We know full well the deeply conceived spirit of malicious destruction which has been evidenced in other lands during this war period. Let us quickly and completely awake to the fact that we too are now fully subject to that same malicious spirit and therefore let us take no chance of misfortune which alertness and abundant caution can avert.

THE AMERICAN CHEMICAL SOCIETY AND THE NATION

Address by BERNHARD C. HESSE before the Detroit Section of the American Chemical Society, March 15, 1917

The American Chemical Society has to-day over 8300 members meeting in 49 local sections in 32 States of the Union and the District of Columbia. In point of numbers it is the largest organization of chemists in the world. Each local section has its own Chairman, Secretary and Executive Committee for the treatment of its local affairs and further, it has representation from among its membership in the Council of the Society in accordance with the size of its membership. The Council of the Society controls the formulation and execution of all the policies of the Society and also receives from the entire membership of the Society by secret letter ballot suggestions for candidates for President, Councilors-at-large and Directors, and from among these suggestions the Council makes the final selection, also by secret letter ballot. The Secretary of the Society, the Treasurer of the Society and the Editors of the various publications of the Society are elected by the Council. Hence, those in positions of authority and responsibility receive that authority substantially directly from the membership and are responsible to and under the control of that membership. In this respect, then, our Society lives up to and practices so nearly as it can be done the great principle embodied in the Declaration of Independence that all governments derive their just powers from the consent of the governed.

The Society holds two general meetings of its Council and of its membership each year, its Board of Directors

meets at the same time also and at such other times as the business of the Society requires.

The object of the American Chemical Society is "the advancement of chemistry and the promotion of chemical research."

In furtherance of these objects the work of the general meetings is carried out in 8 Divisions, namely: Industrial Chemists and Chemical Engineers; Physical and Inorganic Chemistry; Fertilizer Chemistry; Agricultural and Food Chemistry; Organic Chemistry; Pharmaceutical Chemistry; Biological Chemistry; Water, Sewage and Sanitation.

The American Chemical Society publishes three journals, one for pure chemistry, one for industrial and engineering chemistry and a third devoted to coordination of progress everywhere and in all branches and lines of chemistry.

Supplementary to this there are 33 standing and divisional committees appointed annually which look after the subjects confided to their care and 9 of these deal with topics of national scope.

OUR PLAN OF ORGANIZATION THE BEST

This plan of organization is unique in the chemical societies of the world and since the outbreak of the present war, German chemists of prominence have publicly praised this plan and have expressed regret at the absence of such a suitable plan in their own

nated organization among the chemists of their own country, and have cited it as a reason against further subdivision among German chemical societies. While this is not necessarily conclusive yet it is a matter of some satisfaction to have an admission that the chemists of the United States do something better than their professional brethren across the Atlantic. It may, therefore, be stated with confidence as a fact, and not at all as a vainglorious boast, that the American Chemical Society is the largest chemical society and has the best plan of organization of any chemical society in the world.

OUR GOVERNMENTS AND CHEMISTRY

The various states of the Union and their respective municipalities devote a considerable amount of effort and money toward the growth and diffusion of chemical knowledge and the application of chemistry to the welfare of their citizens. Our Federal Government likewise expends much effort and money toward the same ends. In this respect, also, we can invite comparison with any other country confident that it will not result to our disfavor.

OUR PAST POLICY

For the first thirty years or so of its existence the American Chemical Society practically entirely refrained from taking part in shaping national policies or in solving national problems, partly because it was not invited so to do and partly because it regarded its function to be fostering the science rather than the art and the industry of chemistry. Gradually this has been changed and quite markedly so with the founding of its *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY* in 1908, which has come to be regarded as the best publication of its kind in this country. The actual participation of the Society, as such, in shaping policies of national scope did not increase much, if any, until during and after 1914.

OUR ACTIVITIES SINCE 1914

Since 1914 the American Chemical Society has participated nationally by having representation as follows:

- 1—On the Naval Consulting Board.
- 2—On Advisory Committees to the Bureau of Standards and to the Bureau of Mines.
- 3—On the National Research Council.
- 4—In conjunction with the National Academy of Sciences and four Engineering Societies for general lines of cooperation and also on the Nitrate Supply of the United States.

This, in itself, is an achievement and a recognition of no small significance and importance; it is a matter of justifiable pride and satisfaction that we have been able to render national service of worth and effect, but it is largely the result of invitation and not of our initiative. However, we must not dwell upon these results too long nor too exultantly.

OUR FUTURE

This new phase of our activities, upon which we

have entered quite by force of circumstances and not at all with forethought or conscientious, deliberate and comprehensive planning or initiative must give us pause and compel us to consult among ourselves and with our friends as to the responsibilities we are thus assuming and as to the best and most effective way of discharging them patriotically, promptly and comprehensively, all for the best interests of the Nation.

There can be no doubt that if the membership of the American Chemical Society were specifically asked to pass upon these acts of its Council and of its executive officers, that each and all of these acts would be ratified and approved. As a matter of fact, while there has been acquiescence, there has been no such formal ratification and as a further matter of fact, those acts were each and all performed without the specific consent or authorization of the membership itself and in the final analysis the membership must so instruct its officers because for the forty years of its existence the policy of the Society as shown by its acts did not contemplate and has not contemplated any such steps on the part of those it had placed in authority, although there is nothing in that policy and in those acts that could be construed as specifically prohibiting acts of the kind we have performed in the past two years and a half.

WHY WE MUST AUTHORITATIVELY BROADEN OUR FIELD

For those in authority to proceed much further without such specific authority from the membership itself may be fraught with grave danger and may easily leave the door open for internal dissension and strife which could not do otherwise than disturb the magnificent structure of our organization and rob it of its just opportunity to serve the Nation. Those who devised this structure planned wisely and well; they laid their plans as far into the future as they safely could. Three years ago not one of us would have been willing to prophesy this expansion of our activities into the domain of national affairs in the concrete and direct manner that has taken place in the past thirty months. It is for us of to-day to plan as wisely for the future as did they who devised and developed this potentially strong and elastic organization of which every American chemist may well be proud; this structure is now entrusted to our care for its development and safe-keeping. Let us not fail to measure up to the responsibility which the course of events has placed upon us.

WE HAVE NOT FULLY UTILIZED OUR PAST ADVANTAGES

Taking into account the geographical extent and numerical strength of our Society, its exceptionally elastic and adaptable plan of organization and also all that which our federal, state and municipal governments do for chemistry, the question forces itself upon us: Have we in the past made the most of this condition of affairs? I think an impartial inquiry will develop that we have not done so and the reason for

that is not hard to find. We have fostered the science of chemistry in an idealistic manner and have given much less thought to nationality of origin of scientific advancement, than to the actual advancement of the science as a whole; in this we have been encouraged by the general national and international political policy of our Nation, namely that of self-sufficient isolation from the Old World and the general attitude of friend of all the world, and all the world our friend.

OUR PAST ACTIVITIES INCOMPLETE

The events of the past thirty months have not shown that that was an intrinsically wrong course, but they *have* shown that it was not enough; we were all right so far as we went but we did not go far enough; that is, we should also have had an eye on what national advantage we could gain from the general advance of the science as a whole and what national disadvantage would flow from our not making the most of those advances for ourselves and as a Nation.

That is, while our course in the past has not been a mistaken one yet it did include an omission. I believe that we can cure that omission without in any wise interfering with our past policy; in fact, I believe that a cure for that omission will merely strengthen and foster that policy in its own field.

A PROPOSED REMEDY—A BOARD OF CONTROL

As to the remedy, I offer, of my personal initiative, the following plan as a feasible, practical and practicable means of so expanding our activities with authority and authoritatively. This plan is:

I—The membership, by secret letter ballot, to vote on the expansion of our activities to cover all fields of national endeavor, economic, scientific, commercial, industrial and the like.

II—In the event of the adoption of such an expansion of policy, the Society to have a Board of Control of National Policies of the American Chemical Society. This Board of Control to consist of five members: the President of the American Chemical Society, the Secretary of the American Chemical Society, the Editor of the *Journal of Industrial and Engineering Chemistry* of the American Chemical Society or of its successor-publication and the two available past Presidents of the American Chemical Society next preceding, each member to have one vote. The President of the American Chemical Society shall be the Chairman of this Board of Control. The Secretary of the American Chemical Society shall be the Secretary of this Board of Control. This Board of Control shall have complete and sole jurisdiction over any and all subjects of national scope to be taken up, shall direct what national matters shall be taken up, and no such work can be taken up without the consent of this Board. Further, as to the manner in and the extent to which they shall be taken up, the Board of Control shall appoint necessary committees and their needful officers and shall direct and supervise the work and reports of all such committees and such committee-reports are not to be made public until approved by the Board of Control and shall be published by the Board of Control in that publication of the American

Chemical Society best adapted thereto and in any additional publications this Board may elect, and shall be communicated to such committees or public bodies as this Board may deem desirable. At each Fall meeting of the Society this Board of Control shall report to the general meeting what it has accomplished since the Fall meeting next preceding, the work in hand and the work in project and all the suggestions for added work or for betterments it may then have received from members of the Society or from others and this report to be printed in full, in the next succeeding issue of the Proceedings of the Society and in any other place or places the Council may designate. At the December letter-poll of members, in alternate years, the membership shall be asked to vote on continuance and discontinuance of the authority for such expansion of our activities and approval or disapproval of the work of the two years next preceding. If such continuance of authority be withheld, this Board of Control shall cease its activities forthwith.

FOR AND NOT OF THE AMERICAN CHEMICAL SOCIETY

It must be remembered that the ultimate work of this Board of Control cannot, in fact, be the opinion or recommendation of the American Chemical Society; all it can be or profess in fact to be is an expression of opinion or the making of a recommendation or a statement of fact *by authority and in behalf of* the American Chemical Society; such an expression of opinion or such recommendation or such a statement of fact in no wise prohibits any member or members of the Society from disagreeing or from publicly expressing their disagreement or non-concurrence in any way that they see fit so long as they do not directly or indirectly represent themselves as speaking for or by authority of the Society or of any part of the Society. Therefore, this Board of Control must see to it that membership on the various committees that it may find needful to appoint be conditioned upon fitness, disinterestedness and ability and willingness to ascertain all the facts, draw all the conclusions and make all the recommendations regardless and entirely independent of any personal opinion, prejudice, or interests prospective committee-members may have.

CONFIDENCE AND AUTHORITY/FAITHFULNESS

Under these conditions the final work of this Board of Control would be entitled to respectful hearing without any quarrels or quibbles as to motives, etc., and, as such, to treatment on its merits—even by no matter how hostile a committee, say, of Congress. The work will have been done by authority of the membership renewed each two years, and the work itself will be authoritative because we are utterly sure that a Board of Control to select the best available men for any given task because it would be made up of men who have reached that Board on the initiative of the membership and because that membership considered them to be of that recommended type required for successful leadership and the Society by so doing them had given them its confidence in their quality, honesty and ability; having passed that confidence of their fellow citizens in that way and in some cases

through many years of honorable Society service in addition, the members of this Board of Control can safely be trusted further to conserve the best interests of the Nation and of their Society as well as their own personal honor.

Such a Board of Control, working in such a way ought and would merit and would soon gain and hold the confidence of the public and of those in authority in our government. For the Society, it would attend to it that there be continuity of effort and policy and that new circumstances were promptly met in the best available way and that our efforts were properly coordinated and further would prevent participation in minor matters, because it would be the sole mouth-piece of the Society in matters of national scope. We could depend upon it that such a Board would see to it that all the work would be done from the viewpoint of the Nation as a whole, that the Society would not be used as a cat's paw for individual ends because in matters of this nature we are American citizens first and American chemists afterwards and we must deal with them with the welfare of the whole Nation in mind first, last and all the time; the American Chemical Society cannot under any circumstances permit itself to be maneuvered into the position of spokesman for individual gain but it must at all times embody, present and advocate the best interests of the Nation and of the whole Nation; therefore, it must be circumspect, judicious, prompt, comprehensive and thorough in all such work and must at all times command and deserve the full confidence of the public; it must not promise more than it can perform and must live up to its promises.

SMALL COMMITTEES THE ONLY PRACTICABLE MODE

We must get at all relevant facts, deductions and conclusions and face them whether we like them or not; we must not fear nor solicit political favor, we must be comprehensive, complete, fair and just in our work. To my mind this can be accomplished by a Board such as I have just outlined and now is the time to start in on the work, for, under the most favorable conditions, it will be four or six years before a smooth-working organization can be effected.

From the practical point of view of getting things done, experience unequivocally teaches that to leave the execution of a piece of work to our membership at large is totally inefficient and non-productive of results within any reasonable time. A small committee of 3, 5 or 7 members, having received its general instructions from such a Board of Control, would get somewhere and with a reasonable degree of certainty and accuracy long before the total membership or a majority thereof, would have realized, understood and appreciated the trend, scope and purport of the instructions and of the work to be accomplished. Such a Board of Control, having all national threads in its hands, would attend to it that not too much was undertaken at one time, that the needful cooperation between different committees was forthcoming and relative progress kept in alignment, that the various results were promptly communicated where they would accom-

plish the most, and the entire activity kept in definite relationship to the campaign as a whole—something which the membership as a whole or our Council could never hope to realize or to accomplish.

EXCLUSIVE SPOKESMANSHIP NECESSARY

The title "American Chemical Society" belongs to the Society as a whole and no part nor member of the Society should make use of that title not in harmony with the aims and objects of the Society as a whole. If members, sections, or divisions of the Society disagree with any particular act of national scope of the Society they should in no wise be hampered nor interfered with in full and free public expression of that disagreement but they, on their part, must avoid everything that would tend to give their disagreement the appearance of sanction by the American Chemical Society or any part of it, otherwise confusion must result and consequently the name of the American Chemical Society may come to stand for much less than in reality it should.

SUMMARY

In order to have the greatest weight with legislative and similar committees, those appearing before them, professedly in behalf of the general good, must first show conclusively or at least very persuasively that they have no individual nor collective axes to grind either directly or indirectly. This would be taken care of by the plan just outlined which would be embedded in our membership, would take its right of existence from that membership and, based upon its record, must go back to that membership once every two years for a new lease of life. Secondly, they must show conclusively or persuasively that they know what they are talking about and that they are competent to perform the work they offer to perform. For this we shall have to rely upon the judgment of this Board of Control to pick the best men available for any particular piece of work. With a Board constituted as outlined this seems to me a matter of very small risk and of a very great degree of certainty.

Further, this Board being charged with the initiative and the sole and exclusive spokespersonship for the Society in matters of this kind would be put on its honor and on its mettle to see to it that important national matters were promptly discerned and properly treated as they arose and that not too much was attempted at any one time and that the scope of the work was confined to practical limits, all of which things a large body such as our Council and certainly our membership could never hope to accomplish.

THE AMERICAN CHEMICAL SOCIETY CAN ONLY GAIN

In so exclusively delegating the initiative, direction and execution of its participation in national affairs does the Society or do its sections or divisions relinquish anything fundamental? I think the answer must be "No." The membership itself cannot do this work nor can the Council and it is, therefore, a question of getting something constructively done nationally as against getting nothing done at all. The only risk that we run is that of placing all our national activities in the hands of five men. But all

these men have already been tried and found true to our best interests and there is no real reason to believe that they would not continue so to be true.

As I see it, there is a positive added advantage in having such a Board of Control because the participation of the Society in national affairs should increase rather than decrease. As matters now stand, the President of the Society, who is generally new to such responsibilities, may appoint any committees he deems needful, inclusive of committees on affairs of national scope; while this plan would take away from him the sole appointing power of such national committees he would be given definitely and specifically four experienced advisors who must act with him and all five must act in concert; the President is thus officially given specific and experienced help in problems of national scope and the Society *gains* by having five men decide, guide and control its conduct in these matters as against but one, a usually inexperienced man, under our present arrangement. As against this we have loss of such rights as sections and divisions may now have for action in national affairs, but these rights should be formally surrendered, to the end that national action by the Society may be given greater force and effect; if at any time this Board of Control abuses its powers or is derelict in its duties such sectional or divisional rights can be recovered and exercised in the manner provided. To my mind, this temporary and controllable parting with sectional and divisional rights can only be in the interest of all since there can really be but one leader and we must all get back of the leader and should not be pulling in different directions.

THE POSSIBLE FIELDS

Those of our members who have accepted positions on committees and boards of national scope on behalf of or for our Society have every right to expect authoritative, prompt and efficient coöperation from the Society should occasion therefor arise and this without any strings tied to it, and they should have it. A Board of Control, such as suggested, will enable our Society to give that coöperation in the most efficient, authoritative and effective manner available and far better than any we could give under our present arrangement.

Questions of conservation of water power, mineral products, forest products and the like will no doubt offer additional opportunities to such a Board as also will questions of developing and diversifying our internal manufactures and trade, our export trade, transportation of materials, hours of labor, old age, accident, sick and pension funds, workmen's compensation acts, coordination of instruction, investigation and research, in addition to those national questions in which we have heretofore or only recently participated. Now that Congress, by creating a Tariff Commission, has conceded that Congressional committees such as the Ways and Means Committee and the Finance Committee of the Senate are unequal to the task of ascertaining fundamental facts and of determining what are fundamental facts, opportunity is given us to aid in that direction unhampered by the

claptrap, sophistry, legerdemain, unfair tactics and browbeating that seem to be inseparable from so many congressional committee investigations, and paying attention solely to the merits of the subject; we will be in good position then to make recommendations to Congress as to specific tariff-treatment, something which the Tariff Commission itself cannot freely do. No doubt there will be further opportunities of aiding in other national fact-ascertainties which are not or cannot be efficiently executed by congressional committees but must be done by special commissions or the like.

To my mind, the time has come when we must think in terms of the Nation, with our eye on the map of the world and on our national requirements, but without in any wise diminishing our support of the science itself.

CONCLUSION

On the assumption that the membership will decide that the Society should systematically take definite part in all relevant national matters I suggest the foregoing plan as containing a fairly comprehensive and complete basis from which to construct and develop a real working and workable plan.

And why should not the Society decide to expand nationally? If we wish to live up to the finest and best traditions of a democracy there is every reason why we should so decide and none why we should not. Why are we not as well qualified to initiate and guide relevant national matters' as are legislators or government officials? In fact, we are better qualified than either or both and, therefore, we should do it. By evading such opportunity we are not living up to our citizenship nor are we fulfilling our obligations. The American Chemical Society should walk right up to this opportunity and embrace it with enthusiasm and determination. Then—let us not backslide. Let us contribute our share towards making a democracy as efficient nationally as any other form of government. Eternal activity is the price of progress just as eternal vigilance is the price of liberty.

The American Chemical Society has such a comprehensively planned organization and so many points of contact with national endeavor, as expressed in our various divisions of government and our various scientific or technical associations, that it can readily add to its present activities systematic constructive work along lines of national and international polity. This is a gap in our work which we should at once proceed to fill effectively and efficiently lest our national citizenship be reduced to mere lip-service. The plan just outlined is, therefore, submitted as a starting point for such action and because of the great importance of the subject it is given *continued* and careful consideration by the Society.

Finally, whatever kind of national organization is evolved it must have the continued, continuous, prompt and whole-hearted support of the entire membership each of us must give of his strength, time, thought and ability all that he can and wherever he can otherwise those chiefly present and ought not less, aid him.

ORIGINAL PAPERS

FERRO-URANIUM¹

BY H. W. GILBERT AND E. L. MACK

Uranium steel apparently dates from about 1897, when it was stated² that the French Government was trying to make use of uranium steel in guns. Merck's 1907 index (p. 452) states that the only technical use for uranium is in the form of an alloy in the manufacture of gun barrels.

Escard³ states that it is reported that Krupp uses uranium steel in armor plate. There have been various rumors, naturally not capable of direct proof, that Germany is using uranium steel liners in big guns, in the present war.

Fischer⁴ says, "a German firm is putting on the market ferro-uranium to be used in the manufacture of steel. England is also interested in uranium steel and as a permanent supply of ferro-uranium is guaranteed by Messrs. Geo. G. Blackwell Sons and Co., Ltd., of Liverpool, trials on a large scale will be made in the steel industry. The properties of uranium and tungsten steels are similar. Fischer⁵ says, "some of the large (American) steel companies have tried to use uranium in their line of work, but with little or no success."

Tourchinsky⁶ includes without further comment 0.23 per cent in the composition of steels made at the Sonoritz works in 1913.

Commercial use of uranium steel in the United States is quite recent. Keeney⁷ states that in 1915 the Standard Chemical Company worked on the use of uranium in steel and put ferro-uranium on the market. He says, "although the applications of ferro-uranium have not been completely solved, the results are encouraging and indicate that in high-speed steel a small percentage of uranium may be substituted for a very large percentage of tungsten without injuring the cutting qualities of the steel. A high-speed steel showing excellent cutting qualities contained C 0.78 per cent, Mn none, Si 0.16 per cent, P 0.02 per cent, W 8.15 per cent, Cr 3.62 per cent, V 1.81 per cent, U 1.02 per cent." Two or three other American firms are contemplating the commercial production of ferro-uranium.

Comparative tests of uranium steels whose composition is not given, against other high-speed steels, also of unstated composition, have been given by the Standard Chemical Company.⁸ Uranium steel has

been widely advertised as "the last word in high-speed tool steel," and it has also been advertised that "ferro-uranium used in high-speed steels greatly increases strength, toughness and durability, producing a steel that will stand up on the job."

However, the reports of Hoffman and Johnson⁹ were not so favorable, the former stating that a uranium steel with 5 per cent W and 3 to 4 per cent Cr made a very good tool and did good work for say two grindings, but after that did not hold its efficiency and had to be rehardened, and the latter, that a 40-point carbon steel with 0.3 per cent U was disappointing, being red short at ordinary forging heat and altogether uninteresting from a practical point of view.

It is also understood that in most attempts it has been found very difficult to produce uranium high-speed steel free from streaks or seams.

It will be necessary to have more definite data than have yet been published before the real value or lack of value of uranium in steel can be determined. All that can be said at present is that uranium deserves a careful trial both in tool steel and in ordnance, though the former is probably the more promising field.

Although the production of uranium steels was attempted ten years ago, the literature is singularly barren of really definite information on them, and is even more meager in regard to the manufacture of ferro-uranium.

The electrolysis² of fused mixtures of CaO and the oxide of the metal to be produced has been suggested as a method of making ferro-alloys. In a private communication, Mr. Beckman has outlined his process for making ferro-uranium, in which equimolecular proportions of CaO and rather impure U₂O₃ were fused in a magnesite-lined furnace and electrolyzed with an iron cathode and carbon anode. The furnace was not arranged to pour or tap, and the product was chiseled out after cooling. Mr. Beckman stated that he had thus made carbon-free ferros of 60 per cent U, and 9 per cent V with the balance mainly Fe and Si. He kindly sent the writers a small sample whose analysis he did not have, which was made by the above process.

The analysis³ of this sample, the composition of the ferro produced by the Standard Chemical Company,

TABLE I

Ferro	PERCENTAGE COMPOSITION						RATIO TO 10% U	
	U	C	Si	V	Al	Traces	C	Si
Electrolytic.....	57.2	4.2	4.3	Traces	1.5		0.73	0.76
Keeney.....	50.0	3.0	1.0	2.0			0.60	0.20
Commercial No. 1.....	41.2	4.9	2.4	2.3			1.12	0.38
Commercial No. 2.....	40.0	3.5	2.0	...			0.88	0.30
			to					0.75
			3.0					

as given by Keeney,⁴ and the analyses of two shipments of commercial ferro made in 1916 and reported by the purchasers, are given in Table I. The absolute percentage of carbon and silicon in the ferro is not so

¹ Hoffman and C. M. Johnson, in discussion, "Symposium on Electric Steel," THIS JOURNAL, 8 (1916), 949; *Met. and Chem. Eng.*, 15 (1916), 448.

² J. W. Beckman, "An Electrolytic Furnace Method for Producing Metals," U. S. Pat. 973,336, *Trans. Am. Electrochem. Soc.*, 19 (1911), p. 171.

³ By E. L. Mack.

⁴ R. M. Keeney, *Loc. cit.*

¹ To be read at the Kansas City Meeting of the American Chemical Society. Published by permission of the Director of the Bureau of Mines.

² Dennis, L. M., "Uranium," *Mineral Industry*, 6 (1897), 654.

³ J. Escard, "Sur les différents procédés de préparation de l'uranium métallique pur ou à l'état de fonte," *Rev. chim. industrielle*, 18 (1907), 81.

⁴ S. Fischer, "Uranium and Vanadium," *Mineral Industry*, 22 (1913), 773.

⁵ S. Fischer, "The Carnotite Industry," *Trans. Am. Electrochem. Soc.*, 29 (1913), 374.

⁶ K. Tourchinsky, "Nathusius Electric Furnace in the Steel and Tube Works at Sonoritz," *Rev. Russ. Soc. of metallurgy*, through *Rev. de met.*, 12 (1915), extraits, p. 180.

⁷ R. M. Keeney, "Uranium and Vanadium," *Mineral Industry*, 24 (1915), 706. See also J. M. Flannery, U. S. Patents 1,201,625; 1,201,626; 1,201,627, January 2, 1917.

⁸ Standard Chemical Co., "Uranium in High-Speed Steel," *Met. and Chem. Eng.*, 15 (1916), 160; *Iron Age*, 97 (1916), 952.

important as their ratio to the uranium content, so, for comparison, the percentages of these impurities for each 10 per cent U have been calculated and included.

Johnson¹ states that he has encountered so-called ferro-uranium containing 15 to 20 per cent aluminum, and that vanadium was always present, from 2 to 3 per cent up to 28 per cent; he states also that one ferro-uranium analyzed by him contained 15 per cent silicon.

One steel company, according to a private communication, has made ferro-uranium on an experimental scale, in an Acheson graphite crucible, under an indirect arc, using silicon or ferrosilicon as reducing agent, and has produced ferro of 15 to 85 per cent U, with carbon averaging about 4.5 per cent in all lots. Quite a little silicon was also left in the ferro. On the 85 per cent ferro, this would give 0.53 per cent C for each 10 per cent U.

The price of American ferro-uranium in February 1917 was \$7.50 per lb. of contained U, *i. e.*, \$3.75 per lb. for a 50 per cent ferro. A German product was quoted² in 1914 at 450 Marks per kilo for a ferro of about 50 per cent U. A recent quotation³ on uranium oxide is \$3.60 per lb. of 96 per cent U_3O_8 , with special prices on ton lots, equivalent to \$4.40 per lb. of contained U at the price for small lots. This leaves a margin of \$3.10 per lb. U to cover loss of U in reduction, cost of iron, coke, flux, power, labor, interest, depreciation and profit in the manufacture of the ferro.

Partly on account of the price, experiments on uranium steels seem to have been confined to those with a maximum of about 1 per cent U. While it is probable that uranium steels with such high percentages as the 12 to 20 per cent W in some tungsten steels may not be commercially desirable, it would be well to know what the properties are of steels really high in U.

In present practice in the addition of ferro-uranium to steel, $1/3$ to $1/2$ the U is lost. Experience will probably reduce this loss materially, but reports so far indicate that with a ferro much below 40 per cent U the U is not readily taken up and that with a very high U ferro—say 95 per cent, or practically a crude metallic U, the metal burns up so rapidly that much is lost before it can get into the steel. It seems probable that 45 to 65 per cent U will be about the proper percentage. Those who have attempted to use ferro-uranium find that it must be added just before pouring or during pouring, as, if added any length of time before the steel is cast, no U is found in the steel, possibly because of reaction with slag as well as oxidation. The steel should be very hot.

The C and Si ratios in the ferros, whose compositions have been given are so high that, with the $1/3$ to $1/2$ loss of U, these ferros, even if added to a carbon-ferrous iron, would reach the usual limit of carbon for a tool steel when about 3 per cent U remains in the

steel, and in most cases the silicon would also be over the usual limit.

On the other hand, if experiments prove that only very small amounts of U are desirable, ferros of the composition given, or those even higher in carbon, could be used. But until a purer ferro is produced, experiments on steels really high in U and of normal C and Si content will be impossible.

The uranium oxide used in the work described below was produced by the National Radium Institute. It was mainly UO_2 , with some U_3O_8 . This runs about 83 per cent metallic U. The oxide contained about 2 per cent Fe_2O_3 , 0.1 per cent Al_2O_3 , 0.1 to 0.25 per cent V_2O_5 , 0.20 to 0.35 per cent SiO_2 , 0.3 per cent moisture, 1.3 per cent NaCl, 0.15 per cent carbon. Of these impurities, for use in a ferro-uranium made by reduction with carbon, only the Al_2O_3 , V_2O_5 , and SiO_2 can introduce impurities into the ferro. On the basis of metallic U + V + Si + Al, the total impurities that can go into the ferro are less than 0.5 per cent.

Beside the greater purity of this UO_2 than most commercial U_3O_8 , the lower oxide is advantageous in that the first stage of the reduction, from U_3O_8 to UO_2 , has already been accomplished, hence the further reduction, from UO_2 to U, will not require as much energy as would be the case when U_3O_8 is used. In order that the other materials used might approach this standard, a pure ingot iron, and a low-ash coke were used.

UO_2 is not reduced by carbon below $1500^\circ C.$,⁴ and according to temperature measurements on the surface of the slag at the end of successful runs, a temperature of at least 1700° is required for efficient reduction, requiring an electric furnace.

UO_2 has a specific gravity of 10.2, that of iron is a little under 8, and that of metallic uranium is about 18.7. Hence if one melts UO_2 , carbon and iron together without a slag, the iron will stay on top and will not collect the uranium. So it is essential to have some flux present which will combine with UO_2 to form a slag lighter than iron. This slag should also be a good arc-supporter, in order to use the direct arc type of furnace, since the bulk of the reduction seems to go on directly under the arc itself. The slag must not introduce undesirable impurities into the ferro. The furnace must be provided with a lining that will not be strongly attacked by the slag or introduce undesirable impurities, and which will stand up at the high temperature needed.

Attempts to produce the ferro in an indirect arc type of furnace soon showed that there would be an excessive power consumption to get the required temperature, and the direct arc type was then taken as the most promising. The Remondet type, where the arc is deflected onto the charge, might serve, but was not tried, as only single phase power was available, and there was no difficulty in getting materials which were good arc supporters for the direct arc type.

In preliminary experiments it was found that MgO made a very good slag with UO_2 and as it was 61.0 per

¹ C. M. Johnson, "Chemical Analysis of Special Steels," 1914, ed., pp. 298, 299.

² Dr. Haas's price list, May, 1914.

³ Bunte Mineral Co., Mineral Price notes, January 10, 1917.

⁴ H. G. Bousquet, "Reduction of Uranium Oxide by Carbon," *J. Chim. Phys.*, 93, 1906, 488.

thought that Al would not be reduced rapidly enough to produce a very impure ferro, this was tried.

In order first to produce a ferro sufficiently high in U without regard to carbon content, experiments were made with both Girod and Héroult type furnaces with carbon or graphite hearths. Some of the first of these were not tilting or tapping and the product was taken out when cold, but it was soon found that even for preliminary work, a tilting furnace was desirable, since, by tilting the furnace to and fro slightly during the run, a fresh charge can be brought directly under the arc and far better results obtained.

over the graphite hearth, in the hope that it might keep the ferro away from the graphite, but while some of this layer remained unfused, the ferro would break through and touch the graphite, and high carbon ferros resulted, giving a ratio of from 0.9 to 1.3 per cent C for each 10 per cent U, save in Expt. 49, where, after the furnace was cold, a small separate regulus was found that had been kept out of contact with carbon by the UO_2 layer. This piece, 49 B, analyzed 50 per cent U, 0.62 per cent C, or 0.12 per cent C per 10 per cent U.

It is evident that ferro-uranium can be readily pro-

TABLE II—RUNS IN TILTING FURNACES, GRAPHITE HEARTH— Al_2O_3 IN SLAG
Experiments 47, 48, 49, 50 and 65: Layer of UO_2 on Hearth

Expt. No.	Lbs. Fe	Lbs. Slag-Formers Charged with Fe				Lbs. Old Slag Charged	Lbs. Lbs.		Time C	Furnace at Start	Lbs. Lbs.		Time C	Furnace at Start	Lbs. Lbs.		PERCENT ANALYSIS OF PRODUCT					Ratio to 10% U
		Al_2O_3	CaO	UO_2	UO_2		SiO_2	Coke			SiO_2	Coke			SiO_2	Coke	U	C	Si	Al	C	
39	3.0	1.0	0.25	1.0	4.0	1.25	1	8	Cold	51	4.75	47.5	4.2	0.3	Not det.	0.89	0.06	0.07	
40	4.0	5.25	1.5(b)	1	12	Cold	60.5	8.1	42.5	4.5	0.3	Not det.	1.06	0.07	1.0(f)	
41	4.0	0.5	0.3	0.5	6.0	1.25	1	3	Cold	58.5	10.8	45.0	4.2	0.4	Not det.	0.94	0.10	1.0(f)	
44	3.5	2.0 (No. 43)	...	6.5	1.5	1	0	Cold	59	6.0	52.0	5.8	0.5	Not det.	1.12	0.10	1.04	
45	3.5	2.0 (No. 43)	0.5	6.5	0.25(c)	1	48	Hot	30	7.0	39.0	5.2	1.6	2.0	1.33	0.41	1.0(f)	
47	4.0	0.9	6.4	1.5	1	0	Cold	40	8.5	55.0	5.9	1.07	...	1.0(f)	
48	4.0	8.0	...	6.0	0.7	1	10	Cold	40.5	6.6	45.0	4.85	1.08	...	1.0(f)	
49	4.0	3.75	...	3.5	0.5	...	32	Cold	36	3.0	29.5	2.55	0.87	...	1.0(f)	
50	4.0	1.0	10.6	0.9(d)	1	52(e)	Cold	51(e)	1.5(f)	50.0	0.62(g)	0.3	...	0.12	0.06	1.0(f)	
65	4.0	3.0(a)	8.75	0.6(d)	1	12	Cold	50.75	8.0	38.0	5.8	1.0	...	1.53	0.26	1.0(f)	

(a) Plus 1.0 CaF_2 . (b) Charcoal. (c) For reduction of SiO_2 . (d) Coke at end, after adding UO_2 not mixed with it. (e) Total.

(f) Taken from furnace when cold. (g) Sample poured 3 min. after coke was charged. (h) Second pour. (i) This piece not in contact with graphite.

(j) This piece probably not in contact with graphite.

Hence a small tilting, single-phase Héroult type furnace, with a graphite hearth, was built. This furnace, and those later used, all took 600 to 750 amperes at 60 to 90 volts; with 90 to 95 per cent power factor, i. e., some 30 to 60 kw. It was regulated either by the length of the arcs or by regulating the voltage. The iron was charged into the furnace, slag formers added, the furnace heated till iron and slag were fluid, then the charge proper (UO_2 mixed with coke) added slowly and the furnace then heated 20 to 30 minutes more before pouring the ferro. Results in this furnace are shown in Table II.

duced on a carbon hearth with very little loss of U, but that there will be 4 to 5 per cent carbon in the ferro, and that without water-cooling of the hearth a layer of UO_2 cannot be satisfactorily preserved.

A magnesite hearth was tried in the same furnace shell as was used with the graphite hearth, with the Al_2O_3 slag and with excess carbon in the charge and ferros of 33 to 40 per cent U, 4 to 5 per cent C, produced, but the magnesite hearth was ruined in one to three heats. A zirkite hearth was ruined in one heat. Small scale tests of silica and chromite were made, but neither stood up and they introduced, respectively,

TABLE III—RUNS IN STATIONARY WATER-COOLED FURNACE
Experiments 54, 56, 57 and 58 on Magnesite Hearth. Experiments 61, 62, 63 and 64 on SiC Hearth

Expt No	Old Slag in Hearth	Lbs.				Lbs.		Lbs.		Ferro-Silicon (50%)	Time	Kw. h.	Lbs. U-free	Lbs. Ferro in Regulus	PER CENT ANALYSIS OF REGULUS				Ratio to 10% U
		Fe	CaF ₂	Al ₂ O ₃	CaO	UO ₂	Coke	CaC ₂	U						C	Si	Al	C	
54	28.0(a) (Nos. 45, 49 and 50)	4.0	...	1.0	0.5	1.0(e)	1	20	42.75	2.0	3.5	46.0	1.3	1.3	Trace	0.28 0.28
56	18.0 (No. 55)	3.0	...	0.4	...	3.0	0.75(f)	1	30	40.75	2.0	1.4	28.0	3.4	1.8	4.9	1.21 0.65
57	23.0 (Nos. 55 & 56)	4.0	1.25	0.6(e)	1	15	40.75	2.25	2.25	33.0	2.7	1.4	0.7	0.82 0.42
58	8.0 (No. 57)	4.0	1.3	0.6	...	4.0	0.5(e)	53	40	...	6.0	1.6
61	1.5	4.0	...	1.25(b)	10.0(f)	0.6(e)	1	18	40	...	4.5	45.0	3.7	0.3	...	0.82 0.07
62	11.0 (No. 61)	3.7	11.0(g)	None	2.0(g)	42	...	6.25	12.0	3.5	0.7	...	2.92 0.58	
63	25.0 (No. 62)	3.9	None	0.9	0.5	1	...	40.5	...	5.25	9.0	2.5	4.5	...	2.78 5.0	
64	19.0 (No. 63)	3.0	0.5	0.75	40	...	4.0	35.0	3.9	1.4	...	1.12 0.40	
(a) Plus 1 lb. fine magnesite. (b) Also 0.35 BaO. (c) In bottom. (d) In charge. (e) Alone. (f) Mixed with UO ₂ . (g) Also 0.3 Na ₂ CO ₃ .																			

(a) Plus 1 lb. fine magnesite. (b) Also 0.35 Br_2O_3 . (c) In bottom. (d) In charge. (e) Alone. (f) Mixed with UO_2 . (g) Also 0.3 Na_2CO_3 .

In Expts. 39-41, 16.75 lbs. UO_2 were charged, and 24.65 lbs. ferro averaging 44.5 per cent U were obtained. The UO_2 charged was equivalent to about 14 lbs. metallic U and 11 lbs. metallic U were obtained in the ferro, or nearly an 80 per cent recovery, not counting the U in the metal and slag (about 3 lbs.) left in the furnace which bring the loss down to about 10 per cent. In other words, the loss of uranium is very small. There is a slight orange sublimate, apparently UO_3 , given off in small amounts, some of which condenses on the electrodes.

In Expts. 47-50 inclusive, a layer of UO_2 was fused

large amounts of Si and Cr. Hence, a magnesite hearth, and later a carborundum hearth, water-cooled in order to maintain a layer of frozen UO_2 or slag over it, was tried in a stationary furnace. The product was dug out when the furnace was cold. This was usually in two parts, one which had not gotten under the arcs, as the furnace could not be rocked back and forth to stir the charge, and which had only a trace of U, the other the regulus, in the center. The results are given in Table III.

The Al_2O_3 in the slag introduced Al into the ferro. This may be more of an apparent than a real impurity,

as Al_2O_3 and uranium oxides form a fluid slag, and as small amounts of Al might be expected to be oxidized before the bulk of the U is, the Al might even to some extent protect the ferro from loss of U and the Al_2O_3 be eliminated as a fluid slag instead of held as infusible Al_2O_3 inclusions, as when Al is used alone. It is possible that a Fe-U-Al alloy that would give a fluid slag on oxidation might be found to reduce the trouble from streaks and seams in uranium high-speed steel or at least prove a good deoxidizer and scavenger for steel. However, the present purpose is to produce a ferro-uranium as free as possible from all impurities. Experiments were made with other slags: one of B_2O_3 -CaO- UO_2 was not satisfactory, but a CaO-CaF₂- UO_2 slag worked fairly well.

For the preparation of pure uranium from the oxide, Kuzel and Wedekind¹ suggest the use of metallic calcium, while another patent² suggests the use of CaC₂

shell 18 in. × 18 in. × 14½ in. high in the body portion, and with a hearth portion 11 in. × 11 in. × 4½ in. deep extending downward from the bottom of the body portion, was made up, mounted on trunnions, provided with pouring spout, and the hearth portion arranged for water-cooling by being surrounded with a perforated spray pipe, the holes in which were at such an angle that the streams hit the main or upper bottom just outside the junction with the sides of the hearth portion, causing sheets of water to cover the junction and flow down the sides.

A pan 15 in. × 15 in. × 3 in. deep suspended by corner posts extending down from the main bottom was hung with its bottom 1 in. below the hearth bottom. A hole was cut in the center of the bottom of the pan of such size that it did not drain the cooling water all off, but some ran over the edges.

This covers the bottom and the lower 2 in. of the

TABLE IV—TILTING FURNACE.

CHARGE PROPER IN POUNDS— Disregarding Slag Left in Furnace										FURNACE WATER-COOLED HEARTH									
Expt. No.	Fe	CaO	CaF ₂	Mill Scale	Old Slag	UO ₂	Coke	Time Hrs.	Furnace at Start	Kw. h.	Lbs. Poured	Percentage Analysis of Product	U	C	Si	Ratio to 10% U	Si	REMARKS	
66	4	5	0.9	1	10	Cold	53.5	4.0	58.0	2.4	1.0	0.42	0.17	SiC hearth & sides. Little CaO & CaF ₂ used or needed. Ferro touched SiC sides.	
67	4	5	0.8	45	Hot	33	7.3	44.5	2.25	1.0	0.51	0.23			
68	4	5	0.7	1	10	Cold	53	6.5	37.5	2.1	3.0	0.58	0.80		
69	4	5	0.6	40	Hot	28.25	5.4	37.5	1.75	2.0	0.47	0.54			
70	4	5	0.6	32	Hot	18.25	6.5	25.5	4.2	2.5	1.64	0.98			
73	...	0.2	0.2	5.0	2.5	5.2	1.0	1	10	Cold	47.5	5.8	70.0	1.7	3.8	0.25	0.55	Magnesite hearth, carbon sides in this and all subsequent runs. 5 lbs. mill scale + 1 lb. coke charged before UO ₂ and rest of coke.	
74	...	0.2	0.2	5.0	...	5.2	1.0	40	Hot	28.25	5.9	60.0	2.4	2.4	0.40	0.40			
75	4.0	11.0 (No. 74)	...	0.85	1	5	Cold	50.0	8.9	51.5	2.05	2.5	0.40	0.49	No. 71 slag contaminated with SiC. Too much slag in furnace, slag too stiff, magnesite spalled from roof.	
76	4.0	4.5 (No. 74)	7.0	0.8	40	Hot	30.0	6.5	48.0	1.65	1.75	0.35	0.37			
77	4.0	0.1	0.2	...	5.0 (No. 76)	3.0	0.8	1	0	Cold	46.75	6.8	45.5	2.0	4.0	0.44	0.88		
78	4.0	8.3.5 (No. 71)	10.0	0.8	40	Hot	27.5	6.9	46.0	2.1	1.8	0.46	0.39			
79	4.0	0.1	0.2	12.0	0.8	40	Hot	21.75	3.0	33.0	2.6	1.4	0.79	0.43			
80	4.0	0.3	0.3	...	6.0 (No. 79)	6.0	0.8	1	2	Cold	48.75	5.2	67.0	1.1	0.9	0.17	0.14	Slag stiffened by spalled mag- nesite from roof. Ferro touched carbon walls. A. C. generator temporarily out of commission. Used D. C. at 50 volts 800 amps. on these two. This voltage would hold only one arc, so one electrode always touched slag or ferro, giving high carbon. 10 in. on each electrode used in the two heats. Fresh lining of UO ₂ -CaO- CaF ₂ put in before No. 85 (not contaminated with SiC)—change all added in center from No. 86 on.	
81	4.0	0.2	0.2	...	7.25 (No. 79)	5.0	0.8	40	Hot	25.0	6.8	53.5	2.4	1.2	0.45	0.23			
82	4.0	0.1	0.1	...	8.75 (No. 79)	4.0	0.8	32	Hot	23.5	8.0	45.0	3.6	1.2	0.80	0.27			
										5.0(a)	2.0(a)			
85	4.0	0.1	0.6	9.0	0.8	1	10	Cold	50	5.2	64	3.25	0.35	0.51	0.06	Furnace cooled 2½ hrs between Expts 87 and 88. No. 91 slag contained some embodied No. 91 ferro. Too much CaF ₂ slag too fluid ferro splattered around the carbon sides, giving a high-car- bon normal. No. 96 and 97, entire charge added together. Ferro not hot enough to pour properly.	
86	4.0	...	0.6	10.0	0.8	1	50	Hot	33	14.9	68.5	5.00	0.25	0.73	0.04		
										5.0(a)	2.0(a)			
87	4.0	...	1.4	13.0	1.0	1	10	Cold	50.5	4.2	65.5	1.5	0.45	0.21	0.07		
88	4.0	...	2.7	10.0	0.8	1	7	Warm	52	6.6	59	1.3	0.60	0.22	0.10		
89	4.0	...	0.9	9.0	0.8	42	Hot	33.5	9.2	56.0	1.2	0.65	0.22	0.12			
92	0.75	5.5	9.0 (No. 91)	4.0	2.0	1	10	Cold	50.5	9.5	63.5	2.15	0.65	0.34	0.10		
93	1.25	5.5	9.0 (No. 91)	6.0	2.0	0	53	Hot	38.25	12.5	63.0	1.75	0.90	0.28	0.11		
94	1.25	5.5	9.0 (No. 91)	8.0	2.0	0	55	Hot	30.75	10.6	72.0	2.4	0.60	0.32	0.08		
95	2.40	6.0	...	9.0	2.0	1	15	Cold	45.00	3.2	58.5	3.65	1.20	0.62	0.21		
										4.75 (5.0(a))			
96	1.50	6.5	...	12.0	2.0	1	3	Hot	35.50	7.5	63.0	2.15	0.75	0.34	0.12		
97	1.50	6.5	...	13.0	2.0	1	11	Warm	41.25	4.75 (5.0(a))	43.0	2.15	0.10	0.50	0.16		

(a) Taken out when furnace was cold.

or CaC₂ plus ferrosilicon. At arc temperatures CaC₂ will be decomposed into C and Ca, both of which should take part in the reduction. According to Expts. 62-64 (Table III), coke appears a more effective reducing agent than CaC₂, with or without ferrosilicon.

As the CaO-CaF₂ slag was fairly satisfactory and as the water-cooling preserved a frozen layer of slag over the lining of the stationary furnace, the next step was to combine these in a tilting furnace. An iron

sides of the hearth portion continually with quite a volume of water, while the upper 2½ in. of the sides are cooled by sheets of water. The water falls from this pan into a large pan beneath the furnace, connected to the sewer.

A neater job could have been made by completely enclosing the hearth portion and spraying thick and outlet pipes, but the open system was used instead of a closed one for greater safety in case something should go wrong and the bottom cut through, and, in order that the cooling might be watched.

An apron on the front of the furnace below the pan

¹ H. Kuzel and E. Wedekind, French Patent 419,004, Class VIII, 2, Application Oct. 13, 1909, granted Oct. 15, 1910; published Dec. 24, 1910.

² Electro Furnace and Smelters, Ltd., London, German Patent 247,993, Class 40, Group 15, Application Apr. 8, 1911, patented June 11, 1912.

ing spout (which is $1\frac{1}{2}$ in. above the main bottom) prevents the water from splashing into the ladle or mold, when the furnace is tilted to pour.

A carborundum lining was first used, both in the hearth and on the sides, but the sides were attached by spattered slag, crumbled off, and contaminated the ferro with Si. Had sides as well as hearth been water-cooled, this lining would have served.

Then split magnesite brick ($1\frac{1}{4}$ in. thick) were used in the hearth, and carbon on the sides. For sometime the charge was added between the electrodes and the outside of furnace, with the idea of making sure that the slag did not melt clear to the magnesite. It was found, however, that this was not necessary, and all charging was finally done in the center, between the arcs. Until a high CaF_2 content of slag was maintained, and until center charging was begun, the slag built up in the sump and after a few heats the ferro was brought up so far that it touched the carbon sides and gave high carbon ferros. To prevent this, some of the slag had to be removed from time to time and added to subsequent charges. After chiseling out some slag the rest was roughly shaped into a sump and the furnace heated without charge till the slag was melted, to form a tight frozen lining. In a run, the slag was first melted, the iron charged and melted, then the charge proper slowly added, and heating continued till the CO flame grew weak. The slag never poured out of the furnace with the ferro, but all remained in the furnace. The electrode consumption averaged 1 in. on each 2 in. diameter graphite electrode for each 26 kw. h. used, but much of this was due to oxidation in the air while cooling, so the electrodes were pulled out of the furnace while pouring, which would not be the case in a steadily-run commercial furnace.

The results in the water-cooled tilting furnace are given in Table IV on page 345.

Better results were obtained when the iron was charged in the metallic state, than as oxide (mill scale).

Including UO_2 for slag and lining, there was charged in Expts. 85-97 (see Table IV):

	Lbs. U	Lbs. Fe
151.8 lbs. UO_2 equivalent to.....	125.7	2.1
18.65 lbs. CaO
1.6 lbs. CaO
20.0 lbs. Fe equivalent to.....	..	20.0
35.5 lbs. mill scale equivalent to.....	..	25.7
15.0 lbs. Fe for remelting equivalent to (see Table V).....	9.7	4.7
16.2 lbs. coke.....
	135.4	52.5
There was obtained 107.45 lbs. Fe equivalent to.....	Lbs. U	Lbs. Fe
and 85.0 lbs. slag equiv. to.....	63.4	40.9
	60.0	7.8
	123.4	48.7
	123.4	48.7

Loss, lbs. 12.0 3.8

Loss calculated on 75.4 lbs. U actually used, 16.5 per cent; on 44 lbs. Fe actually used, 8.5 per cent.

Loss calculated on total U, 9 per cent; on total Fe, 7.5 per cent.

Most of the loss was due to fine particles carried out by the CO flame (this might be reduced by briquetting), some to spatter, some to volatilization of UO_3 or of a fluorine compound, and some to mechanical loss in charging and pouring. Two of the thirteen heats included above were on remelting, and the loss therein makes the loss calculated above, too high, 15 per cent being probably nearer the true figure.

The average Si in the last 11 runs in Table IV (all others in that table being contaminated by SiC) was under 0.7 per cent.

The average carbon in all 26 runs, good and bad, of Table IV was under 2.5 per cent. Excluding those where the ferro touched or spattered against the carbon sides, which would not occur if the furnace had water-cooled magnesite sides, the average of 21 runs is under 2 per cent carbon. That of the three runs 87-89, in which the best conditions obtained, was 1.33 per cent C.

The power consumption in 6 runs, 87-89 and 92-94 was under 4 kw. h. per lb. for ferro averaging 63 per cent U, 1.8 per cent C, and on heats 89 and 94, with the furnace fully hot, about 3 kw. h. per lb., pouring about 9 lbs. per heat. In a large commercial furnace, the power consumption should be much lower than in the little experimental furnace.

For a commercial furnace, assuming a capacity of 200 lbs. ferro per heat, 200 kw. (say 100 volts, 1200 amperes per phase), on a three-phase tilting direct arc furnace of the Héroult type, would probably not be too much, as the best results on the ferro come when it is heated very hot, though such a furnace would be overpowered for steel. To withstand the high temperature, the thin magnesite walls and bottom (say $2\frac{1}{2}$ in. thick) should be strongly water-cooled so as to maintain a solid UO_2 lining within them. The roof should be of carbon bricks on the inside, as the usual silica roof would drip and contaminate the ferro. The center of the roof should be open for charging.

A three-phase direct arc furnace like the Héroult is preferable to a single-phase like the Girod, and rather large carbon electrodes should be used, to give as many and as large arcs as are practical, since there is little reduction outside the arc itself.

Fluorspar alone is the best flux tried, if Al is to be kept out of the ferro. Its amount should be so regulated that the slag is not so stiff as to hold ferro in emulsion, and not so fluid as to spatter badly under the arc. The slag was good when 60 lbs. UO_2 (excluding that reduced and poured out as ferro, but including 30 lbs. used as original lining) and 10 lbs. CaF_2 had been charged.

Bleecker¹ suggests first making ferro alloys high in carbon, by reduction with carbon, then crushing the ferro, mixing it with iron oxide or oxide of the other metal in the ferro, and remelting, in order to decarbonize. Or, he states, one may first make a high carbon alloy and decarbonize by later adding to the molten ferro iron oxide or the oxide of the other metal. Remelting iron high in carbon with iron oxide to refine it is of course steel-making routine, and Moissan² and Escard³ both long ago described decarbonizing metallic uranium high in carbon, by heating it with uranium oxide. Table V gives some results on refining high carbon ferros.

The finely crushed ferro emulsified badly with the slag, particularly in Expts. 83 and 84 when the slag was extra stiff because of adventitious magnesite.

¹ W. F. Bleecker, U. S. Pat. 1,094,114, Apr. 21, 1914.

² H. Moissan, trans. by V. Lenher, "The Electric Furnace," 1904 ed., pp. 167, 170.

³ J. Escard, *Loc. cit.*

TABLE V—REMELTING FERROS FOR REFINING
Tilting Furnace, Water-Cooled Hearth

Expt. No.	CHARGE PROPER IN POUNDS											Furnace at		Lbs. Ferro	Percentage Analysis			
	Disregarding Slag in Furnace											Time Hr. Min.	Start		Kw.-H.	of Product		
	ANALYSIS FERRO			Slag	UO ₂	Mill Scale	CaF ₂	Ferro	C	Si								
71.....	6.0 (No. 70)(a)	25.5	4.2								2.5	None	5.0	1	0	Cold	49
83.....	9.0 (No. 82)(a)	45.0	3.6	1.2	9.0 (No. 82)	5.0	0.75	1	20	Cold	55	4.0	56	1.7	1.6		
84.....	7.0 (No. 65)(a)	38.0	5.8	1.0	7.0 (No. 82)	1.75	0.75	..	50	Hot	31.25	4.0	47.5	2.45	1.45		
90.....	7.0 (No. 89)(a)	56.0	1.2	0.65	3.0	1.2	1	..	Cold	49	2.25	43.0	0.95	1.55		
91.....	9.0 (No. 86)(a)	68.5	5.0	0.25	6.0	2.5	..	50	Hot	36	5.0(b)	66.0	1.8	0.75		

Expt. No.	RATIOS PER 10% U			RECOVERY (POUNDS)			REMARKS				
	Original Ferro C	10% U Refined Ferro C	10% U Refined Ferro Si	In Ferro Charged C	In Ferro Charged Si	In Ferro Recovered C	In Ferro Recovered Si				
71.....	1.64	0.98	0.25	1.28	1.50	0.25	0.15	1.25	0.03	0.16	SiC hearth & walls, walls crumbled and contaminated Ferro with Si
83.....	0.80	0.27	0.30	0.29	4.05	0.25	0.11	2.70	0.07	0.06	Magnesite hearth
85.....	1.53	0.26	0.52	0.30	2.67	0.41	0.07	1.90	0.10	0.06	Magnesite hearth
90.....	0.22	0.12	0.22	0.12	3.56	0.07	0.04	0.97	0.024	0.035	Magnesite hearth. Increase in Si probably due to siliceous impurities in CaF ₂
91.....	0.73	0.04	0.27	0.11	6.17	0.45	0.02	4.62	0.126	0.053(c)	
								3.30	0.09	0.038(d)	

(a) Crushed to pea size and smaller. Plus any ferro left in furnace from preceding run.

(b) Taken from furnace in regulus, when cold. (c) Poured. (d) Regulus.

(a) Crushed to pea size and smaller. Plus any ferro left in furnace from preceding run.

(b) Taken from furnace in regulus, when cold. (c) Poured. (d) Regulus.

In all of these runs the recovery of the ferro charged was poor, much less being poured than was charged. There was always some spatter, small globules of ferro being shot up into the air above the hearth, oxidizing, and dropping back into the hearth, the Fe_2O_3 thus produced tending to decrease the percentage of U in the recovered ferro, as metallic U in the ferro will be oxidized by Fe_2O_3 . The experiments indicate that it is probably desirable to produce a low carbon ferro in one operation, rather than first to make a high carbon ferro and then to refine it.

Vanadium has not been determined in most of the ferros. It cannot average as high as 0.25 per cent; though individual ferros, made with a large amount of fresh UO_2 , will run a trifle higher than the average because V is more readily reduced than U, while one made from a charge consisting largely of old slag from which the V is already largely extracted will run lower than the average. A few analyses of the ferros indicated that probably 0.4 per cent and certainly not over 0.5 per cent is the maximum. Traces of V were present in all.

As V is used in almost all tool steels, the very small amount of V that would be introduced into steel by the ferro-uranium certainly would not be classed as a harmful impurity, though for experimental work on the value of U in steel it is desirable to have a ferro-uranium as low as possible in V in order not to have another variable to contend with in the V.

It appears that by using a pure UO_2 , a low-ash coke, and a pure iron as raw materials, with CaF_2 as slag former, and using a tilting direct arc type furnace with water-cooled magnesite hearth and sides, it should be possible to produce commercially, without a second refining operation, ferro-uranium of any desired U content, say 40 to 70 per cent, with carbon averaging below 2.0 per cent, silicon below 0.75 per cent, vanadium below 0.5 per cent, and with aluminum, sulfur, phosphorus and manganese all so low as to be negligible.

If experiments with such a ferro show that uranium steels high in uranium are not valuable, but that a little uranium is useful, and if the amount required is so low that the carbon introduced by a high carbon ferro is harmless, then the furnace might have an uncooled carbon hearth, and the ferro would contain 4 to 5 per cent carbon.

If uranium is found useful only as a deoxidizer or

scavenger of oxygen and nitrogen, aluminum would not be harmful and might be advantageous, and the slag former might be wholly or in part Al_2O_3 .

Grateful acknowledgment is made to the Department of Chemistry at Cornell University for the use, under a cooperative agreement, of its laboratory facilities, which are particularly well adapted to a problem of this nature.

ITHACA, NEW YORK

INFLAMMABILITY OF CARBONACEOUS DUSTS IN ATMOSPHERES OF LOW OXYGEN CONTENT

By H. H. BROWN and J. K. CLEM

Received November 20, 1916

INTRODUCTION

As was stated in a previous paper,¹ if dust could be entirely confined within the machinery of a mill in which combustible dust is produced, and a method could be found for preventing explosions in these machines, a long step would be taken in the prevention of dust explosions in mills. To keep a dust cloud from forming in the machines appears to be almost, if not utterly, impossible. It is possible, however, by proper cleaning to remove foreign material from the grain and thus lessen the possibility of a spark being formed in the machine which might ignite the dust. But cleaners and separators do not always take out all the foreign material, so that even under the best conditions foreign materials may get into the machines, or other conditions develop which might cause sparks, or other sources of heat, to be formed within the machine, thus creating a very dangerous condition. However, if there were present within the machine an atmosphere which would not support combustion, the dust could not ignite and an explosion could not take place.

For some time the possibility of preventing explosions within machines by the use of inert gases has been under consideration. In an article on "Coal Dust Explosions and Their Prevention," J. Hargreaves recommends a low oxygen content in the atmosphere of the mine as a preventive measure. The writer states in part as follows:

The only way to absolutely prevent dust explosions is to reduce the oxygen percentage below the lower limit, which varies with the different dusts.

¹ Ind. Eng. Chem., Anal. Ed., 9, 177 (1917).

A reduction of 2 per cent in practice will do this for all mines, but to get a guarantee of absolute immunity $17\frac{1}{2}$ per cent oxygen is the figure. A $17\frac{1}{2}$ per cent oxygen atmosphere is ideal for a coal mine, if it were not too expensive to obtain, which should not be the case.¹

He recommends not over 1 per cent carbon dioxide in this atmosphere, as a higher percentage would be dangerous from the point of view of respiration.

Referring to decreasing the oxygen content of the atmosphere he states:

"This method is, in my opinion, the only one which can be thoroughly applied to mines or machines making inflammable dust."

The most likely source of such inert gases around a mill are the flue gases. These contain a large amount of nitrogen, 79 per cent, the other 21 per cent containing varying amounts of oxygen and carbon dioxide. Under normally good working conditions the oxygen content is about 11 per cent. Small amounts of carbon monoxide are often present, especially when the oxygen content is low, but this is usually under one per cent. For use in enclosed machines the carbon dioxide content would not necessarily have to be as low as in a mine or in an atmosphere where men were working so this would not have to be removed from the flue gases before they could be used in the grinding systems of mills.

The purpose of this investigation was to determine to what amount the oxygen content of the air must be reduced in order to prevent the propagation of explosions of various carbonaceous dusts.

EXPERIMENTAL

APPARATUS—The Bureau of Mines has made a number of tests upon the inflammability of coal dusts in mixtures of air and natural gas. For this work the apparatus used in the usual testing of coal dusts was adopted with but one change. This was an auxiliary attachment to the base plate for putting the gas into the globe.¹ It consists of a brass tube lying just above the glass injection funnel and passing upward through the base plate at the right of the funnel. After passing through the base plate it extends upward for a distance of 1 in. and then encircles the top of the funnel. The portion of the brass tube forming this circle has eight small holes, spaced at equal intervals from each other, drilled through its upper wall. The outward end of the brass tube is connected to the gas holder.

GAS MIXTURES—The gas mixtures used contained approximately 79 per cent of nitrogen, the remaining 21 per cent being made up of carbon dioxide and oxygen.

To obtain the gas mixtures, commercial carbon dioxide, oxygen and nitrogen were used. The gas mixtures were made in a large gas holder, the amount of each gas used being measured roughly by the height of gas in the holder. The mixtures were then analyzed before and after each series of tests.

METHOD OF OPERATION—To test the inflammability of the dusts in these gas mixtures in the apparatus

referred to above, it was necessary to displace all the air in the globe with the gas mixture. Evacuating and refilling were considered, as were other methods, but the only method which proved to be practical was to allow a sufficient amount of the gas to enter to displace all the air. To determine the amount of gas necessary to displace the air in the globe (capacity of 1390 cc.), measured amounts of a gas containing 9.5 per cent carbon dioxide and 11.2 per cent oxygen were allowed to flow into the globe through the gas injecting tube around the top of the funnel, and to force the air out of a valve in the tube to which the pressure gauge is attached.

A sample taken after 4.5 liters had been allowed to flow into the globe showed 8.2 per cent CO_2 and 13 per cent oxygen. Four and a half liters more were allowed to flow into the globe. A sample taken showed 9.6 per cent CO_2 and 11.4 per cent oxygen.

Nine liters of the gas were allowed to flow through another globe. A sample of the gas in the globe showed 9.5 per cent CO_2 and 11.4 per cent oxygen.

These results indicate that 9 liters of gas will displace all the air in the globe. Therefore, to be certain that all the air is displaced, 10 liters of gas were allowed to flow into the globe before each test. The gas flowed at a rate of 0.9 to 1.0 liter per minute.

To blow the dust into this gas mixture by a puff of air would change the oxygen content and introduce an appreciable error. Therefore, a second connection was made to the gas holder so that gas could be drawn from it and compressed by a vacuum and compression pump, into the bulb attached to the funnel which contained the dust to be tested.

The method of testing was, therefore, not unlike that used for testing the explosibility of carbonaceous dusts in air, except that the explosion flask was filled with a known gas mixture and the dust was injected by the same gas mixture under a pressure of 20 cm. of mercury. The heating of the igniting coil was so regulated that the dust might be injected as soon as possible after all the air had been displaced. This was done to obviate any possible change in the gas mixture by leakage or any other way.

SERIES OF TESTS—A few preliminary tests were made with dusts which gave an indication of the lower limit to be expected. Five typical dusts were then tested, using the following gas mixtures:

Per cent O_2	Per cent CO_2	Per cent N_2
16.9	4.0	79.1
15.0	5.6	79.4
14.1	6.8	79.1
13.9	6.1	80.0
13.4	7.6	79.0
12.8	7.6	79.6
12.2	9.0	78.8
10.9	9.2	79.9
0.8	0.0	99.2

Pittsburgh Standard Coal Dust was tested with the following gas mixtures:

Per cent O_2	Per cent CO_2	Per cent N_2
19.8	1.2	79.0
19.2	1.9	78.9
18.1	2.8	79.1
16.9	4.6	78.5
16.0	8.8	75.2
0.8	0.0	99.2

It will be observed that the sum of the oxygen and carbon dioxide content does not always add to 21

¹ "Inflammability of Carbonaceous Dusts."

per cent. This is due to the inaccurate method of measuring the gas as it was mixed. These figures are the mean of two analyses made before and after each series of tests. In no case was there a variation of over 0.2 per cent in the two analyses.

As in all cases where no inflammation was noticeable, a pressure was obtained above that given by the blank—that is a test made without any dust—it was thought that these might be due to a decomposition caused by the dust striking the hot coil and not due to a slight ignition. To determine this, a series of tests was made using 99.2 per cent pure nitrogen in the globe. With all grain dusts a pressure of 0.4 to 0.5 lb. more than the blank was obtained, that is, a pressure of 0.6 to 0.7 lb. The average of 0.6 lb. was therefore taken as the zero correction, in all tests where gas mixtures are used. Coal dust gave a pressure of 0.2 lb. more than the blank, or a pressure of 0.4 lb. This pressure was taken as the zero correction for coal dust.

RESULTS—The results obtained with the five typical dusts and coal dust are given in Fig. I, the average lbs. pressure being plotted against the percentage of oxygen in the gas mixture. This method was adopted

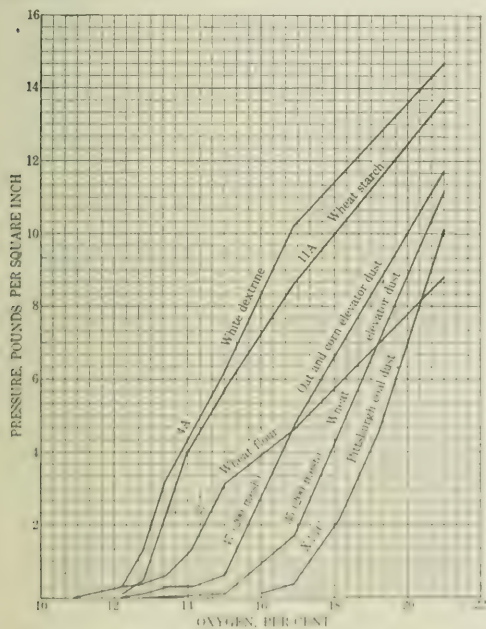


FIG. I

instead of plotting pressures against percentage of CO_2 , since it is the amount of oxygen in the air rather than the amount of carbon dioxide that determines inflammable limits. If the carbon dioxide replaced the oxygen in air, then plotting against carbon dioxide would give the same curves because the balance of the 21 per cent would be oxygen. But in the gas mixtures used, the carbon dioxide was sometimes one per cent lower than would be required to make the sum of it and the oxygen up to 21 per cent. This one

per cent or less is nitrogen, an inert gas, and, therefore, would have a similar effect to that of the carbon dioxide in preventing combustion.

The values as given in the curves are the average of all results obtained in each series of tests. For the pressures above 2 pounds, the results given in each series were quite uniform and concordant. This is also true for pressures averaging under 0.5 lb. But those results between 0.5 lb. and 2 lbs. are less uniform.

It will be observed that these curves are quite similar in their direction, falling very rapidly as the percentage oxygen is decreased until a point is reached where the curves flatten. This point is in nearly every case at pressures near or less than 1 lb. It is considered that rapid oxidation will take place if the oxygen content of the atmosphere is above that indicated by the break in the curve, but cannot take place if the oxygen content is less than this amount.

CONCLUSIONS—Although no large scale tests have been made with which to compare these results, from the general action of the dusts in the tests, it may be concluded that an explosion of a grain dust cannot be initiated in a gas mixture containing 12 or less per cent of oxygen, the remainder being inert gases. And this limit could be extended to 14 or 14.5 per cent of oxygen if elevator dusts alone are considered. The results would suggest that the maintaining of an atmosphere of inert gases in all systems grinding or handling carbonaceous materials which form dangerous dusts would be an effective means of preventing many dust explosions; for even though an ordinarily dangerous amount of dust may be present and a spark or other source of heat may be formed, the dust would not be ignited or an explosion be propagated because the oxygen content of the atmosphere would be too low to support combustion.

The results of these tests show that a lower oxygen content in the inert gas mixture is necessary to prevent an explosion of grain dust than would be required to prevent a coal dust explosion. And, the results obtained with coal dust would indicate that a lower oxygen content in the mine atmosphere would be necessary to prevent a coal dust explosion than was recommended by Harger.¹ However, his recommendation of 17.5 per cent oxygen was very close to that determined by the authors.

It may be noted in this connection that the results published in a previous paper show that with one exception coal dust is less inflammable than the other dusts used in the tests with inert gases. This one exception is wheat flour, a comparatively coarse dust.

Large scale tests are being planned to demonstrate further the effectiveness of this preventive. The results which may be obtained then may alter the above results slightly. However, it is considered, as a result of the present tests, that an inert gas mixture containing 12 per cent or less of oxygen will prevent a dust explosion from starting or propagating.

THE THERMAL DECOMPOSITION OF BENZENE

By J. E. ZANETTI AND G. EGLOFF

Received January 20, 1917

HISTORICAL INTRODUCTION

The discovery of diphenyl by Fittig¹ in 1862 by the action of sodium on brombenzene opened up a new field in organic chemistry. His method, however, was costly and it was not till Berthelot² in the course of his classic researches on pyrogenetic reactions found that benzene, when passed through a red hot tube, decomposed chiefly into hydrogen and diphenyl, a much cheaper method of preparation, that impetus was given to the chemistry of that compound and methods of improving the yields were worked out by various investigators.

Berthelot found that by passing vapors of benzene through a red hot porcelain tube, at the rate of one gram per minute, he obtained hydrogen and a liquid product, from which he isolated diphenyl and other hydrocarbons which he claimed to be "chrysene" benzerythrine, and "bitumene." He stated unequivocally that between the boiling point of the undecomposed benzene and that of the diphenyl, there was no intermediate compound, and that no naphthalene, styrolene, or anthracene were formed. From the gas, which consisted of almost pure hydrogen, he claimed to have obtained a small quantity of acetylene, though the presence of hydrogen sulfide³ interfered with the test for that compound and rendered it uncertain.

Following Berthelot's discovery, Schultz⁴ introduced several improvements and pointed out the influence of rate and temperature. Instead of passing the vapors from boiling benzene through a hot porcelain tube, he used a hot iron tube and dropped the benzene into it at the rate of 1 drop every 3 seconds. Later, he used 100–200 g. per hour and a not quite "white-hot" tube. Schultz' yields were 50 to 60 per cent of the benzene used. Luddens⁵ used a CO₂ stream to carry the vapors of benzene along the hot tube, a method likewise followed by Hübner.⁶

Schultz⁷ studied also the tarry products obtained along with diphenyl, and identified *p*- and *m*-diphenyl benzene and claimed that Berthelot's "chrysene" was only a mixture of diphenylbenzenes and another hydrocarbon melting at 266° C. He obtained also another hydrocarbon melting at 196° C., which gave a compound with picric acid, whereas none of the others would. Berthelot⁸ objected to Schultz' correction, basing his objections on analytical data and put forward the claim that Schultz' product was impure and consisted of a mixture of diphenylbenzenes with "chrysene."

Schmidt and Schultz⁹ made an exhaustive investigation of the tarry products from the benzene decomposition and obtained the following products:

	M. P.	Picrate
(1) Diphenyl	70.5°	None
(2) <i>p</i> -Diphenylbenzene	205°	None
(3) <i>m</i> -Diphenylbenzene	85°	None
(4) Triphenylene	196°	Red needles
(5) Benzerythrine	307–308°	None
(6) Oily hydrocarbons		
(7) Pitch (b. p. above 450°)		

¹ Ann., **124** (1862), 276. ² Ann. de Chim., [4] **9** (1866), 445.

³ From the thiophene in benzene. Thiophene not yet discovered.

⁴ Ber., **5** (1872), 682; Ann., **174** (1874), 201; Ber., **9** (1876), 547.

⁵ Ber., **8** (1875), 870. ⁶ Ann., **209** (1881), 339. ⁷ Ibid., **174** (1874), 230.

⁸ Bull. soc. chim., [2] **32** (1874), 437. ⁹ Ann., **203** (1880), 118.

They again claimed that Berthelot's "chrysene" is identical with their "triphenylene." In their experiments, they used the method previously employed by Schultz, using a rate of 1 drop every 3 seconds. The yield of *p*-diphenylbenzene was 40 g. from 2 kg. of benzene.

Olgiaiti¹ obtained diphenylbenzenes by likewise passing benzene through a red hot tube and collecting the 320 to 420° C. fraction of the decomposition products.

Haber² found that below 900° C. benzene was not decomposed and that only above 1000° C. was it effected with the formation of diphenyl. Haber noticed the formation of other crystalline compounds along with diphenyl but did not investigate them; he remarked that naphthalene was not obtained.

From that time on, owing to the importance of the use of benzene for carbureting water gas, many studies of the decomposition of benzene have been published. McKee³ studied the decomposition of benzene by passing its vapors through a copper tube heated electrically and determining the specific gravities of the recovered products and their appearance under the polarizing microscope. He made no attempt whatever at determination of the chemical composition of these products. The temperatures were accurately measured and mention is made of the regulation of the rate, but it is not given. His temperatures varied between 448 and 765° C. and the only conclusions he drew were that the amounts of decomposition and the specific gravities increased with the temperature. Ipatieff⁴ found that benzene in the presence of iron gave diphenyl and hydrogen above 600°.

Smith and Lewcock⁵ passed benzene vapors at varying rates through a red hot iron tube in the presence of various catalyzers and using varying temperatures. The catalyzers used were oxides of calcium, lead, aluminum, barium peroxide, etc., but as they remark, the action may not have been purely catalytic, since some of the oxides were reduced to the corresponding metals or lower oxides. They find that the yield of diphenyl is not increased by using temperatures above 720°.

Recently, Hollins and Cobb⁶ have found that benzene is not decomposed below 800° when a mixture of hydrogen and methane saturated with benzene vapor was passed through a hot tube.

Rittman, Byron and Egloff⁷ studying the decomposition of aromatic hydrocarbons by passing benzene through an iron tube 6 ft. long at the rate of 200 cc. per hour, using varying temperatures and pressures, state that they obtained naphthalene and doubtless diphenyl, though they did not isolate it.

Summing up in review, the decomposition of benzene by heat takes place in such a way as to split off two or more hydrogen atoms from the ring, forming diphenyl and diphenylbenzenes. No investigator, previous to Rittman, Byron and Egloff, has claimed to

¹ Ber., **27** (1894), 3387.

² J. Gasbel., **39** (1896), 377–382, 395–399, 435–439, etc.

³ J. Soc. Chem. Ind., **23** (1904), 403.

⁴ J. Russ. Phys. Chem. Soc., **39** (1907), 681.

⁵ J. Chem. Soc., **101** (1912), 1453–1458.

⁶ Gas World, **60** (1914), 879. ⁷ This Journal, **7** (1915), 1019.

have obtained any naphthalene, and none at all of anthracene or phenanthrene. Indeed, those who devoted any attention to the point, as Berthelot and Haber, state unequivocally that they were unable to obtain any naphthalene. In other words, all investigators, previous to 1915, have been unable to adduce conclusive evidence that the benzene ring breaks up at temperatures below 800° C. and atmospheric pressure, in any except two ways:

(1) Benzene \rightarrow Carbon + Gas,
or, (2) Benzene \rightarrow Condensation Products, by the splitting off of hydrogen from two or more molecules.

Rittman, Byron and Egloff do not state in their publication what test besides the boiling point they used in determining the presence of naphthalene. Since their claims are entirely in opposition to all previous work, that the amounts of material obtained by them were small, that the boiling points of diphenyl and naphthalene, especially when mixed with other decomposition products, are dangerously near together to be of value in deciding the matter, further evidence on that point seemed desirable.

Berthelot's contention that he obtained chrysene was definitely settled by the work of Schmidt and Schultz¹ who proved that the hydrocarbon he believed to be chrysene melted sharply at 196° and not at "about 200°," and further by Lieberman,² who obtained pure chrysene melting at 250° and pointed out that Berthelot's product could not have been that compound.

In connection with other studies on thermal decomposition of hydrocarbons undertaken in this laboratory by one of us,³ it seemed desirable to study more completely the course of reaction of the decomposition of benzene in order to arrive at some definite conclusions regarding its behavior at high temperatures and gradually gain insight into the complicated mechanism of formation of cyclic and polycyclic compounds from straight chain hydrocarbons.

EXPERIMENTAL

The plan of the experimental work consisted in studying the decomposition of pure benzene by passing it at measured rates through a furnace, the temperature of which could be accurately controlled. The plan included the following topics:

- 1—Influence of the temperature.
- 2—Influence of the rate.
- 3—Influence of the metallic catalyzers.
- 4—Composition of the gases.
- 5—Composition of the tar.

MATERIAL.—The benzene used was pure thiophene-free benzene boiling at 80–81° C. of specific gravity 0.881, at 15.5° C. No test for thiophene was given by the indophenene reaction, and on treatment with C. P. concentrated sulfuric acid, no change of color was noticeable in the acid.

Three hundred cc. of benzene were used in each run whenever possible. In some cases, as when nickel and iron were used as catalyzers, at the higher temperatures, not more than one-fourth of that amount could

be used as the deposition of carbon would plug up the tube, and stop the run.

APPARATUS AND PROCEDURE.—The heating apparatus used consisted of a Whitaker-Rittman furnace, the description of which has been given in detail in THIS JOURNAL¹ and will, therefore, not be described here. The arrangement of the apparatus is diagrammatically given in Fig. I. Essentially it consisted of an iron tube 1½ in. in diameter, electrically heated and provided with a rheostat and a pyrometer to regulate and measure the temperature. The pyrometer was a base-metal thermocouple which was compared with a standardized platinum-iridium thermocouple

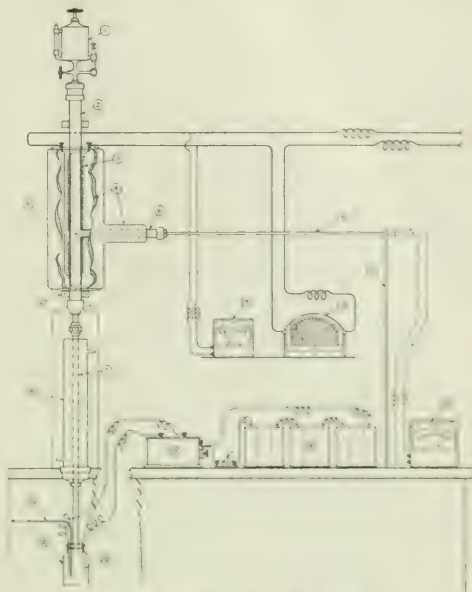


FIG. I—APPARATUS USED IN TESTS

- | | |
|------------------------------|-------------------------------|
| 1—Oil feed cup | 11—Baf for gases |
| 2—Tube of furnace | 12—Electrodes of copper gauze |
| 3—Nichrome wire resistance | 13—Induction coil |
| 4, 5—Magnesia lining | 14—Storage batteries |
| 6—Stuffing box for pyrometer | 15—Pyrometer rod |
| 7—Condenser tube | 16—Pyrometer lead |
| 8—Water jacket | 17—Pyrometer support |
| 9—Support of furnace | 18—Voltmeter |
| 10—Wide-mouth glass bottle | 19—Rheostat |

and found to check up within 5 to 10°, according to temperatures. The temperature could be maintained constant within 5° C. for long periods of time. The benzene was led into the tube from a large oil feed cup with a sight tube by which the rate at flow could be accurately determined by counting the drops falling in a certain time. One drop per second gave a flow of 100 cc. per hour, two drops one and three drops (approx.). These values were determined experimentally, as, of course, the size of the drop will vary with the size of the opening. The benzene did not drop directly into the heated zone, even at the higher rates, but flowed along the sides and evaporated before reaching

¹ *Ind. Eng. Chem.*, **100**, 299. ² *This Journal*, **8** (1916), 631, 1917.

³ *Ind. Eng. Chem.*

the area of high temperature. This is an important point in a vertical furnace since some of the benzene could readily fall through the tube without vaporizing, owing to the small surface of the spherical drop and the short time it would be exposed to heating.

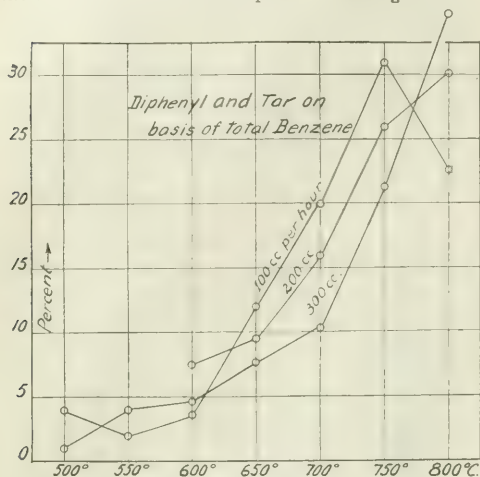


FIG. II—INFLUENCE OF RATE

The condensing apparatus consisted of a piece of iron pipe $\frac{1}{2}$ in. in diameter, 3 ft. long, surrounded by a water jacket. The water cooling was found unnecessary, in fact, detrimental, as the diphenyl was apt to solidify and choke the condenser. The cooling was quite sufficient as was shown by recoveries of 98 per cent of the benzene used in some of the runs where little decomposition to carbon occurs. The receiver consisted of a wide mouth glass bottle provided with two electrodes connected with an induction coil and a set of storage batteries. This arrangement was found very convenient to settle the "fog" from the gases obtained by decomposition at higher temperatures, and afforded a means of accomplishing complete deposition in the receiver. The whole apparatus was washed with benzene before the beginning of a new run in order to avoid vitiating results by decomposition products from a previous run.

The decomposition products of the reactions were distilled in a 500 cc. flask provided with a Ginsky column and a 24-in. condenser for the lower boiling fractions (undecomposed benzene). The residues were transferred to a standard Engler distilling flask and the distillation carried on up to 300° C. Most of the distillate came over between 250 and 275° (diphenyl). A small fraction coming over between 200 and 250°, was collected separately and carefully tested for naphthalene. The residue (tar) was in most cases too small to be fractionated separately, so that the tars from a series of similar runs were added together and fractionated.

CATALYZERS—The catalyzers were pieces of metallic gauze 40 mesh in case of the copper and iron, 40 mesh and 50 mesh in the case of nickel, cut into pieces

10 in. \times 12 in., rolled so as to fit the tube and inserted into the part of the tube above the pyrometer. Frequent changes were necessary as they quickly became coated with carbon. This deposition of carbon was particularly objectionable in the case of nickel and iron where plugging of the tube would occur before much of the benzene could pass through.

GASES—Samples of gas were collected for analysis at the exit from the tar separator. To test for acetylene, a large test tube half filled with an ammoniacal cuprous chloride solution, and provided with a two-hole stopper and a tube reaching to the bottom, was inserted at the end exit from the separator tube. To measure the amount of gas given off in the reaction a Referee meter graduated to 0.001 cu. ft. and provided with a thermometer was placed at the end of the tar separator.

The gases were analyzed over water for unsaturated, by absorption with fuming sulfuric, for hydrogen by passing over copper oxide at 290–300° and for methane by explosion with oxygen.

SOURCES OF ERROR—The chief source of error was the deposition of carbon in the tube and on the catalyzers as well as on the pyrometer rod. This tended to obstruct the passage of the gases and interfered with the temperature measurements. The higher temperatures are probably too low since the deposition of non-conducting finely divided carbon would act as a heat insulator. Since the pyrometer projected into the middle of the tube the temperature measured at the beginning of a run was the actual temperature of the vapors and gases and not merely that of the walls of the tube.

The carrying of undecomposed benzene in the form of vapor by the hydrogen introduces quite an appreciable error in some of the determinations. This

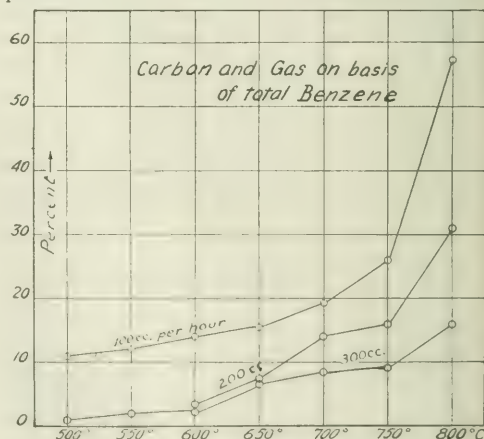


FIG. III—INFLUENCE OF RATE

error increases with increasing decomposition of the benzene and consequent increase in the volume of the gases. At ordinary temperatures (20° C.), the vapor pressure of benzene is 74.6 mm. or nearly 10 per cent of the total volume of hydrogen given off. As

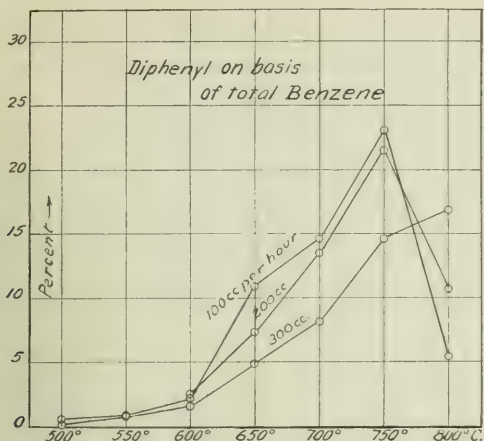


FIG. IV—INFLUENCE OF RATE

there is produced by the reaction, products which dissolve in the benzene and lower its vapor pressure, this amount of benzene in the gas is sensibly lowered. Experimentally we found this percentage to be about 7.3 per cent (see Table III). Calculations of per cent

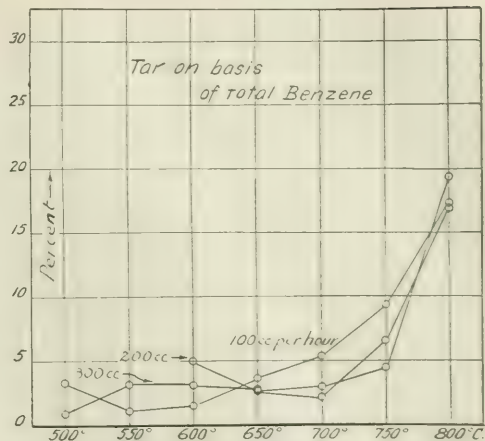


FIG. V—INFLUENCE OF RATE

TABLE I—EFFECT OF RATE (PER CENTS ON BASIS OF TOTAL BENZENE USED)

Temp. ° C.	SP. GR. RECOVERED OILS			PER CENT DIPHENYL AND TAR			PER CENT DIPHENYL			PER CENT TAR			PER CENT BENZENE DECOMPOSED TO FORM CARBON AND GAS		
	100 cc. per hr.	200 cc. per hr.	300 cc. per hr.	100 cc. per hr.	200 cc. per hr.	300 cc. per hr.	100 cc. per hr.	200 cc. per hr.	300 cc. per hr.	100 cc. per hr.	200 cc. per hr.	300 cc. per hr.	100 cc. per hr.	200 cc. per hr.	300 cc. per hr.
500	0.886	...	0.884	4.0	...	1.0	0.6	...	0.1	3.4	...	0.9	11.0	...	1.0
550	0.886	2.0	...	4.0	0.9	...	0.8	1.1	...	3.2	12.0	...	2.0
600	0.887	0.888	0.886	3.7	7.5	4.7	2.2	2.5	1.6	1.5	5.0	3.1	14.0	3.5	2.3
650	0.897	0.891	0.890	14.5	9.5	7.7	10.9	7.4	4.9	3.6	2.1	2.8	15.5	7.5	7.3
700	0.920	0.910	0.896	20.0	16.0	10.3	14.6	13.5	8.1	5.4	2.5	2.2	19.3	14.0	8.0
750	0.950	0.936	0.916	32.0	26.0	21.3	22.6	21.5	14.7	9.4	4.5	6.6	26.0	16.0	8.7
800	0.956	0.950	0.945	22.7	6.8	34.0	5.4	10.7	16.9	17.3	19.4	17.1	57.3	31.0	16.0

decomposition on basis of "actual benzene used" (total benzene benzene recovered) should be corrected by subtracting from the "actual benzene" the amount of benzene vapor which theoretically could be recovered by cooling the gases to a very low temperature. This correction may amount to nearly 13 per cent of the benzene used.

This correction applies likewise to the "per cent of carbon and gas" formation, if the latter is found by subtracting from the total benzene the amounts of diphenyl and tar obtained.

For this reason the percentages calculated in this paper are given on the basis of "total benzene." Moreover, in some cases, especially at lower temperatures, the amounts of "actual benzene" are so small as to

low as 500°. In all cases below 600°, the amounts decomposed are small, but quite appreciable, and leave no doubt that diphenyl and other decomposition products are formed at those temperatures. This is quite in opposition to the claims of Ipatieff and of Haber¹

but the precautions taken in these experiments to prevent contaminations from a previous run and the fact that we obtained diphenyl repeatedly at temperatures as low as 500° can leave no doubt on this point.

If the added percentages of diphenyl and tar as giving the total amount of synthetic products (diphenyl, diphenylbenzenes, etc.) formed, are plotted against temperatures, there is no marked regularity below 600° owing to the fact that the percentages are so close together as to come within the limits of experimental error. Above that temperature, the decomposition proceeds with regularity, being greater in the case of the slower rate which attains a maximum at 750°. Above that temperature, the decomposition to gas and carbon (Fig. III) proceeds so rapidly in the

TABLE II—EFFECT OF CATALYSIS (PER CENTS ON BASIS TOTAL BENZENE)

Temp. ° C.	SP. GR. RECOVERED OILS				PER CENT DIPHENYL AND TAR				PER CENT DIPHENYL				PER CENT RESIDUE TAR				PER CENT GAS AND CARBON			
	None	Cu	Fe	Nickel	None	Cu	Fe	(a) (b)	None	Cu	Fe	(a) (b)	None	Cu	Fe	(a) (b)	None	Cu	Fe	(a) (b)
500	0.884	...	0.884	0.884	1.0	...	1.9	...	0.1	...	0.8	...	0.9	...	1.1	...	1.0	...	1.0	...
550	0.884	0.884	0.884	...	4.0	1.3	2.7	...	0.8	0.4	0.8	...	3.2	1.2	1.9	5.3	...
600	0.886	0.885	0.885	0.884	6.0	9.0	2.7	4.7 0.0	1.6	1.0	1.8	0.8 0.0	3.1	1.1	1.6
650	0.890	0.889	0.887	0.885	7.7	5.0	7.0	3.3 2.2	4.9	3.1	3.9	1.9 0.8	2.8	1.9	3.1	1.4	8.0	30.0 70.0
700	0.896	0.900	0.898	...	10.3	11.3	12.0	...	8.1	9.8	2.2	1.5	4.4
750	0.916	0.926	0.912	0.884	21.3	23.3	11.0	5.0 0.0	14.7	18.1	8.6	0.8 0.0	6.6	5.2	3.4	4.8
800	0.945	0.936	0.906	...	34.0	11.7	10.0	...	16.9	8.6	17.1	3.1	9.8

(a) 40 mesh Nickel

(b) 50 mesh Nickel

introduce very large percentage errors if results are calculated on that basis.

DISCUSSION OF DATA

INFLUENCE OF RATE—The results regarding the influence of rate are given in Table I and Figs. II and III. Decomposition begins, even with the faster rates, as

low as the 500° rate at 500°. The effect of rate on the percentage of synthetic products, the gas and carbon formation being slower in the case of the slower rate, its effect on the synthetic products is less marked and although the percentage of synthetics is greater at

¹ See historical introduction.

800° than at 700°, the rate of increase is much smaller than in the previous 50° rise. Finally, in the 300 cc. rate, the amount of gas and carbon being much smaller than in either of the previous cases, its influence on the synthetics is scarcely noticeable, and their rate of increase is the same between 750 and 800° as between 700 and 750°.

If now we split the "synthetics" into their components and plot these separately (Figs. IV and V), we find that diphenyl decreases markedly above 750°, except in the case of the 300 cc. rate where there is a small increase. In any case, the rate of diphenyl formation is markedly diminished. To counterbalance

cases of reactions in the gas phase. It must be also remembered that, not being a product of the reaction, $2C_6H_6 \rightarrow C_{12}H_{10} + H_2$, it may act in this case as a true catalyst.

The action of copper, iron and nickel as catalyzers is much the same as that observed by one of us¹ in connection with the decomposition of straight chain hydrocarbons. The action of the copper is almost nil up to 700° C. At 800°, however, a marked decrease in the diphenyl and tar formations takes place with consequent increase in the carbon and gas. There may be a question whether this decrease is due to specific catalytic action or merely to increased surface.

Whatever question there may be regarding the copper, there can be none regarding nickel and iron.

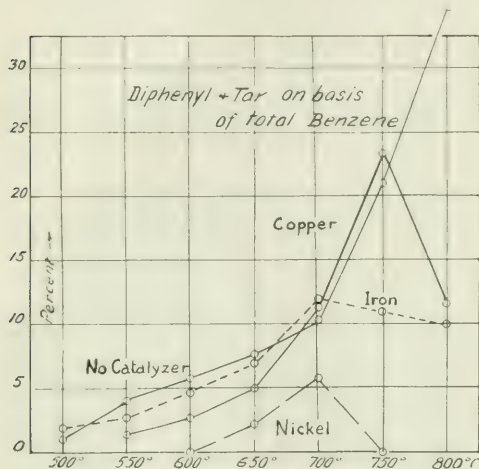


FIG. VI—INFLUENCE OF CATALYZERS

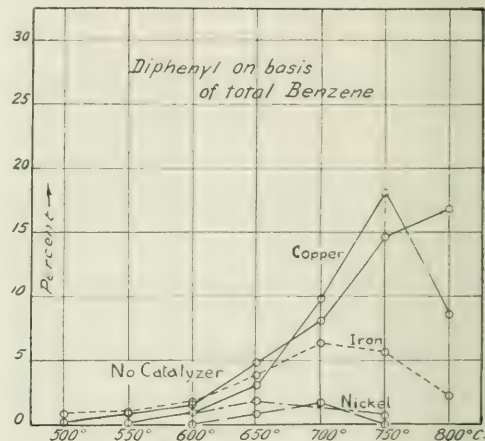


FIG. VII—INFLUENCE OF CATALYZERS

this, we find that in all cases the rate of tar formation increases very markedly from 750 to 800°. It would then appear that the tar formation occurs at the expense of diphenyl and that the diphenylbenzenes and other condensation products are formed by the action of diphenyl on benzene.

INFLUENCE OF CATALYZERS—The catalyzers studied were copper, iron and nickel. For the sake of uniformity, wire gauzes of the same mesh were used, except in the case of nickel when two different meshes were used. The rate in these cases was 300 cc. per hour.

The graph with "no catalyst" is given for the sake of comparison. It is, of course, a question whether the finely divided carbon which forms abundantly at the higher temperatures is not itself a catalyst. As, however, the amount formed on the sides of the tube was the same in all cases, its influence, so far as that amount is concerned, is negligible for purposes of comparison. As to whether a product of a reaction can be called a catalyst, it must be borne in mind that at the higher temperature the speed of the reverse reaction, $6C + 3H_2 \rightarrow C_6H_6$, is immeasurably small, and that the action of the finely divided carbon may be in the nature of a surface action, so important in

These are true catalyzers for the reaction $C_6H_6 = 6C + 3H_2$ (see Fig. VII). Of course, the surface exposed has a marked effect on the action as may be gathered from the results obtained with two different meshes of nickel gauze.

GASES—Analyses of the gases are given in Table III.

Temp. ° C.	LITERS PER 100 CC. BENZENE USED		PERCENTAGES OF TOTAL GAS		
	Total Gas	Hydrogen	Unsaturated	Hydrogen	Residue
500	2.8	2.6	7.2	90.8	2.8
550	4.2	3.9	7.7	89.9	2.4
600	8.5	7.8	7.2	89.8	3.0
650	12.7	11.8	7.2	90.6	2.2
700	28.3	26.2	7.3	88.3	4.4
750	49.5	36.1	7.3	90.5	2.2
800	63.7	59.2	7.1	91.8	1.1

The per cent of "unsaturated" is so constant and corresponds so well to the amount of benzene vapor that it cannot be ascribed to any other cause.

Careful tests for acetylene with ammoniacal cuprous chloride proved absolutely negative. Of all investigators of the thermal decomposition of benzene, Berthelot is the only one to report acetylene,² and he was none too sure about its presence, owing to the interference of sulfur compounds in his benzene which generated H_2S .

¹ Loc. cit. See historical introduction

It seems to us that if acetylene is formed by the thermal decomposition of benzene at atmospheric pressure, we should expect some of the condensation products that it forms with benzene, such as naphthalene, styrolene, anthracene, etc.,¹ whereas none of these products has been reported² and in fact, Berthelot positively declares they are not formed.

In the analysis of the gas, there always remained a residue after combustion of the hydrogen over copper oxide, which could not be exploded with oxygen. This residue, which amounted to about 2.5 per cent, was undoubtedly nitrogen. The very large volume of the system and the necessity of taking gas samples before the almost inevitable plugging of the tube with carbon, made it practically impossible to sweep

tained without the introduction of an enormous percentage error and for the present only the qualitative results can be reported.

CONCLUSIONS

From the above data, as well as from those of previous investigators, it seems settled that the decomposition of benzene at high temperatures (600–800°) takes place in accordance with the following reactions:



At temperatures below 750°, the reaction velocity of the diphenyl formation is greater than that of carbon and hydrogen. Above that temperature, the velocity of the carbon-hydrogen reaction becomes very great and decomposes the benzene before other condensation products can be formed.

It seems of interest to remark on the stability of the benzene ring and on its complete decomposition to carbon and hydrogen without appreciable quantities of intermediate products, such as acetylene, ethylene, ethane or methane at high temperatures. No conclusive evidence has thus far been brought forward to show that the ring is broken at high temperatures with formation of any products but carbon and hydrogen.

The remark of Rittman, Byron and Egloff¹ that diphenyl is not an equilibrium product but merely an intermediate one seems to be borne out by our results with this difference, however, that whereas those authors, as well as McKee,² believed the equilibrium to be Benzene \rightarrow Diphenyl \rightarrow Naphthalene; it is, in fact, Benzene \rightarrow Diphenyl \rightarrow Diphenylbenzenes.

There have been no catalyzers so far brought out that catalyze the formation of diphenyl. Those studied by Smith and Lewcock proved ineffective and those presented in this paper catalyze only the formation of carbon.

FORMATION OF NAPHTHALENE Owing to the fact that this compound was reported present in the decomposition of benzene, by Rittman, Byron and Egloff, very careful tests both as to melting and boiling points and formation of picrate were made on the first fraction that came over on distilling the reaction products, after the undecomposed benzene had boiled off. The boiling point of naphthalene is 218°, whereas that of diphenyl is 254°. If any naphthalene were present, it would appear in the first fraction of the distillate which should come sensibly below the boiling point of diphenyl. The first fraction after the separation of the benzene did boil much below diphenyl and for that reason was separately collected, crystallized repeatedly and treated in alcohol solution with picric acid, according to the method given by Millson.³ In no case was a melting point higher than 70° obtained using a standard picric acid benzene solution, neither was the slightest presence of naphthalene points obtained, though the method was carried out with extraordinary care both against pure naphthalene and

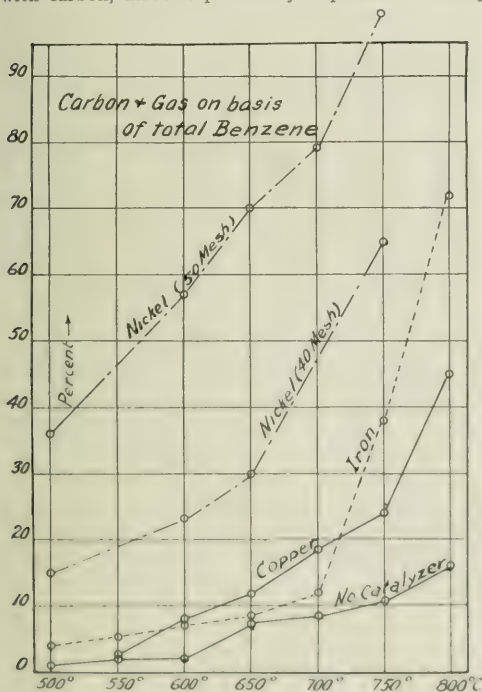


FIG. VIII. INFLUENCE OF CATALYZERS

out all the air from the apparatus with the hydrogen produced in the reaction.

TAR The tarry compounds remaining after 275° were redistilled and extracted with alcohol, according to the method of Schmidt and Schultz.⁴ We were able to obtain without difficulty the same compounds separated by those authors: *m* and *p* diphenylbenzenes, melting at 86° and triphenylene 196°, this last giving a compound with picric acid. The amount of tar not obtained from each separate run was so small that no quantitative relation of the influence of rate on the formation of its individual constituents could be ob-

¹ Bull. Soc. Chim., 7, 218, 228, 306.

² Except naphthalene by Rittman, Byron and Egloff, loc. cit.

³ Ann., 202, 118.

⁴ Trans. Faraday Soc., 7, 1911, 200.

⁵ J. Ind. Eng. Chem., 27, 1000, 1001.

⁶ Identification of the compounds by comparison of their spectra with those of pure compounds.

mixtures of naphthalene and diphenyl in proportions from 1 : 1, to 1 of diphenyl : 0.01 of naphthalene.

As a further test the accumulated diphenyl from all experiments, amounting to about 1 kilogram, was distilled in a large flask and the first few cubic centimeters of distillate collected and submitted to the same tests with negative results.

The presence of naphthalene in Rittman, Byron and Egloff's product at atmospheric pressure can be ascribed by the writers only to the fact that those authors used commercial benzene, which doubtless contained toluene. This last on heating with benzene gives naphthalene as shown by Carnellay¹ by passing mixtures of benzene and toluene through a red hot tube.

The specific gravity of the benzene used by Rittman, Byron and Egloff at 15° was 0.879, whereas that of the one we used was 0.881 at 15.5°. The difference is small indeed but it tends to show the presence of some toluene (0.871 at 15.5°) in the material used by those authors.

SUMMARY

I—The thermal decomposition of benzene has been studied at temperatures varying from 500 to 800° C. and atmospheric pressure.

II—The chief products are diphenyl, diphenylbenzenes, carbon and gas. The formation of diphenyl begins at as low a temperature as 500°.

III—No acetylene was found in the gas, which consisted of hydrogen saturated with benzene vapor, and no naphthalene in the decomposition products, tending to show that the thermal decomposition of benzene at atmospheric pressure takes place with the formation of condensation products in which the benzene ring apparently remains intact, or with the formation of hydrogen and carbon.

IV—The effect of rate on the yields of diphenyl has been studied. The slower rates are more favorable to the formation of diphenyl. The optimum temperature is in the neighborhood of 750°. Above that temperature, diphenyl benzenes as well as carbon and hydrogen form readily.

V—The catalytic action of copper, iron and nickel has been studied. Iron and nickel favor the decomposition to carbon and hydrogen. The action of copper is not marked except above 750°, when the formation of carbon is accelerated.

Further work upon these topics is now in progress in this laboratory.

DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
NEW YORK CITY

RUBBER HOSE FOR USE ON AEROPLANES

By PERCY A. HOUSEMAN²

Received December 18, 1916

The enormous increase in the world's output of aeroplanes during the last three years has rendered important a systematic inspection of materials used in their construction.

One of the materials requiring detailed examination

¹ *J. Chem. Soc.*, **37**, 712.

² Formerly Chief Examiner, Aeronautical Inspection Department Laboratories, London, England.

is rubber hose, which is held to be the most desirable material for conveying gasoline from the tank to the engine on aeroplanes.

It was found, at the time that a system of inspection for aeroplane materials was initiated in England, that the quality of the rubber being used was quite unsatisfactory. This was probably due in a large measure to the unfamiliarity of the rubber manufacturers with the properties required of gasoline-resistant rubber hose. They appear in some cases to have endeavored to adapt their regular types of material, such as steam- or water-hose, for use with gasoline, with results which were sometimes disastrous to the life of the aeroplane and to its pilot.

The Underwriters' Laboratories of Chicago have published (May, 1914) their requirements for rubber hose to conduct gasoline, and their tests are very thorough. When the hose is to carry gasoline on aeroplanes some modification of the Underwriters' examination seems desirable. Bursting, tensile, and stretch tests on the original hose are described by the Underwriters, and tensile strength is also determined 24 hrs. after gasoline immersion. It may be pointed out that after such a period the rubber recovers, with little deterioration, its original physical properties. It is important to obtain a hose which will show good physical behavior while immersed in gasoline or immediately after removal therefrom. Bursting and tensile tests were given up as specification tests by the writer because, although they furnish helpful information, it was found that they were not adequate to detect tubes which would behave badly towards gasoline when used on aeroplanes.

In drawing up specifications for gasoline-resistant rubber tubing the following tests were carried out, and found to be suitable for controlling the quality of the tubing.

They are intended to amplify and not to supplant the specifications of the Underwriters' Laboratories.

(1) FLEXIBILITY—The tube is bent to a circle having a diameter (*D*) which varies according to the inside diameter of the tube (*d*) as shown below:

<i>d</i>	<i>D</i>
Up to 1/2 in.	8 times <i>d</i>
1/2 in. to 1 in.	10 times <i>d</i>
1 1/2 in. to 1 1/4 in.	12 times <i>d</i>
Above 1 1/4 in.	14 times <i>d</i>

The diameter of the tube so bent should not change at any point by more than 10 per cent from its original diameter.

A tube of poor flexibility will show a permanent weak spot if bent sharply a dozen times at the same place.

(2) IMMERSION IN GASOLINE—At first an immersion test of 200 hrs. in cold gasoline of about 0.720 sp. gr. was used. It was found that approximately the same effect can be attained in a shorter time by boiling in gasoline for 1 hr. under a reflux condenser, followed by 24 hrs.' standing in gasoline at room temperature. The approximate increase in weight and volume of the sample (about 3 in. long) is recorded for correlation with the results of the other tests. The decrease in bore at the narrowest part of the tube is also noted

and should not exceed 25 per cent, otherwise the supply of gasoline to the engine may be seriously diminished, especially for tubes of less than $\frac{1}{2}$ in. internal diameter.

The adhesion of the rubber to the canvas fabric must remain good, and the "nerve" of the rubber must not be seriously impaired when examined immediately after the gasoline treatment.

This test for strength of adhesion of rubber to canvas, and for retention of "nerve" of the rubber is open to the objection of being too vague, but it was not found expedient to incorporate standardized tests for these properties, and in actual practice no difficulty was ever experienced in judging whether or not a sample passed the test. This test is also a rough guide to the amount of free sulfur present, crystals of sulfur being deposited from a tube containing an excessive amount.

(3) PERMEABILITY TO GASOLINE—A 14 in. length of the tube is held vertically and plugged with a glass stopper at the bottom. A glass tube is fitted to the top, and is filled with gasoline to a head of 12 in. above the top of the rubber tube, and then loosely stoppered. The length of rubber tube exposed to the action of the gasoline is 12 in. At first the gasoline is absorbed comparatively rapidly by the rubber. The level of the gasoline in the glass tube should not be allowed to fall more than 3 in., additions of gasoline from a known volume being made as necessary. The amount of gasoline which permeates through the walls of the rubber tube is noted during the first and second days, as a guide to the behavior of the sample. During the third 24 hrs., by which time the rate of permeation has become approximately constant, the amount of gasoline passing through the tube should not exceed 100 cc. per sq. ft. of original internal surface of the rubber tube.

(4) DRY HEAT—A piece of the tube is heated for 2 hrs. at 132° C. The rubber should remain elastic after this treatment, and should show no signs of stickiness or brittleness, nor should any surface cracks become visible on stretching the sample.

(5) COLD—The tube is immersed in carbon dioxide snow, which was found to render all tubes brittle while they remained cold. The rubber regains its elasticity on attaining room temperature again, and this test was, therefore, discontinued.

(6) BURSTING PRESSURE—Tests on bursting pressures were carried out before and after the permeability test, but were subsequently given up, as it was found that the quality of the tube could be sufficiently safeguarded by the other tests, and, moreover, the pressure to which the tube is subjected in actual service is very slight.

(7) ACELONE EXTRACT, FREE SULFUR, MINERAL SULFIDES, AND SULFUR OF VULCANIZATION are also determined, and furnish useful information in forming a judgment as to the quality of the specimen under examination. The free sulfur should not exceed 1 per cent of the weight of the finished tube exclusive of the canvas. Excessive free sulfur will be carried by the gasoline into the cylinders of the engine where it may promote pitting.

(8) ASH—A portion of the rubber is incinerated very slowly, and the amount and composition of the ash determined.

(9) QUALITY OF CANVAS—Tests on the quality and strength of the fabric inserted in the tube were contemplated, but it was found expedient to leave to the judgment of the manufacturer the kind of fabric to be used, relying on the tests already enumerated to control the production of a satisfactory tubing.

When the examination of rubber hose for use with gasoline was commenced, great diversity in construction, composition and behavior was found. Some makers appear to have believed that vulcanized rubber is essentially non-resistant to the action of gasoline, and therefore put as little of it in the tubes as possible. Some tubes yielded as much as 75 percent ash, while others gave less than 40 per cent. As great a diversity was found in the composition of the ash. Barium sulfate, lead, zinc, calcium and magnesium were found in a great variety of proportions, each manufacturer carefully guarding his own "mixings" and considering them of vital importance for the production of a satisfactory tube. Some typical figures of ash analyses are appended. The figures for total ash are percentages of the finished tube, excluding the canvas.

TABLE I—TOTAL ASH AND ASH ANALYSES OF GASOLINE-RESISTANT RUBBER HOSE

DESCRIPTION OF TUBE	TOTAL ASH Per cent	PERCENTAGES OF BASO ₄	PB	ZnO	CaO	MgO
French No. 1.....	51	26	10	..	26	10
French No. 2.....	42	20	..	5	34	20
British 1-A.....	72	43	3	4	..	21
British 1-B.....	73	44	35	4	..	4
British 1-C.....	45	51	34	5	..	1
British 1-D.....	45	40	..	5	33	13
British 2-A.....	40	47	..	5	..	37
British 2-B.....	39	10	18	27	26	34
British 2-C.....	38	..	37	..	4	..
British 2-D.....	43	19	18	3	26	4
British 2-E.....	39	..	27	46
British 3-A.....	68	..	36	34	5	..
British 3-B.....	41	24	25	25
British 4-A.....	45	46	..	29	4	10
British 4-B.....	60	77	..	7	12	1
British 5-A.....	59	28	6	7	31	..
British 6-A.....	44	40	15	2	26	..
British 7-A.....	61	..	60	8	..	3

French No. 1 was not a very good tube. The rubber was somewhat harsh. The tube failed to pass the flexibility test, but was satisfactory for permeability. The adhesion between rubber and canvas at the end of the immersion test was fairly good, but the tube contained as much as 3 per cent free sulfur. The heat test caused obvious deterioration in the quality of the rubber. Barium sulfate and lime are the chief mineral ingredients.

French No. 2 was inferior to No. 1. The rubber was harsh, and its behavior varied along the length of the consignment, indicating probable uneven vulcanization. Mechanical defects, such as local pitting, were to be seen. The adhesion of rubber to canvas after immersion appeared at first sight to be very good, but this was due rather to the canvas which the rubber itself tore. Lime and magnesia are the most prominent oxides, with barium sulfate as a diluent. Rubber hose for use with gasoline on French airplanes is required to contain 44 per cent mineral matter with a margin of 50 per cent, 50 per cent rubber with the same margin, and to have a density of 1.6 g./cc.

British 1-A to 1-D, though all from the same maker, show wide variations in total ash and in the composition of the ash. The bad feature of both 1-A and 1-B was the weakness of the adhesion between rubber and canvas. Separation of the plies occurred spontaneously under gasoline. The other properties of these tubes were satisfactory. 1-D was a good tube.

British 2-A to 2-E, all made by one firm, show less variation in total ash, but much variation in the composition of the ash. 2-A and 2-B represent respectively outer and inner rubber layers of the same tube. The same applies to 2-C and 2-D. The inner layer of rubber proved to be of better quality for use with gasoline than the outer layer. The adhesion between rubber and canvas was bad. Tubes 2-A and B showed high constriction of the bore. All of these tubes contain a considerable quantity of lead, and 2-E is noticeably high in magnesia.

British 3-A and 3-B—3-A showed bad "adhesion;" 3-B very good adhesion, though the rubber was rather "short" after the immersion test.

British 4-A and 4-B—The product of this firm showed great variability in bore-constriction, but the flexibility, permeability, adhesion after immersion test, and quality of rubber after immersion test were all good.

British 6-A was a good tube. *British 7-A* was too harsh.

A large number of other tubes were examined, but most of them showed defects in one or more of the properties tested. Some manufacturers used a certain amount of reclaimed rubber or of rubber substitute, but it is believed that this is not desirable as regards the quality of the product, although it lowers the cost.

One firm made an excellent tube by the use of 45 per cent Para rubber. The mineral ingredients in this tube were lead, calcium and magnesium. This tube withstood the immersion test with hardly any deterioration in the "nerve" of the rubber, and the adhesion between rubber and canvas was scarcely affected. The bore constriction after immersion test was less than 25 per cent on a $1\frac{1}{2}$ -in. tube, and all of the other tests gave good results.

It is probably undesirable to use less than 40 per cent rubber.

In many cases it was customary to insert a spiral of brass or steel wire in the bore of the tube so as to improve its flexibility. This practice is unnecessary if the walls of the tube are made fairly thick, and in the case of the brass spiral constitutes a possible source for the entry of copper into the rubber.

It was found that a decided improvement in some of the properties of gasoline-resistant rubber hose could be achieved by changing the manner in which the canvas was inserted. The usual method was to friction the canvas with a very thin layer of the rubber mixing, so that in the finished tube there were virtually three plies, an inner layer of rubber, a middle layer of canvas, usually from 2 to 4 turns according to the size of the tube, and an outer layer of rubber. When a tube made in this manner is subjected to the immersion test the three layers expand at different rates, resulting often in spontaneous separation. The canvas layer expands hardly at all, and so the expansion of

the inner layer of rubber is forced inwards, with consequent constriction of the bore. A better method of construction consists in spreading a definite layer of rubber on the canvas, so that in the finished tube the thickness of rubber between each turn of the canvas is at least twice as thick as the canvas itself. A cross-section of a tube made in this way shows the canvas to be distributed as a spiral through the whole thickness of the wall of the tube. Such a tube shows improved flexibility and better behavior under the immersion test, there being less tendency to separation between rubber and canvas and a smaller constriction of the bore. For tubes up to $\frac{3}{4}$ in. internal diameter, two turns of canvas are sufficient. Between $1\frac{1}{16}$ in. and $1\frac{1}{4}$ in., three turns are desirable, and for tubes larger than $1\frac{1}{4}$ in. internal diameter 4 turns of canvas should be used. The larger sizes are used for oil or water.

The inner layer of rubber on all tubes for carrying gasoline should, of course, be seamless. A seam on the inner rubber would facilitate penetration of the gasoline to the canvas, which would then function as a wick for the distribution of gasoline throughout the wall of the tube.

A satisfactory material for protecting a cut end of tubing from absorption of gasoline may be made from a mixture of about 4 parts gelatin with 1 part glycerin, with the addition, if desired, of a small quantity of formaldehyde or potassium bichromate. Such a solution might even be run, while warm, through the whole length of the rubber tube, so as to form a protective film on the inner surface. Rubber hose for gasoline is, however, now being made in Great Britain of a quality sufficiently good to need no protective film, and there is, moreover, the possibility of portions of such a film becoming detached and causing partial choking of the tube. When the hose is not to be cut the ends may be best protected from absorption of gasoline by being capped.

In testing a large consignment, a sample should be taken from at least every 100 ft. in order to guard against lack of uniformity in quality, such as would be caused by uneven vulcanization or variability of the mixing.

In storing gasoline-resistant rubber hose the usual precautions should be taken for protection from strong light, and from extremes of temperature. As a matter of safety a tube should not be used which is more than 6 months old.

The testing of rubber hose for use with oil or hot water on aeroplanes is less important. Rubber hose for use with oil should withstand 8 hrs.' immersion in castor oil at 100° C. without serious injury to the quality of the rubber, and without any disintegration of the tube. The increase in weight after thoroughly wiping off the oil should be less than 5 per cent. Rubber hose for use with hot water should withstand boiling in water.

The writer had the privilege of being associated with Mr. W. E. Gibbs and Mr. N. W. Barritt in carrying out the work described in this and in the following paper.

GLUE FOR USE ON AEROPLANES

By PERCY A. HOUSEMAN¹

Received December 18, 1916

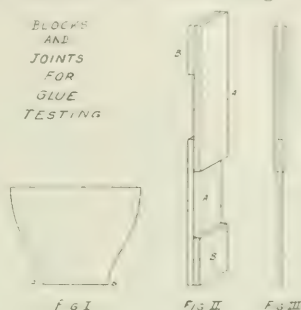
There are many parts of an aeroplane that require the use of an adhesive material. Of these may be mentioned "airscrews" (the collective name for propellers and tractors), hollow spars, booms, ribs, plywood, etc. For some of the small parts, such as the ribs, which are subsequently covered by "doped" fabric, it is not necessary to use the best quality of glue. For other parts; however, it is of vital importance that only the strongest glue be used. This applies particularly to airscrews, which rotate at a very high speed. Airscrews are built up in laminae of walnut or mahogany, usually 7 in number, and each 1 in. thick. It is usual to glue two laminae together, and allow them to remain in clamps for a period of from 6 to 24 hrs. before gluing on the next lamina. The finished airscrew is shaped out after the total number of layers have been glued together and have been allowed to set. The glue is applied hot, and usually by at least two workmen, in order to cover the surface as quickly as possible. The temperature of the gluing room is kept above 70° F. It would, of course, be an economy to glue at one operation all of the laminae of an airscrew, but this is not possible when a cake glue is used, on account of the rapidity with which the hot solution sets. Attempts have been made to overcome this difficulty by the use of "liquid" glues, but these have usually proved unsatisfactory. One French liquid glue contained some hygroscopic material, and failed to set in 14 days. "Liquid" glues should be used only on work in which great strength under widely varying conditions of temperature and humidity is not of prime importance. Bone glue should never be used on aircraft work. The best results are obtained from skin or hide glues.

In working out a method for the examination of glue some attention was given to such chemical and physical tests as moisture, ash, nitrogen, strength of jelly, viscosity, percentage precipitable by alcohol (Stelling's test),² etc., but while the information furnished by these tests was of interest, it was not found possible to correlate definitely the results obtained, with the value of the glue for aeroplane work.

A method was therefore developed to test the strength of a glued joint under various conditions. Experiments were made with blocks of biscuit-ware, as recommended by Rideal in his book on "Glue and Glue Testing." Messrs. Doulton, of London, kindly made the necessary blocks, which had a base (ab) 1 in. square, similar in design to that shown in Fig. I.

Two such blocks were glued together under various conditions of strength of glue solution, temperature, method of application, pressure of clamping, etc. The blocks were pulled apart in a cement testing machine with automatic application of the load, but as uniform results could not be obtained, the stone blocks were abandoned. More uniform results were obtained

with wood, which also has the advantage of giving results more nearly comparable with those obtained under actual service conditions. Pieces of carefully selected straight-grained walnut were used, and from them a number of different types of joints were prepared, and used to illustrate different kinds of stresses. The type of joint finally adopted is that shown in Fig. II. This joint gives by no means a true shear, as was easily seen by examining under polarized light a celluloid model made to scale. A stress more nearly approaching pure shear would probably be obtained with a joint like that shown in Fig. III, made up from pieces 9 in. \times 2 in. \times 1/4 in. but for the purpose of obtaining comparative results, that shown in Fig. II answers well and has the advantage of simplicity.



The wood is exposed for 24 hrs. to a temperature of 35° C. before making the joint. The test pieces (A) are 9 in. \times 2 in. \times 3/8 in. These were roughened by a toothed plane, as it was found that a roughened surface gives a stronger joint than a smooth one. The distance pieces (B) are 3 in. \times 2 in. \times 3/8 in. The area of the glued surface of the joint to be pulled apart is 4 sq. in. To prepare the glue, it is broken into small pieces and is soaked over night in the requisite amount of water. For the gelatine types of glue, 1 part by weight of glue to 2 parts by weight of water gives a desirable concentration, while for "Scotch" glues 1 part of glue to 1.25 parts of water gives the best results. For other types of glue the water required usually falls within these limits. The soaked glue is dissolved by warming to 60° C., and the solution is applied at that temperature. The joints are clamped under moderate pressure for 48 hrs., and are tested after a further 24 hrs. For each sample of glue, the following three tests, each in duplicate, are carried out on the joints prepared as described above.

(1) REGULAR TEST—The joints are pulled apart in a Buckton and Wickett or in a Riedel (Philosophical) Testing Machine and the breaking strain per sq. in. of glued surface is recorded. The experimental variation is less than 5 per cent, most of which may be ascribed to unavoidable variations in the wood.

(2) HEAT TEST—The joints are subjected to dry heat in an electrically heated oven for 2 days at 84° C., and then pulled apart, and the breaking strain is recorded.

¹ Formerly Chief Examiner, Aeronautical Inspection Department, Laboratories, London, England.

² Chem. Ztg. 30, 461.

(3) **IMMERSION TEST**—The joints are completely immersed in water at 20° C. for 12 hrs., and are then pulled apart, and the breaking strain recorded.

Tests (2) and (3) are intended to throw light on the behavior of an airscrew under the extreme conditions of a tropical climate and high humidity. Tests were also made with moist heat, and on immersion followed by dry heat, but were discontinued. The last named test was found to be too drastic, all glues giving very low results.

The whole procedure outlined above is an arbitrary one, and for this reason it is necessary rigidly to standardize and adhere to the technique of the method, in order to obtain comparable results. When the break occurs in the wood, as frequently happens in the regular test, one can, of course, only say that the glue is stronger than the wood, and record the figure at which the wood breaks.

TABLE I—INFLUENCE OF ADDITION OF PHENOL OR CONCENTRATED AMMONIA TO GLUE ON STRENGTH OF GLUED JOINT

GLUE TESTS:	REGULAR	HEAT	IMMERSION
Gelatin A.....	644 627	459 425	504 ...
Gelatin A + 5% Phenol.....	532* 616	476* 627	621 ...
Gelatin A + 10% Phenol.....	677* 845	369 487	560 660
"Propeller" Glue.....	464	470 464	540 504
"Propeller" Glue + 5% Phenol.....	526 593	393* 506	553 560
"Propeller" Glue + 10% Phenol.....	610 632	315 429	560 565
"Scotch" Glue.....	548 571	448 470	448 470
"Scotch" Glue + 5% Phenol.....	688* 723	425 425	532 548
"Scotch" Glue + 10% Phenol.....	694 694	414 453	436 476
Gelatin A.....	627 644	459 565	504 549
Gelatin A + 25% Ammonia.....	610 655	616 688	800 875
"Propeller" Glue.....	464	464 470	540 504
"Propeller" Glue + 25% Ammonia.....	520 532	580 609	648 783

The figures represent breaking strain in lbs. per sq. in. of glued surface of the standardized joint. Breaks in the wood are indicated thus *.

Addition of phenol to the glue improves the regular test. The influence on heat tests and on immersion tests is not marked, but the tendency is to raise them slightly. The addition of 5 per cent phenol to a 1 : 2 gelatine solution, depressed the setting point of that solution from about 26 to 18° C., while 10 per cent phenol caused the solution to be still viscous at 5° C. The addition of 5 per cent phenol to glue solutions to be used on aeroplane work is, therefore, to be recommended, both because of its tendency to increase the strength of the joint, and also on account of its action in depressing the setting point.

Ammonia causes the glue to set more rapidly. It was found to have the unexpected effect of raising the figures for heat and immersion tests, while leaving regular tests little affected.

The Germans appear to have used a casein glue on some of their aircraft. An analysis of a Swiss glue of this type showed its composition to be about 66 per cent casein and 23 per cent mineral matter. The latter was composed of soda, silica, lime and alumina. About 1 per cent of petroleum was present in the powder. This casein glue is prepared for use by rubbing up with cold water. It requires about 3 days for the joint to set, but has the advantage that all the laminæ of an airscrew can be glued together at once.

The following test figures were obtained on joints made with the Swiss casein glue:

Regular	Dry Heat	Moist Heat	Immersion
581 658	526 661	438 465	672 862

The immersion test is particularly high.

Casein glues are very generally used for cementing together the "veneers" on ply-wood which finds extended use on the fuselage and other parts of the aeroplane. One English firm uses a mixture of casein, lime, and blood, which yields a cement very resistant to water. A three-ply board made with such a cement will withstand an immersion test in water at 50° C. for 12 hours without any separation of the plies, though the strength of this cement on a "regular" test is inferior to that of a hide glue.

Another firm of ply-wood manufacturers uses lime and casein only, in the proportion approximately of 4 parts by weight of lime to 7 parts by weight of casein. Casein and borax form a good mixture, but are, of course, more expensive than casein and lime. Casein glues cannot be kept more than a few hours after mixing with water, so that a batch when mixed must be completely used, or the residue wasted.

When a new glue is intended for use on airscrews, the tests described above should be supplemented by a practical test of spinning a trial airscrew made with the new glue.

HIGHLAND PARK, LLANERCH, PA.

A STUDY OF CERTAIN FERMENTS WITH A VIEW TO DETERMINING A METHOD FOR THE DIFFERENTIATION OF PASTEURIZED MILK FROM RAW MILK

I. REDUCTASES

By RICHARD EDWIN LEE AND MELVIN GUY MELLON

Received May 1, 1916

INTRODUCTORY

The enthusiasm and skill with which many of the problems relating to the distribution, composition and action of a class of substances known as *enzymes* or *ferments* have been attacked in recent years have contributed much data of importance to the biological chemist and sanitarian.

Some of these ferments are so widely distributed in living tissues of members of both the animal and vegetable kingdoms that it has been suggested by one well-known investigator "that the properties of these substances might almost be turned to account as a general chemical test for vital activity." While this may seem like an exaggeration of their significance and although the precise rôle of these substances in the life of the cell has not yet been determined, it is undoubtedly true that they are concerned in a great many of the most important biochemical processes with which we are familiar. And furthermore, regardless of the fact that very few, if any, of these substances have been isolated in a pure condition,¹ they have, without doubt, as have other compounds, a definite chemical composition; and through the exercise of definite chemical affinities, they are able to produce alterations in other compounds.

Holding to this view, Traube² formulated his theory of fermentation, for example, upon two distinct chemical propositions: *first*, that the ferments are defi-

¹ It would probably be more accurate to say that we do not know whether a specific enzyme has, or has not been prepared in the pure state.

² *Theorie der Fermentwirkungen*, Berlin, 1888; *Ueber Aktivierung des Sauerstoffs*, 18, 659-675.

nite chemical compounds elaborated from protein as a result of the combined action of heat, water, and oxygen, and are present not only in the lower organisms but also in the tissues of the higher forms, where they are responsible for biochemical processes; *second*, that the ferments are powerful reducing agents and oxygen carriers, capable, in the capacity of chemical go-betweens (*Vermittler*), of effecting the transfer not only of free oxygen to easily oxidizable substances, but also the transfer of combined oxygen from one compound to another.

In accordance with this theory, he was led to divide ferments into three classes:¹

(a) *Verwesungsfermente*—those combined loosely with oxygen, forming unstable compounds which give up their oxygen to other substances less readily oxidized.

(b) *Reductionsfermente*—those which combine with the oxygen of water, the hydrogen going to effect the reduction of some passive body.

(c) *Höchste Fäulnisfermente*—those which cause putrefactions in which hydrogen is set free.

Although there is not complete agreement among investigators as to the exact mechanism by which the alterations are effected, there is very general belief that they act catalytically, and, therefore, partake of the nature of ferments; that is, enzymes may be regarded as organic catalysts.

As is well known, they are very unstable, being generally destroyed by an exposure to a temperature outside of relatively narrow limits; and inasmuch as they have optimum, maximum, and minimum temperatures, and thermal death points, they resemble micro-organisms.

Usually action ceases at 0° C.; the optimum for most types lies between 30 and 50° C.; they are soon destroyed at temperatures above 70° C., and almost instantaneously by boiling water. Likewise they are remarkably sensitive to the action of mineral acids such as HCl and various poisons² such as HCN, SO₂, HgCl₂, C₂H₅NH₂ and CHCl₃.

It is in virtue, however, of these facts which have been pointed out, *viz.*, the wide distribution of these enzymes in the animal and vegetable kingdoms and their sensitiveness to various physical and chemical agents, that they have become of great importance to the biological chemist and sanitarian, as enabling them by means of specific tests for these enzymes to form correct conclusions regarding the character and condition of certain foodstuffs; *i. e.*, these tests have enabled the chemist to say whether the food is *raw* or has been *heated*.

Among the first of these enzymes to be discovered and to have its properties studied is the group now known as the *oxidases*. They are among the most widely distributed of all the ferments. These, together with another group known as the *reductases*,

are of particular interest to us in the consideration of the problem presented in this paper, owing to the presence of the former (*oxidases*) in milk, and the *probable bacterial origin* of the reductases.

For a number of years it has been a most interesting question as to whether these enzyme reactions could be made the basis of methods for differentiating old milk from new milk, and pasteurized milk from raw milk. Regardless of the controversy which has arisen, a number of investigators have proposed tests in which the reactive properties of these enzymes have been utilized with a view to formulating methods for ascertaining the "sanitary condition" of milk. These investigations seem to be entirely justified when we recall the following well-known facts: (1) Normal fresh milk has the property of decomposing hydrogen peroxide into free oxygen gas and water; (2) ordinary milk possesses the power of decoloring, within certain limits of time, various coloring substances by reduction or removal of oxygen. Although the exact nature of these reactions and the source of the substances in milk influencing them have not been clearly established, there is much evidence which indicates that they are of an enzymic nature.

It is scarcely necessary to point out that there is much uncertainty at the present time as to the accuracy and significance of these proposed tests. There is no question, however, as to the need of them.

Inasmuch as it has often become necessary to pasteurize milk to be sold to the public, because it has not been produced under the required sanitary conditions, the need of a test which will quickly and easily show whether a given sample of milk has been heated or not, is at once obvious. In the effort to meet this want a considerable number of methods have been formulated in the last few years. Unfortunately, most of those proposed are not characterized by exactness or simplicity. However, there seem to be a few methods which have received neither the use nor the study to which they are apparently entitled.

It was this view of the situation which led the authors of this paper to the examination of various methods which have been proposed for the differentiating of raw milk from pasteurized milk with regard to determining their relative accuracy.

The methods which have been proposed may be conveniently divided into two main groups:³

(1) *Methods based upon changes which the protein in milk undergoes when the latter is heated.*

(2) *Methods based upon reactions influenced by the presence of certain chemical ferments in milk.*

An examination of the literature dealing with this subject reveals the fact that only those methods which are included in the second group have proven at all satisfactory. And it will be noted that these are the methods which are based upon the action exercised by the presence of certain enzymes.

In this investigation we have been concerned with but three groups of these chemical ferments: (1) a *peroxidase*, which causes hydrogen peroxide to react

¹ Kastle, *Bull.* 59, Hygienic Laboratory.

² Traube in his later writings used the term *Oxidationsfermente* as preferable to the term *Verwesungsfermente*. This term is employed to signify those ferments which possess the power of taking up free oxygen and carrying it to other passive substances, thereby accomplishing the oxidation of the latter.

³ For a more complete list see article by Harris and Creighton, *J. Biol. Chem.*, 22 (1915), 535.

⁴ Barthel, "Milk and Dairy Products," p. 27.

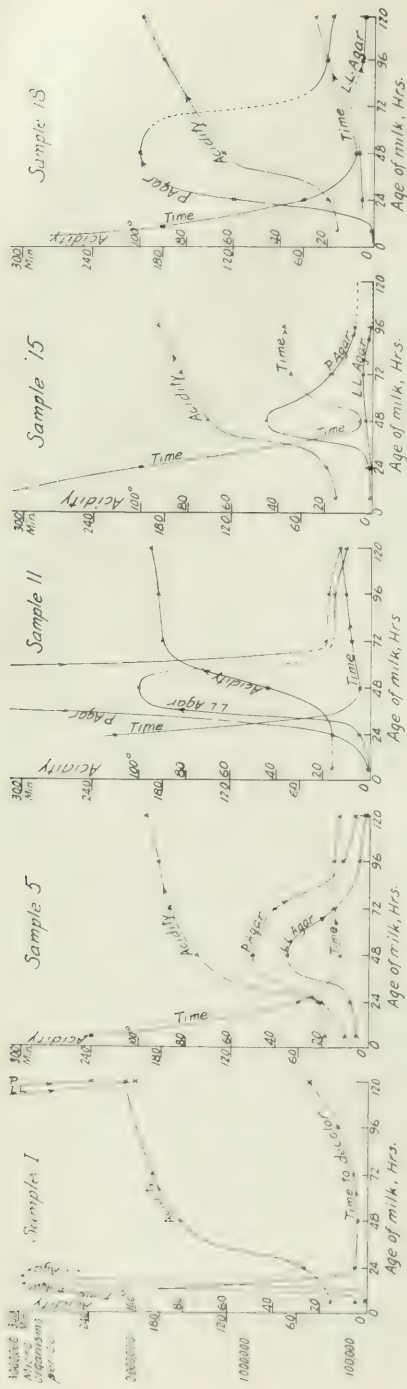


FIG. 1

FIG. 2

FIG. 3

FIG. 4

FIG. 5

with certain (oxidase) reagents, thereby producing change of colors; (2) a *catalase*, which decomposes hydrogen peroxide (with the liberation of oxygen) but is incapable of effecting the oxidation of oxidase reagents by means of the peroxide; (3) the *reductases*, which combine with the oxygen of the water, the liberated hydrogen effecting the reduction of a passive body like methylene blue with attendant decoloration.

Owing to the fact that the peroxidases and catalases are to be taken up in another paper, they will not be considered further at this time as this paper is concerned only with the nature, source, and action of the enzyme which influences the reactions upon which are based the reductase methods.

REDUCTASES IN RELATION TO PROBLEM

The reductases (*Reductionsfermente*) are usually defined as those ferments which combine with the oxygen of water, the hydrogen going to effect the reduction of a passive body like methylene blue.

The reductase test is based upon the fact, first noticed by Duclaux,¹ that ordinary normal cow's milk has the power of converting certain coloring matters, as indigo-carmine, into the corresponding leuco-compound by reduction. He also showed that this property of milk depends upon the microorganisms which it contains.

Neisser and Wechsberg² proposed the use of methylene blue as a reagent for testing the quality of milk. H. Smidt,³ P. Th. Müller,⁴ and Barthel⁵ also worked on this method and came to the conclusion that there existed a distinct parallel between the number of organisms in the milk and the time required, under certain conditions, for a solution of methylene blue to be decolorized. According to Barthel⁶ the reductase test gives approximately the relative number of bacteria in the milk. Van Slyke⁷ seems to agree with this as he maintains that this reducing property appears to depend upon the presence of microorganisms in milk since the larger the number of bacteria, the shorter the time required to produce decoloration.

There seems to be some dispute, however, among other investigators as to the exact origin of the reductase. Konning,⁸ Seligman,⁹ and Grimmer¹⁰ are of the opinion that the reductases are produced by bacteria. However, Seligman states that possibly some reductases may exist as enzymes in milk. Romer and Sames¹¹ are opposed to the enzyme nature of reductase, and state that it is produced by the destruction of the cells of the mammary glands during milking, as the first milkings have but slight reducing properties and the last milkings are highly reducing.

Sames¹² is not only opposed to the enzyme nature of

¹ Le Lait, "Études chimiques et microbiologiques," Paris, 1887.

² Analyst, 26 (1901), 148.

³ Münch. Med. Wochschr., 1900, No. 37.

⁴ Hyg. Rundschau, 14 (1904), 1, 137.

⁵ Arch. Hyg., 56 (1906), 108.

⁶ Z. Nahr. Genussm., 15 (1908), 385; "Milk and Dairy Products," p. 128.

⁷ Modern Methods of Testing Milk and Milk Products, p. 158.

⁸ Milchwirtschaft Zentr., 4, 156.

⁹ Z. Bgg., 68, 1.

¹⁰ Milchwirtschaft Zentr., 6, 243.

¹¹ Z. Nahr. Genussm., 20, 1.

¹² Milchwirtschaft Zentr., 6, 462.

TABLE I

Sample No.	Age Hrs.	Degree of Acidity	Time to Decolorize Methylene Blue	BACTERIAL COUNT (a)	Sample No.	Age Hrs.	Degree of Acidity	Time to Decolorize Methylene Blue	BACTERIAL COUNT (a)
				Plain Agar					Plain Agar
				L. L. Agar					L. L. Agar
1	4	16.5	No Decol.	90,000	11	4	16	No Decol.	15,000
	24	27	10 Min.	10,000,000	11	4	19	Several Hrs.	20,000
	48	82	7 Min.	450,000,000	48	4	5	8 Min.	5,000,000
	72	93	12 Min.	10,000,000	72	95	15 Min.	370,000	370,000
	96	100	25 Min.	4,000,000	96	97	20 Min.	350,000	300,000
	105	105	50 Min.	50,000	120	100	30 Min.	250,000	200,000
2	4	16	No Decol.	500,000	12	8	17	No Decol.	9,000
	24	26	30 Min.	8,000,000	24	18	65 Min.	400,000	150,000
	48	43	25 Min.	10,000,000	48	44	4 Min.	1,500,000	1,000,000
	72	65	15 Min.	1,000,000	72	90	15 Min.	500,000	350,000
	96	96	50 Min.	1,000,000	96	97	14 Min.	400,000	150,000
	120	85	50 Min.	1,000,000	120
3	8	19	No Decol.	150,000	13	4	17	No Decol.	15,000
	24	21	Several Hrs.	160,000	24	20	40 Min.	90,000	10,000
	48	25	Several Hrs.	6,000,000	48	64	10 Min.	8,000,000	3,000,000
	72	72	35 Min.	3,000,000	72	96	18 Min.	2,000,000	1,000,000
	96	95	45 Min.	1,000,000	120
	120	103	45 Min.	1,000,000	120
4	3	15	No Decol.	20,000	14	8	17	No Decol.	13,000
	24	21	28 Min.	80,000	24	18	25 Min.	1,500,000	30,000
	48	72	35 Min.	2,000,000	48	61	4 Min.	5,000,000	60,000
	72	78	35 Min.	2,000,000	72	90	30 Min.	1,500,000	30,000
	96	87	55 Min.	2,000,000	96	93	60 Min.	50,000	5,000
	120	95	75 Min.	100,000	120	96	60 Min.	30,000	...
5	4	18	4 Hrs.	200,000	15	8	15	Slightly, 3 Hrs.	8,000
	24	22	1 Hr.	400,000	24	19	Partly, 3 Hrs.	20,000	3,000
	48	76	25 Min.	1,000,000	48	72	10 Min.	900,000	50,000
	72	87	30 Min.	800,000	72	83	70 Min.	350,000	70,000
	96	92	30 Min.	220,000	96	93	75 Min.	150,000	10,000
	120	97	35 Min.	180,000	120
6	8	19	5 Hrs.	15,000	16	4	19	Partly, 3 Hrs.	8,000
	24	20	4 Hrs.	160,000	24	25	24	25 Min.	100,000
	48	72	10 Min.	4,000,000	48	86	20 Min.	100,000	20,000
	72	88	18 Min.	800,000	72	96	30 Min.	20,000	16,000
	96	99	60 Min.	600,000	96	96	35 Min.	10,000	3,000
	120	120	103	35 Min.	10,000	1,000
7	4	19	6 Hrs.	20,000	17	4	19.5	Partly, 3 Hrs.	10,000
	24	22	2 Hrs.	100,000,000	24	23	20 Min.	100,000	3,500
	48	74	6 Min.	1,000,000	48	86	18 Min.	130,000	70,000
	72	79	40 Min.	750,000	72	96	15 Min.	100,000	55,000
	96	97	30 Min.	500,000	96	96	45 Min.	10,000	2,000
	120	97	30 Min.	500,000	120	100	45 Min.	10,000	2,000
8	4	16	No Decol.	10,000	18	8	16	Slightly, 150 Min.	5,000
	24	17	35 Min.	600,000	24	19	60 Min.	1,200,000	100,000
	48	48	10 Min.	10,000,000	48	64	15 Min.	2,000,000	120,000
	72	90	15 Min.	1,000,000	72	89	40 Min.	400,000	100,000
	96	96	12 Min.	1,000,000	96	98	50 Min.	350,000	80,000
	120	96	12 Min.	1,000,000	120	98	50 Min.	350,000	80,000
9	4	15	150 Min.	10,000	19	8	16.5	150 Min.	5,000
	24	18	90 Min.	100,000	24	17	120 Min.	75,000	20,000
	48	76	10 Min.	1,000,000	48	82	40 Min.	100,000	25,000
	72	76	10 Min.	1,000,000	72	94	60 Min.	80,000	50,000
	96	88	30 Min.	200,000	96	103	60 Min.	30,000	10,000
	120	90	35 Min.	120,000	120	103	60 Min.	30,000	10,000
10	8	19	No Decol.	10,000	20	4	17	Slightly, 3 Hrs.	30,000
	24	59	4 Min.	1,350,000	24	33	15 Min.	400,000	40,000
	48	59	4 Min.	1,350,000	48	100	15 Min.	140,000	20,000
	72	95	10 Min.	1,300,000	72	100	15 Min.	140,000	20,000
	96	102	14 Min.	500,000	96	100	30 Min.	100,000	10,000
	120	107	18 Min.	300,000	120	98	60 Min.	20,000	...

(a) "Standard Methods" as formulated by the American Public Health Association for the bacterial examination of milk were employed in making all bacterial counts.

reductase but insists that Seligman's assumption that the reduction is due to bacteria is too far-reaching. Salus¹ believes that reductase is a product of cell transformation. Oppenheimer² is of the opinion that the reductase is in no way related to the bacteria and that it is merely difficult to distinguish from bacterial reductases.

However, on the basis of the probable bacterial origin of reductase, there have been two tests proposed for its detection:

(1) Schardinger's *M. Reductase Test*,³ which is carried out by adding 1 cc. of Schardinger's reagent M. (viz., 5 cc. of a saturated alcoholic solution of methylene blue and 195 cc. of water) to 20 cc. of milk in a test tube and placing it in a water bath at 45 to 50° C. With this reagent a number of hours is required to produce decoloration.

(2) Schardinger's *F. M. Reductase Test*,⁴ which is carried out by adding 1 cc. of Schardinger's F. M.

reagent (viz., 5 cc. of a saturated alcoholic solution of methylene blue, 5 cc. of 40 per cent formaldehyde, and 190 cc. of water) to 20 cc. of milk in a test tube, placing it in a water bath at 45 to 50° C., and covering the contents of the tube with a layer of liquid petroleum to prevent the access of air. The formaldehyde serves to produce an acceleration in the time of reduction. Lythgoe¹ states that raw milk will decolor this reagent in less than 20 min. and pasteurized milk will take a longer time.

The reaction depends upon the supposed presence of a specific enzyme in milk called aldehyde-reductase, which is more or less quickly destroyed at a temperature above 70° C. when it is not heated above 80° C. the destruction is complete.⁵ Barthel⁶ claims that the enzyme is destroyed more or less rapidly at temperatures above 70° C. and that milk heated to 80° C. does not decolor the color of the reagent so slowly heated to 75° C. for a few minutes or pasteurized for 5 minutes at 75° C. decolors the color in 10 minutes.

¹ *Arch. Hyg.* 75, 471.

² *Arch. Hyg. Int. Experim. Theoret. et Pract.* 1908, 5.

³ *J. Van Nostrand's Modern Methods of Testing Milk and Milk Products*, p. 163.

⁴ *This Journal*, 6 (1914), 922-923.

⁵ *Milk and Dairy Products*, p. 108.

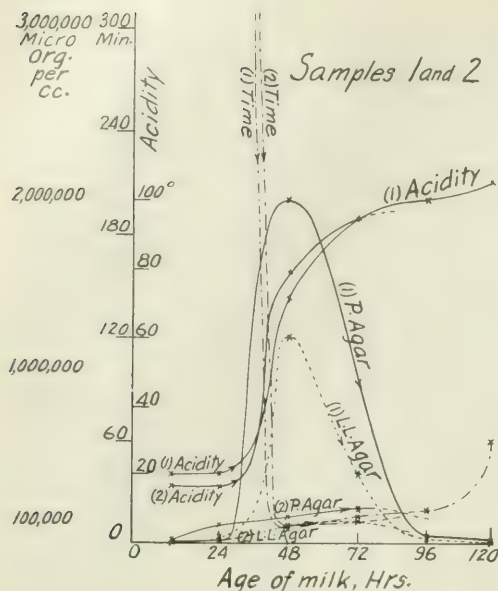


FIG. 6

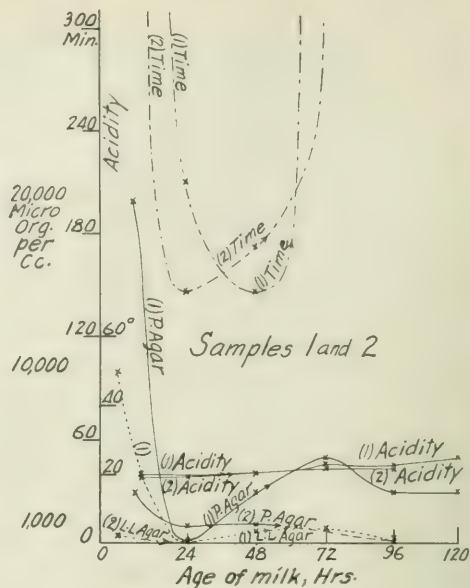


FIG. 7

By means of these reagents it is possible, according to Lythgoe,¹ to get a good idea of the temperature to which the milk has been heated, and also how long it has been heated, since heating the milk destroys the enzyme. Thus, he maintains, this method affords a very good means of distinguishing between raw and pasteurized milk.

As stated previously, there seems to be a difference of opinion as to the origin of the reductase; likewise investigators are far from any agreement regarding any relationship which may exist between the time of methylene blue reduction and the number of bacteria present. Angelici² states that there is absolutely no parallelism between the two. Fred,³ however, holds to the view that most, but not all, milk bacteria reduce methylene blue; and that milk reducing methylene blue in from 15 minutes to an hour contains from 15 to 50 millions of bacteria per cc., and milk requiring 7 hours or more contains less than one million bacteria per cc.

Barthel⁴ states that fresh milk containing 10,000 bacteria per cc. decolorized the methylene blue solution in 11 hrs.; and the same milk four days old containing 17 millions of bacteria per cc. decolorized the solution in 14 min. He further⁵ maintains that when the reduction takes place in less than one hour, the milk has more than 10 million bacteria per cc., and when the time required is from 1 to 3 hrs., the number of bacteria present is from 4 to 10 millions per cc. As a conclusion he asserts that when the reduction requires less

than 1 hour, the milk is bacterially too impure for food; and that good commercial milk should require not less than 3 hours for decoloration.

As a result of the foregoing discussion, therefore, we may conclude that there exists a considerable difference of opinion: (1) as to whether the reductase is of bacterial origin or of animal metabolism; and (2) as to the relationship existing between the time of methylene blue reduction and the number of bacteria present.

EXPERIMENTAL

The following experimental work was carried on with a view to determining by means of the Schardinger F. M. test:

1—The relationship existing between the number of bacteria and the time required to decolorize the methylene blue solution.

2—The influence of time and temperature of pasteurization on milk in its relation to Schardinger's reagent, F. M.

RELATIONSHIP BETWEEN NUMBER OF BACTERIA AND TIME REQUIRED TO DECOLORIZE METHYLENE BLUE

Twenty samples of milk were tested as follows: (1) the acidity was determined by titration with $N/10$ NaOH, 0.1 cc. of the solution being equivalent to 1° of acidity; (2) the time required to decolor methylene blue solution was observed; (3) bacterial counts were made at the time of each test both on plain agar and on lactose litmus agar. Each sample was tested daily for a period of five days, during which time the milk was allowed to remain at the temperature of the laboratory. The results of this work appear in Table I.

The full significance of this data becomes more easily

¹ THIS JOURNAL, 5 (1913), 922-927.

² Clin. Vol., 34, 388.

³ Centr. Bakt. Parasitenk., II Abt., 35, 491.

⁴ Z. Nahr. Genussm., 18, 385.

⁵ Ibid., 21, 513.

apparent when it is presented graphically. In Figs. 1 to 5, graphs have been drawn of 5 of the representative samples of the above series, using separate curves to show the increase in degrees of acidity, the time of decoloration of methylene blue, the plain agar bacterial count, and the lactose litmus agar bacterial count. The dotted portion of the curves indicates the probable course covering the period during which no tests were made, as, for example, on Sundays.

The age of the milk in hours is plotted as abscissas. There are three sets of ordinates: first, the column on the left by which both the plain agar and the lactose litmus agar counts are plotted; second, the middle column expressed in minutes, by which the time of decoloration is plotted; and third, the column on the right expressed in degrees, by which the degree of acidity is plotted. This gives four curves for each sample.

From the data presented in the preceding table and by means of graphs the following conclusions have been formulated:

(1) An increase of acidity occurs with increase of age. In the periods examined this increase was greatest in the majority of cases in the period between 24 and 48 hrs.

(2) Normal fresh milk of good quality does not reduce Schardinger's F. M. reagent in less than 20 min.—the shortest time observed being much longer. When the decoloration was effected in 10 min. or less time, the milk was found to contain at least 1,000,000 microorganisms per cc.

(3) Up to a certain point an increase in the number of bacteria in a given sample is accompanied by a corresponding decrease in the time required by it to decolor the reagent. At this point the maximum bacterial count and the minimum time required for decoloration coincide.

This relationship seems to point to the conclusion that the reductase is of bacterial origin. The tables will show, however, if data for different samples are compared, that no absolute parallelism exists between the time required for decoloring the reagent and the number of bacteria present. This is in agreement with results obtained by Angelici.¹

(4) As the acidity increases beyond this point of coincidence the number of bacteria decreases and the time required for decoloration increases.

(5) The final decrease in the number of bacteria and the increase in the time of decoloration are probably due to the production of acid by acid-forming bacteria, the acid thus produced probably tending to remove the effect produced by the aldehyde reductase and to make the medium unfit for the further growth of certain bacteria.

The foregoing conclusions are in accord with the data obtained in this laboratory over two years ago by F. W. Fabian² working on a similar problem.

In this connection it is noted that it is a matter of record that Lythgoe³ found that normal fresh milk reduced Schardinger's F. M. reagent in less than 20 min. The authors are unable at this time to account

for this discrepancy in the time element, unless it can be attributed to a difference in the standard of milk which is to be regarded as "normal."

Table II is quoted from the report of Mr. Fabian's work to which reference has just been made.

TABLE II (Results by Mr. Fabian)

Sample No.	Minutes Required to Decolorize M.-Blue	Bacterial Count on Plain Agar
10.....	3	17,000,000
17.....	3	35,000,000
5.....	6	12,000,000
14.....	7.5	44,000,000
11.....	9	1,000,000
2.....	13	810,000
1.....	14	720,000
12.....	15	370,000
4.....	15	600,000
3.....	17	560,000
6.....	19	300,000
13.....	20	300,000
20.....	27	220,000
9.....	34	490,000
15.....	32	360,000
19.....	37	300,000
8.....	42	240,000
16.....	45	300,000
18.....	59	120,000
17.....	95	35,000
25.....	120	80,000
22.....	150	110,000
24.....	155	90,000
23.....	180	40,000
21.....	184	20,000

Twenty-five different samples of raw milk were tested with Schardinger's reagent, F. M. A bacterial count was also made of each sample.

EFFECT OF TIME AND TEMPERATURE OF PASTEURIZATION ON MILK IN ITS RELATION TO SCHARDINGER'S REAGENT

Four separate portions of each of three different samples of milk were heated gradually—a rise of 2° C. per min.—in a water bath to 60, 65, 70 and 75° C., and then maintained at these respective temperatures for 30 min. Portions were removed every 10 min. and tested with the reagent. Bacterial counts were made of each sample tested at the various intervals of time. Milk 10 hrs. old was used, as fresh milk 4 hrs. old produced no decoloration of the reagent. The results obtained are given in Table III.

TABLE III

Sample No.	PASTEURIZATION Temp. °C.	Time Min.	Time Required to Decolorize Min.	BACTERIAL COUNT	
				Plain	Agar
1.....	60	0	30	40,000	12,000
		10	70	12,000	2,000
		20	95	6,000	3,500
		30	120	1,000	1,000
		40	60	40,000	11,000
		50	100	10,000	4,000
		60	120	400	None
		70	160	200	None
		80	65	35,000	11,000
		90	No decolor.	200	None
		100	No decolor.	None	None
		110	No decolor.	None	None
2.....	65	0	30	40,000	12,000
		10	70	12,000	2,000
		20	95	6,000	3,500
		30	120	1,000	1,000
		40	60	40,000	11,000
		50	100	10,000	4,000
		60	120	400	None
		70	160	200	None
		80	65	35,000	11,000
		90	No decolor.	200	None
		100	No decolor.	None	None
		110	No decolor.	None	None
3.....	70	0	30	40,000	12,000
		10	70	12,000	2,000
		20	95	6,000	3,500
		30	120	1,000	1,000
		40	60	40,000	11,000
		50	100	10,000	4,000
		60	120	400	None
		70	160	200	None
		80	65	35,000	11,000
		90	No decolor.	200	None
		100	No decolor.	None	None
		110	No decolor.	None	None

These data indicate that both the temperature and the duration of the pasteurization process affect milk

¹ *Chem. Vol.*, 34, 188.

² Working in this laboratory in 1912 in collaboration with the senior author.

³ *This Journal*, 6, 1913, 922-927.

with reference to the time required by the latter to decolorize methylene blue. In general, as either factor is increased the time required for decoloration is increased. Furthermore, the authors found as the result of a larger number of tests than are recorded here that milk heated to a temperature of 70° C. for 10 min. failed to decolor the reagent in several hours. In this latter respect the behavior of samples of milk pasteurized under the stated conditions was identical with that of freshly drawn milk of good grade.

Mr. Fabian found that milk pasteurized at 80° C. for 1 min. behaved towards the reagent in the same manner as milk pasteurized at 75° C. for 3 min. or at 70° C. for 10 min., and that in no case was the reagent decolorized in several hours. Table IV is quoted from Mr. Fabian's report. Samples of raw milk, eight hours old, were used in making the tests indicated.

TABLE IV (Results by Mr. Fabian)

Temp. (° C.) of Pasteurization	Duration of Pasteurization	Minutes Required to Decolorize Duplicates	
60	20	20	19
60	15	16	18
60	10	13	17
60	5	7	10
60	0	3	7
70	20	+	+
	10	+	+
	5	40	42
	0	3	4
75	10	+	+
	5	+	+
	0	4	4
80	5	+	+
	3	+	+
	2	+	+
	1	+	+
	0	3	7

+ Signifies that no decolorization occurred in several hours.

FURTHER EVIDENCE AS TO THE ORIGIN OF REDUCTASE

With a view to obtaining more evidence in regard to the origin of reductase in milk, 5 samples of the latter were pasteurized at 70° C. for 10 min. and then set aside. The samples, in the usual paper-disk-covered bottles, were allowed to "age" at the usual laboratory temperatures. They were tested at intervals of 24 hrs. with the Schardinger reagent and bacterial counts made.

The data obtained by testing the first two samples are presented graphically in Fig. 6.

TABLE V

No.	Age Hrs.	Acidity Degrees	Time to Decolorize	BACTERIAL COUNT ON AGAR	
				Plain	L. L.
1	8	20	No decol.	5,000	300
	24	20.5	No decol.	5,000	
	48	72	8 min.	2,000,000	1,200,000
	72	95	15 min.	1,000,000	400,000
	100	106	18 min.	40,000	8
2	120	106	60 min.	30,000	10,000
	4	17	No decol.	2,500	500
	24	17	No decol.	100,000	5,000
	48	78	10 min.	100,000	30,000
	72	95	12 min.	200,000	125,000
3	4	16	No decol.	1,000	300
	24	18	No decol.	10,000	4,000
	48	25	5 min.	100,000	30,000
	72	93	30 min.	60,000	25,000
	4	19	No decol.	800	450
4	24	20	No decol.	11,400	4,500
	48	74	14 min.	700,000	250,000
	72	98	16 min.	500,000	250,000
	4	20	No decol.	400	300
	24	23	No decol.	8,000	5,000
5	48	76	8 min.	1,000,000	800,000
	72	96	12 min.	800,000	300,000

The experiments reported in Table V yielded results which indicate that milk pasteurized at 70° C. for 10 min. will not decolor methylene blue solution at the expiration of 24 hrs. but will after being allowed to stand for 48 hrs. This points to the conclusion

that reductase is not only destroyed by the pasteurization process but that it is of bacterial origin, the presumption being that no decoloration of the reagent takes place until the bacteria have again multiplied sufficiently.

Mr. Fabian in his work for a similar purpose collected a number of samples of raw milk and after making the bacterial count of each subjected them to a similar set of tests, with the results given in Table VI.

TABLE VI (Results by Mr. Fabian)

No.	Age Hrs.	Time Required to Decolorize	BACTERIAL COUNT ON AGAR	
			Plain	L. L.
1	24	3 (raw)	300,000	110,000
	48	Several hrs.
	72	92 min.
	96	17 min.
	120	2 min.
2	3 (raw)	Several hrs.	220,000	110,000
	24	Several hrs.
	48	70 min.
	72	6 min.
	96	3 min.
3	120	6 min.	310,000	100,000
	3 (raw)	Several hrs.
	24	Several hrs.
	48	35 min.	7,000,000	304,000,000
	72	6 min.
4	92	7 min.
	120	8 min.
	3 (raw)	Several hrs.	150,000	200,000
	24	Several hrs.
	48	10 min.
	72	6 min.
	96	9 min.

The conclusions to be made here are obviously the same as those formulated in the preceding paragraph.

EFFECT OF THE PRESENCE OF FORMALDEHYDE ON MILK WITH REFERENCE TO THE TIME REQUIRED TO DECOLORIZE METHYLENE BLUE

The following work was undertaken in order to ascertain if a so-called "preservative" like formaldehyde influences the action of milk in its relation to the Schardinger reagent. Five different samples of milk, each 8 hours old, were examined as follows: Each sample was tested as regards its acidity, time required to decolor the reagent, and bacterial count; then each sample was treated with formaldehyde (0.5 cc. per pint of milk) and the enumerated tests repeated at intervals of 24 hours. The results are given in Table VII.

TABLE VII

No.	Age Hrs.	Acidity Degrees	Time to Decolorize	BACTERIAL COUNT ON AGAR	
				Plain	L. L.
1	8	20	No decolorization	20,000	10,000
	24	20.5	Slight, 3 hrs.	3,200	100
	48	21	Slight, 3 hrs.	3,000	700
	72	22	No decolorization	5,000	800
	96	23	No decolorization	3,000	28
2	120	23	No decolorization	3,000	None
	8	19	No decolorization	5,000	1,500
	24	19	Slight, 2 hrs.	1,000	35
	72	20	Slight, 5 hrs.	1,200	None
	96	21	No decolorization
3	120	21	No decolorization	100	None
	8	17	No decolorization	15,000	7,000
	24	19	Slight, 5 hrs.	8,000	1,100
	72	20	No decolorization	3,000	600
	96	22	No decolorization	1,500	45
4	120	22	No decolorization	1,400	None
	8	20	Slight, 3 hrs.	40,000	17,000
	24	23	Slight, 7 hrs.	3,000	450
	48	23.8	No decolorization	3,000	250
	72	23.8	No decolorization	1,800	40
5	96	24	No decolorization	2,000	None
	8	16.8	Slight, 4 hrs.	27,000	6,500
	24	18	Slight, 4 hrs.	1,000	600
	48	19	No decolorization	5,500	375
	72	21	No decolorization	6,000	80
	96	21	No decolorization	4,800	None

CONCLUSIONS

The relationships indicated, if not proved, by this rather limited series of experiments are extremely interesting. For example:

(1) The germicidal properties of formaldehyde in relation to microorganisms found in milk are shown in a general way.

(2) Unless it be proven that reductase is formed *within* the milk by purely chemical changes, this series, considered in relation to the foregoing series of tests, points to the conclusion that reductase is of bacterial origin, as the time required for decoloring the reagent was not reduced by allowing the milk to "age," owing presumably to the fact that bacterial growth in the samples of milk was inhibited by the formaldehyde.

(3) The partial decoloration which occurred at first was probably effected by the reductase present in the milk before the formaldehyde was added. The final loss of power of these same samples to effect the same reaction suggests that the formaldehyde may interact with the reductase or counteract its influence in some way. The fact that both of these substances are strong reducing agents does not tend to render the problem more easy of solution.

Since the completion of this work the report of the investigation of Harris and Creighton¹ on the influence of certain poisons on reductase has appeared. Although the list of poisons reported by them as either destroying the reductase or retarding its action does not include formaldehyde, the latter may act in a similar manner. This, however, will be a matter for future investigation.

GENERAL SUMMARY

I—A brief outline has been made of the classification, distribution and reactions of certain enzymes; the possibility of making their sensitiveness to various physical and chemical agents the basis of methods for determining the sanitary condition of certain food-stuffs has been considered.

II—A survey has been made of the work done concerning the source, nature and action of reductase in its relation to certain methods which have been proposed for the differentiation of pasteurized milk from raw milk.

III—The experimental investigation undertaken by the authors of this paper has been described. As the result of this work certain conclusions have been formulated. They are as follows:

(1) Methylene blue as it occurs in Schardinger's reagent, F. M., is not decolorized by:

(a) Normal fresh milk in less than 20 min. When decoloration was effected in 10 minutes or less time the milk was found to contain 1,000,000 or more, microorganisms per cc.

(b) Milk pasteurized at 70° C. for 10 min. unless approximately 48 hrs. have elapsed since the milk was pasteurized, or until the bacteria have had time to multiply sufficiently

(c) Old milk in which the "preservative," formaldehyde, has inhibited the growth of bacteria

(2) Schardinger's reagent, F. M., as a rule de-

colored by normal milk allowed to "age" under ordinary conditions of temperature for 24 to 48 hrs.

(3) Pasteurization increases the time required for the decoloration of the reagent.

(4) In general, no proportionality exists between the time required for the decoloration of the reagent and the number of bacteria in milk. In a given sample, however, a general relation seems to exist between the two up to a given point of acidity.

(5) Inasmuch as there is no absolute parallelism between number of bacteria present in milk and the time required to decolor the reagent but that the relationship seems to exist in a given sample of milk, it would indicate that reductase is of bacterial origin but that not all bacteria found in milk produce this enzyme. (This latter conclusion is in accord with the views of Fred.)

(6) It seems probable that formaldehyde either gradually retards the action of the reductase or destroys it. This is a matter, however, for more careful investigation in the future.

It will be noted that although the conclusions formulated in this paper are not in accord with the entire body of conclusions of any previous worker in this field, yet many of them are in close agreement with certain conclusions of a number of investigators.

HYGIENIC LABORATORY
CARNEGIE HALL OF CHEMISTRY
ALLEGHENY COLLEGE, MEADVILLE, PA.

A STUDY OF THE VOLUMETRIC OR PEMBERTON METHOD FOR DETERMINING PHOSPHORIC ACID, WITH SOME EXPERIMENTS SHOWING THE INFLUENCE OF TEMPERATURE AND THE SULFURIC ACID RADICAL ON RESULTS*

By PHILIP MCG. SHUEY
Received October 20, 1916

There has been a great deal written and said of the volumetric method for determining phosphoric acid, but still many chemists have trouble in its use and manipulation. It has been found by most workers who employ this method that a number of years of careful and patient experience is necessary to master it, and owing to the length of time necessary to acquire this, many chemists have discarded it altogether. The writer has had more than 10 years of practical and constant experience in determining phosphoric acid by this method, both with a large fertilizer concern, and in the phosphate fields of Florida, and possibly some points already mentioned can be emphasized in this paper.

On account of the extreme delicacy of the method, and in order to show how it may be rendered accurate and reliable it might be of interest to include some experiments showing some of the principal causes that bring about disturbances in results. The problem is more interesting, and while on the subject it is made that this article will cover the entire field, it is hoped that it will at least bring the purpose of writing

* *Trans. Inst. Technicians*, 17, 416, 38, 110.

* Presented at 51st Meeting of American Chemical Society, New York City, September 17-20, 1916.

¹ Harris and Creighton, *J. Biol. Chem.*, 22 (1915), 513.

TABLE I—RESULTS BY VARIOUS METHODS OF TREATMENT

1—By dissolving in nitric acid and a few drops of hydrochloric acid.									
2—By adding an equal weight of 50° B _e . sulfuric acid, as in the manufacture of acid phosphate, and then making solution like (1).									
3—By adding twice the quantity of sulfuric acid, as is usually employed in the manufacture of acid phosphate.									
4—By solution in a mixture of 10 cc. sulfuric and 15 cc. nitric acid.									
5—By increasing the sulfuric to 25 cc.									
No.	CUBIC CENTIMETERS STANDARD SOLUTION			SODIUM HYDROXIDE			REQUIRED		
	5° C.	20° C.	30° C.	40° C.	50° C.	65° C.	5° C.	20° C.	30° C.
1.....	30.08	30.15	30.25 } Av. 30.10 } 30.17	30.22 } Av. 30.30 } 30.31	30.65 } Av. 30.65 } 30.65	31.15 } Av. 31.30 } 31.22	1.0023	1.00	0.99905
2.....	30.20	30.0	30.40 } Av. 30.40 } 30.30	30.70 } Av. 30.75 } 30.72	31.10 } Av. 30.95 } 31.02	32.15 } Av. 32.20 } 32.16	0.998	1.005	0.99505
2B.....					31.30 } Av. 31.45 } 31.37				0.9611
3.....					31.25 } Av. 31.25 } 31.25	32.75 } Av. 32.80 } 32.77			0.9648
4.....	30.20	30.20	30.50 } Av. 30.70 } 30.60	31.15 } Av. 31.08 } 31.11	31.40 } Av. 31.50 } 31.45	31.45 } Av. 31.15 } 31.30	0.99802	0.99802	0.98529
5.....	30.10	30.10	30.40 } Av. 30.55 } 30.47	30.95 } Av. 31.08 } 31.01	31.25 } Av. 31.28 } 31.26	31.45 } Av. 31.15 } 31.30	1.00166	1.00166	0.9895
6.....			30.35	30.45	30.50	31.00		0.9934	0.99011
7.....					30.35 } Av. 30.20 } 30.27	30.80 } Av. 30.80 } 30.85			0.99108
8.....					30.95 } Av. 31.15 } 31.05	32.10 } Av. 32.20 } 32.15			0.96618
									0.93312

some chemists, and more particularly those starting out in making analyses of fertilizers, and of the materials which enter into their composition, and show that when properly handled the method is equally accurate, or more so, than the Standard Gravimetric. Dr. F. B. Carpenter, in his very able article, mentions both the advantages and disadvantages of the method, together with details which cause disturbances of results.¹

As a means toward more accurate determinations, a number of modifications of the original method have been proposed. Briefly stated, their principal features are as follows:

1—Richardson's modification for analyzing acid phosphate, which depends upon the removal of sulfuric acid with barium chloride, after making solution in a mixture of nitric and hydrochloric acids.²

2—Separation of the phosphoric acid from sulfuric acid by precipitation with ammonium hydroxide, then, after filtering and washing, the phosphates are dissolved and precipitated in the usual way.

3—Fairchild's modification making the end-point sharper by the addition of barium chloride, after dissolving the precipitate of ammonium phosphomolybdate in an excess of standard alkali.³

It is conceded by those experienced in the method that the details which have the greatest influence on results are temperature and the amount of sulfuric acid radical present; and to show the effects of these important factors on the results, several series of experiments have been made which may be briefly described as follows: The sample of phosphate rock which was adopted by the Fertilizer Division of the Society as a standard for phosphoric acid was taken as a basis for the experiments.⁴ The value of the standard adopted is 30.15 per cent, which was the average of a large number of determinations by the gravimetric method. After weighing out 1-g. portions and putting them into 200-cc. flasks, which had previously been

6—By making solution according to (2), and then adding barium chloride to remove sulfuric acid.

7 and 8—Solutions corresponding to (1) and (2), respectively, only using a standard that has been used in the writer's laboratory for the past 5 years, and which contains much less iron and alumina than the A. C. S. Standard, but which, by coincidence, contains practically the same amount of phosphoric acid.

carefully calibrated, solutions were made according to the descriptions given in Table I.

After making up solutions to mark, and filtering through dry filters, aliquot portions representing 0.1 g. were taken for analysis. After diluting with water the medium for precipitation was regulated in the usual way, by first adding ammonia until alkaline, and then clearing up by the addition of nitric acid. Before making precipitations from Solutions 4 and 5 10 g. of ammonium nitrate were added, as otherwise the precipitation would probably be incomplete in the presence of such a large quantity of sulfuric acid. As an experiment, 10 g. of ammonium nitrate were also added to (2B). In all other cases, however, no ammonium nitrate was added, other than that formed from the reaction between ammonia and nitric acid in getting the proper medium.

With the precipitant at 30° C., precipitation was made at various temperatures as follows:

At 5° C. by adding 50 cc. Molybdic solution, stirring 30 min.
At 20° C. by adding 50 cc. Molybdic solution, stirring 30 min.
At 30° C. by adding 45 cc. Molybdic solution, stirring 30 min.
At 40° C. by adding 35 cc. Molybdic solution, stirring 30 min.
At 50° C. by adding 35 cc. Molybdic solution, stirring 15 min.
At 65° C. by adding 35 cc. Molybdic solution, stirring 15 min.

Filtering and washing was done by the use of 11 cm. filter papers: this the writer regards as being more accurate than filtering under pressure, and when running a batch of 6 or more determinations at a time it is done about as rapidly. The precipitates were all washed free of acid as determined by the addition of a drop of N/4 alkali to the filtrate. It is noteworthy that in making these experiments only 2 or 3 of the duplicate determinations were run at the same time, and therefore the results are more truly checks than had all been duplicated together. Results found by precipitating at the low temperatures, 5 and 20° C., were not duplicated through lack of time, but as would be expected, the figures agree closely when making precipitation from the various solutions at these temperatures.

As the strength of the standard solutions was practically 0.3238 N, and as 0.1 g. of rock was taken for analysis, the number of cc. of solution required should

¹ THIS JOURNAL, 2 (1910), 157.

² Sutton's "Volumetric Analysis," "Schimpf's "Volumetric Analysis," and J. A. C. S., 29, 134.

³ THIS JOURNAL, 4 (1912), 520.

⁴ "Details of Analysis for Standardization," THIS JOURNAL, 3 (1911), 118.

very nearly correspond to the actual percentages, provided there are no disturbing elements to offset the results. In Table I is shown the number of cc. required when precipitation was made at the various temperatures and from the various solutions and the corrective factor for each cc.

It will be noticed what a great deviation there is in the number of cc. of the standard solution required to dissolve the various precipitates formed under the different conditions of temperature, and the varying amounts of sulfuric acid, and that according to the Official Volumetric Method¹ the number of cc. required corresponds to the percentage for anything from room temperature up to 65°, without making any allowance whatever for correction.

While in the Official Method it is not recommended that sulfuric acid be used in making solutions of the material, no distinction, however, is made in the mode of precipitation, whether or not the sulfuric acid radical is present. It is noteworthy that at a temperature of 65° C., much higher results are found on acid phosphate dissolved in nitric acid than when phosphate rock was dissolved in a mixture of sulfuric acid and nitric acid.

By reference to the table under Treatment 2, it will be noticed that the number of cc. of standard alkali required to dissolve the yellow precipitate, when precipitation was made at the various temperatures, varies all the way from 30 to 32.16 cc., a maximum variation of 2.16 cc., which would correspond to 2.16 per cent when not making correction.

If we consider that the addition of 1 g. of sulfuric acid to 1 g. of rock gives 2 g. of acid phosphate, and that the aliquot taken represents 0.2 g., the maximum variation caused by changes in temperature is 1.08 per cent, without correction, and when precipitating at 65° in determining the phosphoric acid in acid phosphate, results will often be 1 per cent higher than they should be.

It was found in making the experiments that there was much difficulty in making results agree when precipitating at 50 and 65°, while at 30 and 40° there was not the least trouble in this respect, the results being extremely regular.

The deviation in analysis of phosphate rock caused by changes in temperature, as shown under (1), is about half of what it is after the addition of sulfuric acid (after the manner of making acid phosphate), the maximum variation being 1.14 cc.

Experiment 3 shows the variation at 30 and 65° after adding double the amount of sulfuric acid, as is usually employed in making acid phosphate. This addition gave a result 0.62 per cent too high, and 0.61 per cent higher than results shown in (2), necessitating a corrective factor of 0.92005 per cc. when precipitation was made at 65°.

Experiment 4, in which solution was made by dissolving in a mixture of sulfuric and nitric acids, shows a variation at different temperatures of 1.24 cc., and with precipitation at 30, 40 and 60° C., the volume re-

quired was from 0.3 to 0.6 cc. greater than in the acid phosphate under (2), but at 65° this quantity was 0.71 cc. less.

It was found that by increasing the amount of sulfuric acid used in making solution to 25 cc., little, if any, difference was made in results.

Experiment 6 shows the analysis after removing the sulfuric acid radical with barium chloride. The results were not duplicated, but they agreed closely with those under (1), in which no sulfuric acid is added.

Experiments 7 and 8 were made to determine whether or not iron and aluminum had a tendency to affect results, the sample being very low in these metals, while the A. C. S. standard is very high. The results were concordant.

The results found at the various temperatures and from the various states of solution show how utterly impossible it is to do correct work when precipitation is made at from 40 to 50 or from 60 to 65°, as mentioned in the Official Method, unless correction is made by the use of a standard, which is run along with the batch under identically the same conditions, and then corrections made accordingly. If work is being done on acid phosphate, it is suggested that a control test be carried on at the same time by adding to a weighed quantity of standard phosphate rock the amount of sulfuric acid used in making the acid phosphate. It was also found by experiment that the sulfuric acid may be added after making solutions in nitric acid with the same results. This suggestion is intended particularly for those who precipitate phosphoric acid at temperatures higher than 30° C. It is advisable, too, that a stirring machine be employed.

Should a sample of fertilizer under examination contain a large amount of organic matter like fish scrap, ground tankage or cottonseed meal, it is suggested that the method of solution be the addition of a mixture of 10 cc. sulfuric acid and 15 cc. nitric acid, boil on a hot plate until black, and then oxidizing the organic matter by the addition of potassium nitrate. Whenever employing this method allow the flask to cool down with the hot plate, otherwise it will crack; then boil with about 100 cc. of water. A portion of a standard sample of phosphate rock is dissolved and treated in the same manner, and the value per cc. found and correction made. It is advisable when precipitating from a sulfuric acid solution to add at least 5 g. of ammonium nitrate.

It has been found also that the age of the molybdc solution may seriously affect results. If a solution is very old and shows a tendency of separating out molybdc acid, it should be discarded and not even mixed with a fresh solution. By keeping the solution in a dark bottle and in a cool place it will be preserved longer. A precipitating vessel that is most convenient is a 3-ounce sealed fat extraction flask fitted with a No. 5 rubber stopper. After adding an excess of standard alkali, the stopper is inserted, and the flask shaken until the yellow precipitate is dissolved. The end point is sensitive to a drop, and therefore the molybdc modification is recommended.

In conclusion it may be stated that with a knowledge of the method and with strict attention to detail, very accurate and reliable results may be obtained, and the fact that it is extremely delicate is a point in its favor. Accuracy, however, will come only with practice.

LABORATORY OF SAVANNAH GUANO COMPANY
SAVANNAH, GEORGIA

THERMOCLINE STUDIES AT KENSICO RESERVOIR¹

By FRANK E. HALE AND JOHN E. DOWD

Received September 30, 1916

The new and enlarged Kensico reservoir is the storage reservoir for the new Catskill water supply nearest to New York City. Owing to the progress made on the dam, the reservoir was filled in the winter of 1915-16. Close watch was kept of the quality of the water in order to utilize it at the earliest possible moment. During construction the water of the Bronx watershed had been held back by the Bronx and Rye Dykes and the Bronx supply fed from Rye Dyke. As soon as the quality of the water permitted, change of draught was made to the new dam and filling continued over the Dykes in order to conserve in the Catskill system as much of the winter and spring flow as possible.

The problem was interesting in that it is not the usual procedure to use water from a reservoir without long standing and possibly blowing of bottom water after stagnation.

TREATMENT OF RESERVOIR BOTTOM

Soil stripped from certain designated portions was used for filling areas of shallow flowage. Swampy areas were covered with sand and gravel to a depth of 12 in. or more. The bottom and a margin of about 30 ft. outside the flow-line were cleared of all buildings, fences, trees, bushes, logs, stumps, high grass, tussocks or clumps of roots of bushes or grass, weeds and rubbish. Stone walls within the 30-ft. margin and to a depth of 20 ft. below the flow-line were removed.

anything approaching the stagnation of summer is avoided. Water first flowed in from the Ashokan tunnel on November 22, 1915, and continued steadily until January 15, 1916, when the water was 123 ft. deep. Filling was resumed February 21, 1916, and continued to full reservoir level which was reached May 23, 1916.

The water entering was of low turbidity and free from *B. coli* in 10 cc., having seen long storage at Ashokan reservoir. The water as it entered the reservoir stirred up the mud of the bottom with the result that the whole volume of water in Kensico reservoir was muddy and showed *B. coli* in many of the tests in 0.1 cc. The turbidity contained fine silt which settled very slowly. The turbidity was still 30 p. p. m. at the end of a month and naturally cleared more slowly in the deeper water. *B. coli* results improved with subsidence of turbidity and time of standing, tests in only 10 cc. being obtained at the end of 3 weeks and at the end of 6 weeks being negative in 10 cc.

Special inspections were started by the Laboratory Division of the Department of Water Supply, Gas and Electricity, and special samples were taken on December 22, 1915. Eight samples taken at different points along the side of the reservoir had an average of only 36 bacteria per cc. (agar 37° C.) and no *B. coli* in 10 cc. within 24 hrs., lactose bile test. In 3 days' time the tests in 10 cc. were positive in 3/4 of the samples. One only gave a test in 1 cc. These results proved the presence of attenuated *B. coli* only, its source being the disturbed mud of the reservoir.

A path was broken through the ice to a point several hundred feet back of the intake at the dam and samples taken from a row boat at the surface and at 50 ft. depth, the total depth of water being 82 ft. These samples were taken, as were all similar samples later, by the method employed for collecting dissolved oxygen samples, *i. e.*, allowing a larger bottle to fill through a small bottle so that the analysis of the water in the small bottle represents the actual conditions at the

TABLE I—QUALITY OF WATER AT VARIOUS DEPTHS, KENSICO RESERVOIR

DATE	PLACE OF COLLECTION	Temp ° F	EXAMINATION			CHEMICAL ANALYSIS (Parts per Million)										OXYGEN		Bacteria per cc. in 10 cc. at 37° C.	Bacillus coli in 0.1 cc. in 10 cc.	Total Microscopic Organisms per Cc.	
			Turbidity P. P. M.	Color P. P. M. Pt.	Odor	Aluminoid Ammonia	NITROGEN AS —				Total Solids	Chlorine	Hardness	Alkalinity	Iron	Free CO ₂	Per cent Saturation				P. P. M. Dissolved
							Free Ammonia	Nitrites	Nitrates												
Dec. 22, 1915	Surface	34	8	20	10	0.116	0.038	0.002	0.15	51	2.2	25	14	0.70	0.9	91.9	13.08	15	0	0	15
	50 ft. Depth	34.7	11	21	25 + m	0.106	0.024	0.002	0.15	50	1.5	25	14	0.60	0.9	90.0	12.67	37	0	0	15
	82 ft. Bottom																				
Jan. 7, 1916	Surface	34	5	16	25	0.088	0.016	0.002	0.15	48	1.0	25	13	0.40	0.4	93	13.25	11	0	0	20
	25 ft. Depth	34.8	5	16	25	0.088	0.020	0.002	0.10	51	1.2	20	13	0.50	0.4			11	0	0	100
	50 ft. Depth	35	4	16	25	0.090	0.030	0.002	0.20	59	1.4	20	13	0.50	0.4	92	13.25	19	0	0	0
	117 ft. Bottom																				

Designated areas within the 30-ft. margin and the reservoir bottom to a depth of 35 ft. below the flow-line were grubbed of stumps and roots. Material was burned, excrement removed, and chloride of lime used.

The time of filling the reservoir was well chosen, late fall, since circulation continues all winter and

depth sampled. These samples were given complete analysis, physical, chemical, bacteriological, and microscopical. Dissolved oxygen and free carbonic acid were also determined at the reservoir. The results are shown in Table I.

The temperature, oxygen-free carbonic acid and other determinations proved the water to be of uniform character throughout. Microscopic organisms were practically absent, oxygen was abundant, 90

¹ Presented at the 53rd Meeting, American Chemical Society, New York City, September 25 to 30, 1916.

per cent of saturation at 50 ft. depth, free carbonic acid very low, and the *B. coli* present only in attenuated form in the 50-ft. sample. The turbidity, which accounted also for the slight excess of iron, was still just sufficient to have caused complaint if turned into service.

On January 7, 1916, a second inspection was made in the same way (see Table I). The shore samples were of similar character, averaging 38 bacteria per cc., and only attenuated *B. coli* appearing in 10 cc. in 4 out of 7 samples.

Samples were again taken from a boat at surface, 25 ft. and 50 ft. depths, the total depth being 117 ft. Owing to the difficulty of winter sampling from a row boat, samples were not taken at a greater depth than 50 ft.: in fact some samples froze and burst the bottles while standing in the boat. The results were similar to the previous analyses.

The water had improved in showing less turbidity, about 5 p. p. m., no *B. coli* in any sample, still lower carbonic acid, and oxygen 92 per cent of saturation at 50 ft. The temperature, oxygen, free carbonic acid, and microscopic organisms for both inspections are plotted in Chart No. 1 and show the absence of stratification or any thermocline, all lines being vertical.

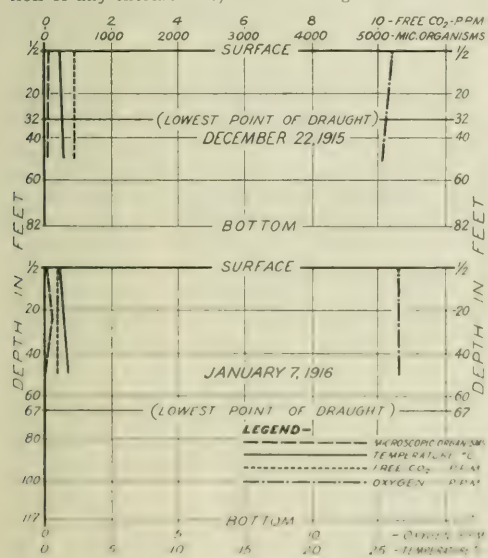


CHART NO. 1 WINTER CIRCULATION
QUALITY OF KENSICO RESERVOIR WATER AT VARIOUS DEPTHS.

As the water rose difficulty was experienced with the pipe line bringing water from Rye Dyke and it became necessary to supplement at the new dam. Service from Rye Dyke was soon discontinued and all draught taken at the new dam, the point of draught being 50 ft. off the bottom, the lowest available. Filling of the reservoir, which was stopped January 15, was continued February 21, and the Dyke flooded until the reservoir was practically full with a depth of 117 ft. on May 23, 1916.

Previous experience with Croton Lake having indicated that there would be no stagnation until summer, special sampling was discontinued until spring. Regular samples were taken 3 times weekly of surface and effluent at the dam and these resulted of excellent quality.

Common reference is made to winter stagnation in reservoirs. It is the opinion of the writers that under usual conditions there is no winter stagnation. In our experience with Croton Lake and with Kensico Reservoir the water circulates and overturns all winter long even to a temperature below that of greatest density. The following table of temperatures taken by thermophone by the Board of Water Supply substantiates this point:

DEPTHS	FEBRUARY 8, 1916	DEPTHS	APRIL 5, 1916
Surface	32.7° F. 0.4° C.	Surface	35.8 2.1
7 ft.	33.9 1.1	14 ft.	36.0 2.2
22 ft.	34.0 1.1	30 ft.	36.1 2.3
62 ft.	34.2 1.2	89 ft.	36.3 2.4
103 ft.	34.8 1.6	129 ft.	36.4 2.4
122 ft. (bottom)	149 ft.

It will be noted that the colder temperatures are at the surface, that on February 8, there was only a difference of 1.2° C. between top and bottom temperatures taken, and on April 5, only 0.4° C. difference, and that all the temperatures on April 5 are higher than those on February 8, proving circulation from top to bottom. The probable explanation of this circulation is that water cooled below 4° C. becomes lighter and when it again increases in temperature grows heavier up to 4° C. Any disturbance as by wind then causes an overturning which temperatures show is profound. Such appears to be the case all winter. Only in the summer does true stagnation take place. The fact that Kensico was filling most of the winter really has no bearing on the results in that the same phenomenon has been noticed at Croton Lake and also there was no water running in from January 15 to February 21, a period of 5 weeks. Again the water entered at the northern end and sampling was at the southern end.

The temperatures obtained on the different dates are shown in Table III.

COMPLETE ANALYSES

On May 22, 1916, the first of a very complete set of analyses was started. Temperatures were taken by a thermophone of the Board of Water Supply, operated by Mr. Glazer. The instrument was of the galvanometer type and readings could be made accurately to 0.1° F. The instrument had been compared with standard thermometers and found to be correct. Temperatures were read at every 5 ft. depth down to 100 ft., then at every 10 ft. depth. When the thermocline developed from its exact position was determined by readings 10 ft. apart. Samples for other determinations were taken at frequent intervals including especially just above and just below the thermocline. Running logs also have been taken from the effluent pipe near the dam, which have demonstrated that the draught is entirely of the water intended.

TABLE III

May 22, 1916				June 29, 1916				July 28, 1916				August 31, 1916			
Depth ft.	Thermocline	Temperatures	Bottle	Depth ft.	Thermocline	Temperatures	Thermophone	Depth ft.	Thermocline	Temperatures	Thermophone	Depth ft.	Thermocline	Temperatures	Thermophone
1	55.1° F.	12.8° C.	55.8° F.	13	2° C.	5	75.1° F.	23.9° C.	1/4	78.3° F.	25.7° C.	1	75.6° F.	24.2° C.	5
5	55.0°	12.8°	5	78.2°	25.7°	...	5	75.6°	24.2°	5
10	54.3°	12.4°	10	77.9°	25.5°	...	10	75.6°	24.2°	10
15	54.0°	12.2°	15	77.8°	25.4°	...	15	75.5°	24.0°	15
20	52.9°	11.6°	20	77.6°	25.3°	...	20	74.0°	23.3°	20
...	21	77.2°	25.1°	...	21	73.7°	23.2°	21
...	22	76.6°	24.8°	...	22	73.5°	23.1°	22
...	23	76.3°	24.6°	...	23	72.1°	22.8°	23
...	24	76.1°	24.5°	...	24	71.9°	22.7°	24
...	25	76.0°	24.4°	...	25	71.8°	22.6°	25
...	30	75.0°	23.3°	...	30	70.8°	22.6°	30
...	35	74.8°	23.2°	...	35	70.5°	22.5°	35
...	40	74.6°	23.1°	...	40	70.3°	22.4°	40
...	45	74.5°	23.0°	...	45	70.1°	22.3°	45
...	50	74.4°	22.9°	...	50	69.9°	22.2°	50
...	55	74.3°	22.8°	...	55	69.8°	22.1°	55
...	60	74.2°	22.7°	...	60	69.7°	22.0°	60
...	65	74.1°	22.6°	...	65	69.6°	21.9°	65
...	70	74.0°	22.5°	...	70	69.5°	21.8°	70
...	75	73.9°	22.4°	...	75	69.4°	21.7°	75
...	80	73.8°	22.3°	...	80	69.3°	21.6°	80
...	85	73.7°	22.2°	...	85	69.2°	21.5°	85
...	90	73.6°	22.1°	...	90	69.1°	21.4°	90
...	95	73.5°	22.0°	...	95	69.0°	21.3°	95
...	100	73.4°	21.9°	...	100	68.9°	21.2°	100
...	105	73.3°	21.8°	...	105	68.8°	21.1°	105
...	110	73.2°	21.7°	...	110	68.7°	21.0°	110
...	115	73.1°	21.6°	...	115	68.6°	20.9°	115
...	120	73.0°	21.5°	...	120	68.5°	20.8°	120
...	125	72.9°	21.4°	...	125	68.4°	20.7°	125
...	130	72.8°	21.3°	...	130	68.3°	20.6°	130
...	135	72.7°	21.2°	...	135	68.2°	20.5°	135
...	140	72.6°	21.1°	...	140	68.1°	20.4°	140
...	145	72.5°	21.0°	...	145	68.0°	20.3°	145
...	150	72.4°	20.9°	...	150	67.9°	20.2°	150
...	155	72.3°	20.8°	...	155	67.8°	20.1°	155
...	160	72.2°	20.7°	...	160	67.7°	20.0°	160

The analyses made May 22 are shown in Table IV. Chart No. 2 shows the temperatures, oxygen, free carbonic acid, and microscopic organisms. It is evident from the chart that a thermocline had begun to form at about 20 ft. depth. Oxygen was abundant at all depths and microscopic organisms at a minimum.

Comparison of the small bottle temperatures with the thermophone proved that the samples came from the depth intended. Some change of temperature in the deep samples is occasioned while drawing up through the warmer water. This difference becomes greater as the surface temperatures become higher.

The tubes were so arranged that the bottles took 2 min. to fill, and it took only about one-half minute to lower to the depth desired.

The analyses show the water to be of remarkably uniform character from top to bottom.

On June 29, 1916, samples were again taken. The results, shown in Table IV and on Chart No. 3, indicate that marked changes have taken place. A distinct thermocline has formed at 16 ft. depth with great increase of temperature of the surface water. Microscopic organisms have increased above the thermocline. Free carbonic acid has increased below the thermocline.

TABLE IV—QUALITY OF WATER AT VARIOUS DEPTHS AT KENSICO RESERVOIR

SAMPLE	DATE (1916)	Place of Collection (ft. back of Dam)	PHYSICAL EXAMINATION		CHEMICAL ANALYSIS (Parts per Million)										BACTERIOLOGICAL EXAMINATION		MICROSCOPICAL EXAMINATION																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																										
			Turbidity	Color	NITROGEN AS—										Bacteria per 100 c.c. at 37° C.	Bacillus coli in 10 c.c.	Total Microscopic Organisms	No. of Standard Units per c.c.																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																									
					P. M.	P. M.	P. M.	P. M.	P. M.	P. M.	P. M.	P. M.	P. M.	P. M.																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
																			Alumina	Ammonia	Free Ammonia	Nitrites	Nitrates	Total Solids	Loss on Ignition	Fixed Solids	Chlorine	Hardness	Alkalinity																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																														
																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																											</

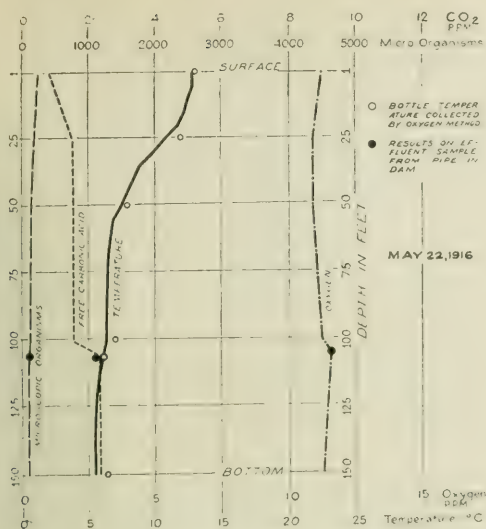


CHART NO. 2 THERMOCLINE FORMING AT ABOUT 20 FEET

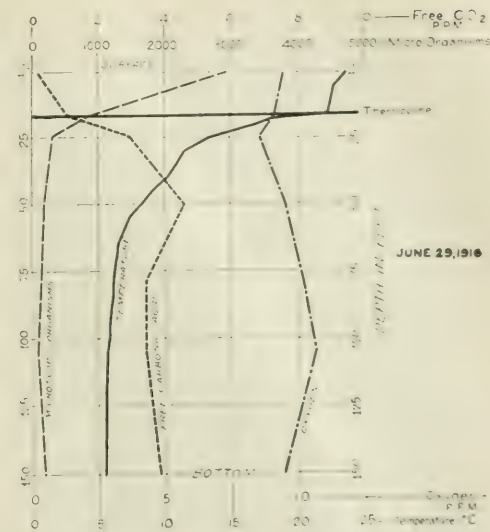


CHART NO. 3 THERMOCLINE FORMED AT 16 FEET

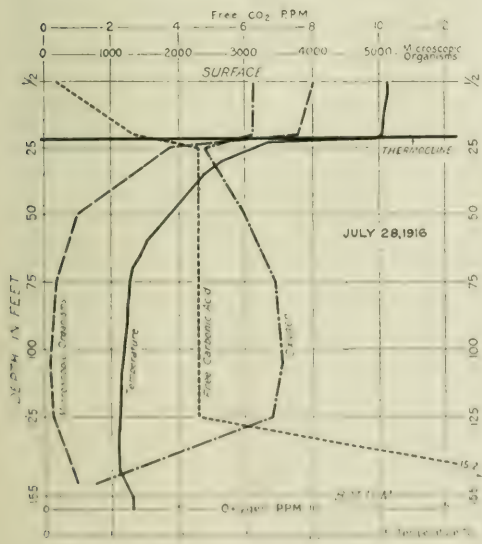


CHART NO. 4 THERMOCLINE AT 22 FEET

QUALITY OF KENNEDY RESERVOIR WATER AT VARIOUS DEPTHS

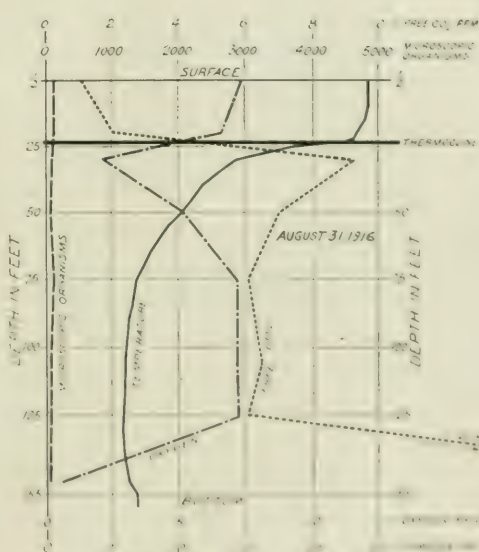


CHART NO. 5 THERMOCLINE AT 23 FEET

and oxygen has begun to decrease just below the thermocline and at the bottom. There was, however, an abundance of oxygen at all depths. The albuminoid ammonia decreased with the microscopic organisms from top to bottom. The reverse was true of free ammonia, nitrite, and free carbonic acid. The bottom samples alone showed high bacteria.

The next set of samples was taken July 28, 1916. The results are shown in Table IV and on Chart No. 4.

The thermocline is very sharply defined at 23 ft. depth. Between 21 ft. and 23 ft. there was a difference of 8° C., whereas for each foot above and below these points there was but a difference of 1 degree difference. Other changes were more sharply marked. The oxygen was very scarce below the thermocline and is nearly exhausted at the bottom. The free carbonic acid has greatly increased at the bottom accompanied by high free ammonia, nitrite,

and amorphous matter. Microscopic organisms have greatly increased above the thermocline and somewhat below, the curve conforming to the temperature curve very closely. Free ammonia showed certain changes also, increasing from zero at the surface to a maximum just below the thermocline, reducing again to a minimum at point of draught (105 ft.) and increasing again to the bottom. Nitrite and nitrate showed a slight increase from top to bottom.

For the first time *B. coli* appeared in both samples above the thermocline, also at mid depth and at bottom. The numerous regular samples taken of the effluent have, however, only a few times given a positive test for *B. coli* in 10 cc.

Another odd feature is a slight rise in temperature at the bottom, probably due to earth temperature. While not sufficient to cause overturning in the quiet water of that depth, this probably accounts for the gradual increase during the summer in the temperature of the water below 75 ft. depth.

On August 31, 1916, another set of samples was taken. The results are shown in Table IV and on Chart No. 5. The thermocline is sharply formed at 23 ft. depth. The oxygen dip below the thermocline and at the bottom is striking. This is accompanied by heavy amorphous matter at both points due to the death of microscopic organisms which for some reason have almost disappeared at all depths. Particularly striking is the reciprocal relationship between the oxygen and the free carbonic acid, the latter increasing greatly just below the thermocline and exceedingly at the bottom. The bottom sample also shows an exceedingly high color with accompanying high iron. The turbidity, free and albuminoid ammonia, amorphous matter, oxygen, and free carbonic acid all show the effect of stagnation and leaching of the bottom.

The albuminoid ammonia decreased from the surface to the point of draught and then increased to the bottom. The amorphous matter increased from the surface to the sample just below the thermocline, where oxygen is low, then decreased, to increase again at the bottom.

The water was in satisfactory bacteriological condition throughout.

The increase in temperature at the bottom, extending for 15 ft., is again noticeable.

In conclusion attention is called to the fact that, although the reservoir was recently filled, draught was begun almost at once and all through the summer deep draught has been maintained at 50 ft. from the bottom. The water obtained has been clear, cold (43° F.), free from *B. coli* and low in bacteria. Microscopic organisms have been avoided, although heavy growths have occurred at the surface of a type producing on decay disagreeable pig-pen odors. The water has also contained abundant oxygen. The draught of 27 to 30 m. g. d. has had no effect whatever on the water in the Reservoir. Similar results with larger draught have been obtained at Croton Lake for several years.

The fact of continuous winter circulation is also

emphasized although the data here presented in connection with Kensico Reservoir is not as complete as it should be.

The progressive changes in character of the water at various depths accompanying the formation of the thermocline have been striking. Just below the thermocline and at the bottom oxygen has diminished to near exhaustion. Elsewhere it has been abundant. Reduction in oxygen has been accompanied by increase in free carbonic acid, the two curves being reciprocally opposite in character. The free carbonic acid was at a minimum above the thermocline, increasing below. Microscopic organisms increased greatly with increase of temperature above the thermocline.

A slight increase in temperature in the bottom water was noticeable, a phenomenon we have never noticed elsewhere.

MT. PROSPECT LABORATORY, DEPARTMENT OF WATER SUPPLY
FLATBUSH AVE AND EASTERN PARKWAY
BROOKLYN, NEW YORK

IS THE RECOVERY OF THE NITROGEN IN SEWAGE SLUDGE PRACTICABLE?

By WILLIAM R. COPELAND

The answer to the question as to whether it is or is not practicable to recover the nitrogen in sewage and sewage sludge will depend upon three factors:

- (1) The amount of nitrogen contained.
- (2) The cost of recovering and disposing of the nitrogen.
- (3) The market value of the nitrogen.

Sewage may be defined for the purposes of this article as the liquid and water-borne wastes discharged into the city sewers through drains from houses, buildings, factories and streets, together with more or less water which seeps into the sewers from the ground.

In view of the great variety of sources and modes of collection of such waste liquors, sewage contains a variety of elements that change in composition with the source, season of year, day of the week and hour of the day. As nitrogen is an important constituent in many of the compounds, such as fecal matter, urine, horse manure, hair, meat scraps, etc., in sewage, the amount varies widely, both in regard to the portion which is dissolved and to the portion held in suspension by the liquid.

Recovery of nitrogen, from the standpoint of this paper, has to do principally with the nitrogen in suspension, because that is the portion which appears in the greatest quantity in the sludge. The total obtained will vary both with the treatment process used and with the volume contained by the raw sewage. To illustrate these points the following data are taken from Metcalf and Eddy's "American Sewerage Practice," Volume 3:

TABLE I—COMPOSITION OF DRY SEWAGE SLUDGE		PER CENT
SOURCE OF SAMPLE	SLUDGE OBTAINED FROM	NITROGEN
Frankfort-on-Main.....	Plain sedimentation	2.85
Columbus, Ohio.....	Septic tank	1.40
Essen.....	Imhoff tank	1.22
Philadelphia.....	Imhoff tank	1.20
Worcester, Mass.....	Chemical precipitation	2.77

¹ Presented at the 53rd Meeting of the American Chemical Society, New York City, September 25-30, 1916.

Some additional data compiled by J. R. McClintock, Consulting Engineer, of New York, from published reports of other sewage disposal plants, are given in Table II.

TABLE II—ADDITIONAL DATA UPON THE COMPOSITION OF SEWAGE SLUDGE
(Basis of 10 Per cent Moisture)

SOURCE OF SAMPLE	SLUDGE OBTAINED FROM	PER CENT NITROGEN
Brooklyn (Williamsburg).....	Dickson (Yeast) process	1.4
Columbus Testing Station.....	Grit chamber sludge	1.2
	Plain sedimentation tank	1.6
Philadelphia Testing Station.....	Plain sedimentation tank	1.2
Cleveland Testing Station.....	Plain sedimentation	1.4
	Septic tank	1.3
Gloversville Testing Station.....	Imhoff tank	1.2
	Plain sedimentation	2.3
	Septic tank	2.2
Worcester M. & E. Vol. III.....	Plain sedimentation	2.7
	Septic tank	2.7
Atlanta.....	Imhoff tank	1.5

The gist of the data given in these tables is that the sludge which has been obtained heretofore by the best known processes of sewage treatment contained from 1.2 to 3.0 per cent of nitrogen. These figures are low and show that the sludge did not possess as much nitrogen as the amount contained by the raw sewage would lead us to expect. This condition may be explained by the fact that a large share of the colloidal matter carried by the sewage ran out in the effluent flowing away from the tanks and took nitrogen with it; or in the case of chemical precipitation works the lime added drove nitrogen off in the form of ammonia and diluted the portion remaining by increasing the amount of inert mineral matter. Moreover, various authors state that from 10 to 60 per cent of the volume of the solids deposited by sewage in the sludge digestion chambers of Imhoff tanks and other forms of septic tanks, is converted into soluble or gaseous form. Much of the albuminoid ammonia is thus changed into free ammonia and free nitrogen which escape in the liquor or bubble out at the gas vents.

Within the last two years, however, a new method of sewage purification by the so-called "Activated Sludge" process has been tried out in various cities of America and England. One of the distinctive features of this process is that the colloidal and suspended matters of the sewage are collected in the sludge. If this is not reaerated or overaerated the solids are not liquefied to such a large degree as they are in septic tanks, and therefore the nitrogen does not escape.

For example, the digested sludge accumulates in Imhoff tanks at a rate of from 1 to 10 cu. yds. per 1,000,000 gals. of sewage treated; whereas, by the activated sludge process 20 to 80 cu. yds. or more may be deposited in the settling tanks, varying widely, of course, with the strength of the sewage and the water content of the sludge.

TABLE III—ANALYSES OF MILWAUKEE CITY SEWAGE BEFORE AND AFTER TREATMENT BY IMHOFF TANK AND BY ACTIVATED SLUDGE
Results in Parts per Million

Month	1915	SAMPLE	Suspended Matter	NITROGEN AS				
				Ammonia	Or	Albu.	Ni	Ni
				Free	Albu.	minid	N	Ni
							trate	trate
Aug.		EFFLUENT	253	11.6	7.88	29	0.18	0.13
		Imhoff	108	16.3	6.10	27	0.19	0.13
		Activated sludge	14	3.8	3.19	6	0.29	6.00
		Sewage	300	13.5	8.81	29	0.28	0.14
Sept.		EFFLUENT						
		Imhoff	116	18.4	7.10	27	0.12	0.09
		Activated sludge	8	8.1	2.72	9	0.14	8.01

The Milwaukee sewage testing station carried on a series of experiments during the summer of 1915 where the city sewage was treated by the Imhoff and activated sludge processes simultaneously. Analyses of the sewage effluents and sludges are given in Table III.

Samples of digested sludge from the Imhoff tank and of the fresh activated sludge were also collected and analyzed in August and September. While it is not correct to say that these sludges represent all of the raw sewage passed through these tanks during August and September, it is fair to assume that they are typical of the sludge which was being produced by those processes at that season of the year. Therefore, the analyses of the sludges are given in Table IV.

TABLE IV—ANALYSES OF SAMPLES OF IMHOFF AND ACTIVATED SLUDGES OBTAINED FROM MILWAUKEE SEWAGE

Date	SAMPLE	Nitrogen Reported as NH ₃ on a Basis of Sludge Dried to 10 Per cent Moisture	
1915			
Aug.	Imhoff sludge.....	2.87	3.82
	Activated sludge.....	5.71	4.97
Sept.	Imhoff sludge.....	3.88	8.69
	Activated sludge.....	8.69	9.00

The data given in Table III show some interesting facts. For example, the Imhoff effluent contained on an average more than 100 pts. per m. of suspended matter, whereas the effluent from the activated sludge process contained only about 10 p. p. m.; the Imhoff effluent contained more free ammonia than the raw sewage, whereas the activated sludge effluent contained only one-third as much. The Imhoff effluent contained almost as much albuminoid ammonia as the raw sewage, whereas the activated sludge effluent contained only about one-third as much. The Imhoff effluent contained almost as much organic nitrogen as the raw sewage, whereas the activated sludge contained only one-third as much.

What became of the nitrogen carried by the sewage?

Evidently most of the nitrogen in the sewage treated by the Imhoff tank passed out in the suspended and colloidal matters carried by the effluent.

The activated sludge process, on the other hand, converted the free ammonia into nitrate and stored up the undissolved albuminoid ammonia and organic nitrogen, as indicated by the large amount of nitrate in the effluent and high nitrogen content of the activated sludge.

In short, analyses of this material when dry show that activated sludge contains from 4 to 4½ per cent of nitrogen, and sludge from certain industrial plants such as packing houses may carry even more.

When it comes to recovering this nitrogen, however, we meet with a serious difficulty. Inasmuch as the sludge gathers in the settling tanks it contains from 98 to 99 per cent of moisture and the bulk of this water must be removed before the dry material can be sold for fertilizer.

Several methods of desiccating the sludge have been tried, such as settling, passing the mixture through centrifugal machines, pressing and drying.

The best information now available points to a combination of settling and desiccation as a preliminary process. By this means the water will be cut

down from about 99 to 96 per cent. On passing the concentrated residue through a press the moisture can be cut down to 75 per cent. The press cake can be dewatered in a dryer to 10 per cent moisture or less.

More than thirty samples of activated sludge have been dewatered by sedimentation, decantation and pressing at Milwaukee.

It is an interesting and notable fact that two different types of press can handle the settled sludge without requiring the addition of lime. Many experts and manufacturers of presses have held heretofore that sewage sludge could not be pressed advantageously without lime because of the gummy or gelatinous nature of the colloids in the sludge; but the facts remain that the sludge is not as gummy as was expected and it presses fairly easily down to 75 per cent of moisture.

In order to try out the feasibility of further dewatering the sludge four samples of the press cake were sent to fertilizer plants and dried there on a commercial scale. Three of these tests were made in a steam jacketed (indirect heat) dryer and one in a semi-direct heat dryer.

In each case the tests proved to be successful from three standpoints:

1—The sludge dried readily to a satisfactory mechanical condition.

2—The processes did not require much power.

3—Little nitrogen, if any, was driven off or lost by drying.

From the mechanical standpoint, therefore, the recovery of nitrogen in sewage sludge is practicable.

With regard to the question of cost, however, the situation at the time of writing is not so clear. The pieces of apparatus used for settling the raw sludge and drying the press cake were not designed to handle activated sludge in the most economical manner, but were requisitioned as being the best commercial apparatus available at the time.

By comparing the behavior of activated sludge with such matters as packing house tankage I estimate that this sludge can be dewatered so that the recovery of the nitrogen in it will probably cost upon present evidence about \$8.00 to \$12.00 per ton of material containing 10 per cent of moisture, depending upon a variety of local factors. These figures are intended to cover interest charges, depreciation, repairs and renewals, and a liberal provision for labor and fuel, as well as the cost of resetting and decanting of the water of the original sludge, and expenses for handling, freight, and marketing the finished product. Obviously, the total cost per ton will be somewhat more in the case of a small plant than for a large one. For a very large plant, where fuel and labor are relatively cheap, it is possible that further experience will reduce the cost below the lower limit in the range here given.

The dried samples of sludge were analyzed and the data obtained are given in Table V.

TABLE V ANALYSES OF COMMERCIAL DRIED ACTIVATED SLUDGE
BASIS OF 10 PER CENT MOISTURE

Sample No.	Character of Dryer	Per cent of			
		Nitrogen as Ammonia		Available Phosphoric Acid	
1	Semi-Direct Heat	4.36		0.70	
2, 3 & 4	Indirect Heat	4.76	4.86 5.06	0.81	0.47 0.39
Average of 4 Samples		4.68		0.57	

These analyses may be supplemented by the following tests:

TABLE VI—ADDITIONAL ANALYSES OF ACTIVATED SLUDGE PRESS CAKE

Date of Collection	Per cent of Nitrogen Calculated to Ammonia (Basis of 10 Per cent Moisture)
May 3, 1916	5.74
June 20, 1916	4.65
June 13, 1916	4.88
June 14, 1916	4.92
June 16, 1916	5.01

The data obtained at Milwaukee as cited in Tables V and VI indicate that dry activated sludge (basis of 10 per cent moisture) will contain 4.6 to 5 per cent of nitrogen figured as ammonia and 0.6 to 0.7 per cent of available phosphoric acid. In addition to this our data show that the dry product contains about $\frac{1}{4}$ to $\frac{1}{2}$ per cent of potash and from 3 to 4 per cent of fatty material. At present prices the nitrogen is worth \$2.50 per unit (or per cent). In normal times this nitrogen would be worth about \$2.00 per unit. The phosphoric acid is worth about \$0.50, and the potash may be worth something in the future, although the best that can be said of it at present is that it will assure for the fertilizer a more ready sale.

The fat present in the Milwaukee sludge is negligible. It would not pay to recover the fat nor will the fat injure the selling qualities of the dried sludge.

SUMMARY

Summing the whole situation up, then, we see that the dried sludge has a market value upon present figures of \$9.00 to \$15.00 per ton of material containing 10 per cent moisture. The total cost of getting this product and placing it on the market will probably run from \$8.00 to \$12.00 commercially per dry ton, depending upon local conditions. For large plants this cost may possibly be reduced as a result of further experience.

The activated sludge containing 4 per cent or more of nitrogen is much nearer a commercial possibility than the sludges obtained by the older methods of treatment, such as chemical precipitation, septic tanks, or the Imhoff process, which the data given in Table I indicate to contain only $\frac{1}{2}$ to 3 per cent of nitrogen.

In case the question arises as to the possibility of finding a market for the dried activated sludge, it should be added that raw materials containing nitrogen, phosphoric acid and potash are capable of being worked up readily as a base for making high-grade fertilizers, and as they are not very plentiful they are in good demand.

Presumably, however, large cities such as New York, Chicago, etc., by installing this activated sludge process, would produce so much raw material of this character that the product would have to be parcelled out among a number of manufacturers. It is even possible that the production might be sufficient to reduce the price.

However, the dried sludge is a good fertilizer just as it stands and contains enough value to pay for sale and distribution in quite a large local market.

The data given in the preceding pages indicate, therefore, that the recovery of the nitrogen in sewage sludge has at last been brought within the range of a commercially practicable problem.

SEWAGE TESTING STATION
MILWAUKEE, WISCONSIN

STORAGE RESERVOIRS AS A FACTOR IN THE PURIFICATION OF SURFACE WATERS¹

By S. T. POWELL

The impounding of surface waters in storage reservoirs has been practiced for years, but the primary object of such treatment has been the conservation of the supplies or the physical improvements to the water to be derived from sedimentation. Until within a few years past very little was known concerning the hygienic improvement that takes place in water retained in storage basins. Dr. Sedgwick² made note of this fact in a paper which he read before the New England Water Works Association. He pointed out that it was but fifteen years ago that he advanced the theory that it was in "stagnant" rather than in running water that the greatest bacteriological purification takes place. At that time this statement caused considerable discussion on account of this seemingly radical theory. Since that time so much has been learned concerning the chemical and bacterial efficiency of storage reservoirs that it is improbable that any sanitarian would attempt to disprove this general statement.

For a time a number of cities in this country depended wholly upon this method of purification but, as stated by Mr. George W. Fuller,³ "this method is expensive and seldom tried at present." With our present knowledge of water treatment, aside from the economic standpoint, it is doubtful if the public would be content with this form of purification as a complete or sufficiently safe one. Considered merely as an adjunct to filtration or sterilization preliminary to such treatment, storage reservoirs are particularly efficient and the purification to be derived in this way far outweighs certain disadvantages that are at times encountered in the course of storage. It is in respect to a consideration of the value of stored water as a preliminary method of purification prior to ozone sterilization that it is dealt with in this paper.

During the past fifteen months the writer has been afforded an opportunity to study conditions in the Herring Run storage reservoirs used in connection with the ozone plant of the Baltimore County Water and Electric Company. The raw water supply is obtained from Herring Run, a small stream which flows through a rather thickly populated district in Baltimore County adjacent to Baltimore City.

Previous to ozonization the raw water is stored in two shallow reservoirs holding approximately eighty million (80,000,000) gallons, permitting about a 3-weeks storage period. These reservoirs are used in tandem, the water flowing from the first to the second basin through an outlet chamber with gates at different levels so as to draw the water from near the surface at all times. Since undertaking a study of conditions that exist in these reservoirs weekly samples of the raw water and of the effluent have been made. The results obtained, particularly the bacterial data, are

of unusual interest, considering the fact that the reservoirs are quite shallow, averaging probably less than 10 ft. in depth, and that the period of storage does not exceed 3 weeks.

The physical and chemical improvement to the water passing through these basins has been quite marked at all seasons of the year, but these removals have in no sense been abnormal. There has been an average reduction in turbidity of 14.2 per cent during the period covered by these tests, with a maximum removal of 35.3 per cent during July, 1915. The efficiency of storage here in respect to the removal of turbidity has not been as great as at other places with the same detention period. This is due to the fact that during periods of high water, when the raw supply contains the greatest amount of suspended solids, the influent gates have been closed and the necessary daily pumpage has been drawn from storage. The removal of the color effected by these reservoirs has been marked, averaging 15.0 per cent, but contrary to expectation the greatest color reductions have been in the spring and fall and not during the summer months as has usually been noted by observers in studying the bleaching effect of sunlight upon stored water. The greatest bleaching effect is normally to be obtained during the warmest months of the year, on account of the more active oxidation of the organic coloring matter and by the direct decolorizing effect of the sunlight. Stearns,⁴ in studying these conditions in ten reservoir supplies of Boston, reported color reduction of from 9 to 69.5 per cent for periods of from one to nine years. Low color reductions were claimed by Mr. Stearns to be due to "color absorbed from reservoir beds" and this in a measure offsets the normal decolorization due to storage.

The reason the color reduction has been less here in summer is believed to be due not entirely to the absorption of organic substances in the reservoir bottoms but to the fact that during the summer months the algae growths are always prolific. Many of these growths⁵ are chlorophyll-bearing organisms and, due to disintegration, the chlorophyll is scattered throughout the water and this tends to lessen the bleaching effect of the sunlight. In addition to reduction in color and turbidity there has been consistent removal of organic matter from the water as shown in Table I.

TABLE I. SHOWING PERCENTAGE REMOVAL OF CHEMICAL CONSTITUENTS DUE TO STORAGE IN THE HERRING RUN RESERVOIR

CONSTITUENTS	PERCENTAGE REMOVAL
Color	15.0
Turbidity	14.2
Total Residue	6.5
Volatile Matter	6.5
Mineral Residue	0.1
Consumed Oxygen	2.0
Total Iron	0.004
Free Ammonia	0.004
Albuminoid Ammonia	0.004

(a) These determinations have not been made throughout the entire year.

The physical and chemical improvement to be gained by storage cannot be discussed, yet the hygienic betterment derived by the diminution of the

¹ Presented at the 53rd Meeting of the American Chemical Society, New York City, September 25 to 30, 1916.

² Dr. Wm. T. Sedgwick, "Water Supply Sanitation in the Nineteenth and Twentieth Centuries," N. E. W. H. Assoc., 1916.

³ Geo. W. Fuller, "The Purification of Water from Standpoints Other than the Hygienic Aspect," *Trans. Am. Soc. Eng. and Demography*, 1913.

⁴ Ralph H. Stearns, "Disinfection of Water by Storage," N. E. W. H. Assoc., 1916.

⁵ S. T. Powell, "The Effect of Ozone on Algal Growths," A. C. W. Assoc., 1914.

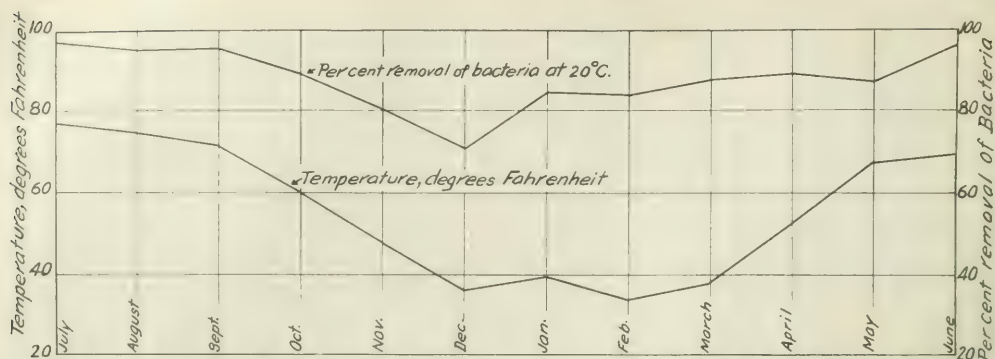


FIG. I.—PERCENTAGE REMOVAL OF 20° C. BACTERIA EFFECTED BY STORAGE RESERVOIR AT HERRING RUN IN COMPARISON WITH THE AVERAGE MONTHLY TEMPERATURES

bacterial count is of far greater value. The careful and exhaustive studies of Dr. A. C. Houston of the Metropolitan Water Board of London has clearly demonstrated the fact that by storage alone a very high percentage of the bacteria can be removed.

The bacterial reduction obtained in the Herring Run reservoirs has been quite high, but the efficiencies have varied with the seasons. There has been a direct relationship between the atmospheric temperature and the efficiency of these reservoirs in the elimination of the bacteria growing at 20° C. From Fig. I it will be seen that the greatest bacterial removal was during July, when the average temperature was the highest during the year. From then on there was a gradual and uniform falling off in the bacterial efficiency until January, when the sudden rise in temperature was followed immediately by an increased efficiency in the percentage removal of this type of bacterium. It will be noted also from Fig. II that the destruction

in the removal of these types was considerably less than for the saprophytic bacteria. This condition has been noted by Houston,¹ Don and Chisholm² and others, and explained by the fact that in summer the active growth of the saprophytes creates an environment antagonistic to the life of the blood temperature germs. Recently the writer has made series of tests in the laboratory which tend to show that the rate of removal of the 38° bacteria, and particularly *B. coli* forms, is far more rapid in the presence of active growths of saprophytes than where such organisms are absent from the water.

Numerous theories have been advanced to account for the beneficial effect to surface waters brought about by storage. There is a general consensus of opinion, however, that the purification effected is due to no single cause but to the combined results of equalization, sedimentation and inanition or devitalization of the bacteria. The advisability of retaining surface

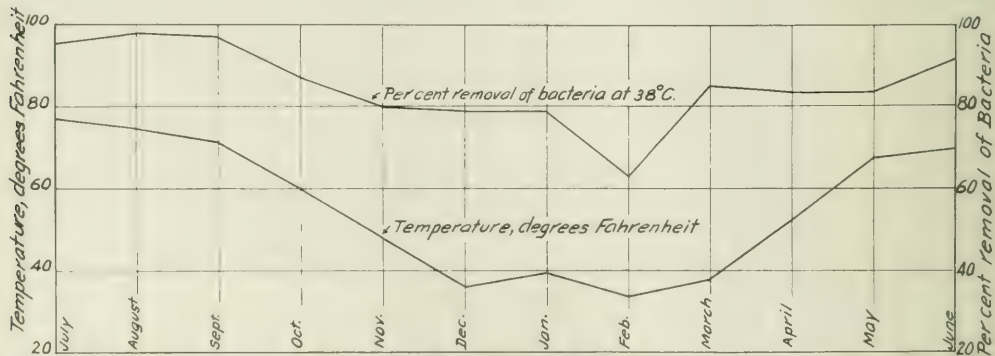


FIG. II.—PERCENTAGE REMOVAL OF 38° C. BACTERIA EFFECTED BY STORAGE RESERVOIR AT HERRING RUN IN COMPARISON WITH THE AVERAGE MONTHLY TEMPERATURES

of 38° bacteria appears to be less affected by temperature changes than that of the 20° organisms.

It is interesting to note that during the summer months the percentage removal of blood temperature microbes was greater than 20° bacteria, but during the colder months the growth of these organisms was more persistent and the efficiency of the reservoirs

waters in storage reservoirs to a condition of sterility in respect to the pathogenic bacteria the supplies may contain is an uncertain and questionable procedure

¹ Dr. A. C. Houston, "The Purification of Water by Storage," *Trans. 15th Congr. Hyg. and Demography*, 1912. *The Eighth Annual Report of the Metropolitan Water Board of London*, 1914.

² Don and Chisholm, "Modern Methods of Water Purification," 1913.

from an economic as well as practical viewpoint, but the bacterial reduction produced by comparatively short detention periods prior to final purification by means of filtration or sterilization with chemicals has much to appeal to the practical side of this question. The potent advantages in favor of such preliminary treatment are the reduction of all forms of

bacterial life, but particularly the removal to a very large extent of the pathogenic germs, and the general physical and chemical improvements of the water ensuring more uniform control and economical operation of the final purification system, due to the equalizing effect that reservoirs of this type produce.

100 W. FAYETTE STREET
BALTIMORE, MARYLAND

LABORATORY AND PLANT

AN EXPERIMENT IN THE EDUCATION OF CHEMICAL ENGINEERS¹

THE TWENTY-FIFTH ANNIVERSARY OF THE AUDUBON SUGAR SCHOOL

By CHARLES E. COATES

In these days of preparedness, the training of chemical engineers has taken on a consequence which is interesting both to the college and the country at large. The part which the chemist has played in modern development, we have known in a way for some years, of course, but we are appreciating now as never before, the vital and imperative importance to our nation of a body of men who cannot only discover chemical principles but can also apply them industrially.

At the same time, it has been generally acknowledged that college courses in Chemical Engineering have hitherto been lacking in some essential ingredient. Numerous efforts have been made to remedy this state of affairs. Among the most recent are the industrial fellowship system of the Mellon Institute and the plan lately outlined by the Massachusetts Institute of Technology, accounts of which have appeared in *THIS JOURNAL*. The English journals are full of new schemes for the training of chemical engineers; indeed practically all the larger schools have changed such courses materially within the past few years. In view of this and inasmuch as experience, after all, is the only safe guide in the jungle of educational theory, it has been thought that a brief sketch of the origin and development of the Audubon Sugar School might not be untimely.

Few people realize how very largely the sugar industry of to-day is a chemical industry. A little over a century ago, when sugar was first made from beets, the root was low in sucrose and the process gave a poor yield of an inferior grade of sugar with an almost valueless molasses. The chemist and the agronomist, working together, slowly raised the sucrose content of the beet root until it was more than doubled; the chemist and engineer, working together, slowly improved the processes until a good yield of sugar was turned out, practically pure, and both the molasses and all the other by-products became sources of profit and not of loss. In consequence the net cost of beet sugar fell year by year until it became a serious competitor of cane sugar and, finally, it was offered at prices closely approaching the cost of cane sugar production.

The sugar planters of Louisiana, as a class, are cer-

tainly among the most intelligent agriculturalists in America. Seeing the increasing gravity of the situation, they decided to meet the competition of beet sugar by the same methods which made that competition possible. In the late eighties they called to Louisiana Dr. W. C. Stubbs and established, under his direction, the Sugar Experiment Station at Kenner, Louisiana, which was subsequently moved to Audubon Park, on the outskirts of New Orleans. This station was financed entirely by the planters of Louisiana. A complete sugar house was erected on a scale large enough to give commercial results, and altogether, perhaps \$100,000 worth of equipment was obtained either by purchase or gift.

As soon as the work was fairly under way, it became evident that there were many leaks in the sugar industry as carried on in Louisiana and that these could be stopped by proper scientific control. But when the planters began to look for chemists and engineers, they were simply not to be obtained. Up to that time, the cane sugar industry throughout the whole world had been carried on largely by rule of thumb. Few men scientifically trained in sugar chemistry were to be found outside of Europe. In 1890, therefore, at a meeting of the Louisiana Sugar Planters' Association, it was decided to establish, in connection with the Sugar Experiment Station, a school for the training of experts in sugar work. This was placed under the direction of Dr. Stubbs and was opened in 1891 as the Audubon Sugar School. So far as I know, this was the first instance in America in which any industry established both laboratories for the scientific investigation of its problems and a school for the college training of men to put the theory into practice.

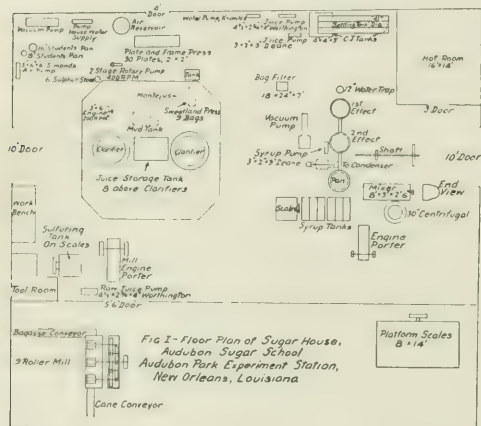
POST-GRADUATE CHARACTER OF WORK

As first outlined, the Audubon Sugar School was intended to appeal mainly to graduates of schools of engineering, and the course was distinctly post-graduate in character. The faculty was composed of some of the ablest men in the country, special stress being laid on research work. It soon became evident, however, that the number of college graduates who appreciated the opportunities in the sugar industry was quite small, and that the demand for training came mainly from men who had not received very much undergraduate training. Moreover, there was a number of applicants from tropical countries, whose ordinary studies had been of such a type as to make it impossible for them to take up the ordinary, the advanced

¹ Presented at the 53rd Meeting of the American Chemical Society, New York City, September 25 to 30, 1916.

scientific work offered in the Sugar School. At the outset, therefore, the greater number of students were special students, very un-uniform in educational training, which, of course, handicapped the school materially. The course was two years in length, classes were held at the Experiment Station, and during the sugar season the students did the actual work in the fields, in the laboratory, and in the sugar house.

The school was successful from the outset and, in a couple of years, more students were applying for admission than could well be accommodated. In the meantime the Sugar Experiment Station was taken over by the State of Louisiana as part of the Louisiana State University, and the Planters' Association withdrew its financial support. With limited funds, the increasing demands upon its staff along purely research lines, and the growing magnitude of its routine work, the Station found it impossible to handle students also. In 1896 the school was, accordingly, incorporated with the Louisiana State University, preserving



the name by which it had become known. In 1908 its numerical importance was such that it was reorganized as a college of the University.

From the first the writer and his colleagues were given a free hand by President Boyd in formulating the course of study, and changes were made year by year as experience or circumstances dictated. As the instruction was now given by the regular university staff, the students were, of necessity, ordinary college students, subject to the college entrance requirements. Moreover, as the chemical, mechanical, and agricultural subjects having to do with sugar technology had to be based upon chemistry, physics, mathematics and the biological sciences, it was necessary to require these subjects of all those taking up the purely sugar work. The enforcement of these two regulations worked, at the beginning, to eliminate a number of applicants whom the University would have been glad to welcome, if possible. They were, for the most part, men of maturity, from 25 to 40 years of age, who had had

previous experience in sugar house work, and were anxious to supplement their experience with a certain amount of theory. For several years the University received these men as special students, but it soon became evident that, in spite of their laudable ambition, they were, in nine cases out of ten, merely wasting their time. They were taught certain things in a mechanical way, such, for instance, as how to polarize sugar, but they did not know the principles on which these things depended and their studies did not lead them anywhere. They were deceiving themselves in thinking they were studying sugar chemistry when they were merely becoming chemical mechanics. Only after it was too late did they recognize the necessity for the foundations and the utility of short cuts to learning. From the beginning, the writer counselled these men against their undertaking, but, as they were ordinarily both intelligent and self-confident, he could not keep them from following their own ideas. Finally, the advanced courses were closed to students of this type. We expected some criticism at first, but none came. The questions which were asked by certain men as to why they could not be admitted were readily answered to their complete satisfaction.

As men of this class present, collectively, a problem of a general nature, I may say here that I do not believe that it is possible to receive them in the same classes with the ordinary college student. The latter is presupposed to have a certain fairly uniform preparation for his work; the preparation of the former, on the other hand, is almost always inadequate and much has been forgotten of what had once been known. The college student, therefore, can be taught in the conventional way, but men of maturity must be taught each as a separate problem, with different difficulties to solve. Then, again, the college student is joyfully ignorant of practical experience and responsibilities, and the college teacher must bring these home to him as best he may; the practical man, on the other hand, has learned them in the school of hard knocks, and not infrequently comes better equipped than his teacher, so that what is good advice to one man is a platitude to the other. But the greatest difficulty in teaching the practical man lies in his unwillingness to fill in the gaps in his training. He probably knows no mathematics, and without this he cannot study to advantage college physics, without which problems in mechanics and machinery are unintelligible. The same holds along other lines.

The purpose of the school when first organized was to offer to the citizens of Louisiana the opportunity to secure such training as would qualify them to enter most advantageously the sugar industry of the state. The underlying idea, therefore, was to train men who would be competent to manage plantations which both grew cane and made sugar; that is to say, they were to be trained in agriculture, engineering and chemistry.

FOUR-YEAR COURSE CHANGED TO FIVE

The course, as formulated in 1897, was four years in length. During the last two years the students

spent the sugar season at the Sugar Experiment Station at Audubon Park in practical sugar house work. It soon became clear, however, that a satisfactory foundation could not be given to high school graduates in two years, so, in 1899, the course was made five years in length, the first three years being devoted entirely to foundation subjects and all technology being avoided. During the fourth and fifth years the student was sent, as heretofore, to the sugar house at Audubon Park, returning at the end of the sugar season and taking up his work for the rest of the year. At the end of the fifth year the graduates received the degree of Bachelor of Science. Here, too, there was a little dissatisfaction. The Sugar School students thought that if the Engineering students received their B.S. degree at the end of the fourth year, so should they. At the end of the fifth year they could then receive another degree. There was a certain specious justice in this claim, but it was not granted. At the end of the fourth year the

students than it could well care for and they have been men of an exceptionally high class, which merely goes to prove again that, in matters educational, if a thing is well worth while the best men do not count the price, whether in time or money. So far as the writer knows, this was the first five years' course in Chemical Engineering ever offered in this country.

From the beginning, there was a strong demand for the graduates of the Sugar School. Ordinarily they were placed six months before they graduated and, as they made good without any exceptions, the requests became year by year more pressing. Most of the larger sugar houses began to put in laboratories and chemical control slowly displaced the old rule of thumb. About 1901, the demand for chemists became so great that two or three of the best fifth-year men were allowed to omit the second year of the practical course at Audubon Park. Instead they were sent to a sugar factory where they were paid the regular salary of an assistant chemist and worked through



FIG. II.—GENERAL VIEW OF PLANTS AT EXPERIMENT STATION, AUDUBON SUGAR SCHOOL.

sugar school student would not be sufficiently trained. If he were to receive a degree then, however, he would be more than likely not to appreciate the deficiencies in his training. A degree is a *summum bonum*—an end in itself to most college students. These students were also anxious to get into practical work. Why work a year longer for a degree when they already had a degree? This argument would have been conclusive with many students and most parents. So the course was fixed at five years and the student got his B.S. degree in five years instead of four. This was done because the five years were necessary and those who did not like it were told that it was a rule of the school and could not be changed. The results justified the means and to-day the students take special pride in this particular feature of the course.

There was some fear, at first, on the part of the authorities, that a five years' course would drive away the desirable students, but such has not been the case. As a matter of fact, the Sugar School has had more

the season under strictly commercial conditions, returning to the University when the season was over. It was immediately apparent that these men had gained something which gave them a marked advantage over those students who were taking the routine fifth-year course at Audubon Park, but it was a little hard to tell wherein this advantage lay. Perhaps each man had benefited in a different way. To one it gave self-confidence, to another an appreciation of actual working conditions, to a third a knowledge of men as distinguished from boys; to all, a certain sense of responsibility and a maturer point of view.

FACTORY WORK IN FIFTH YEAR

The fifth year practical course had been formulated and carried out at Audubon Park and in the laboratories with great care. It contained many things which the student, by going to the factory, would not get, and which it was desirable he should get. In the actual factory practice was permitted with some degree of

reluctance and a little fear that we were making a concession to a popular demand. But its undoubted advantage, largely psychological, over the routine course was so marked that in 1903 the sending out of the fifth-year students became a part of the established policy of the School and has remained so ever since. The planters met the movement more than half way and have given the students every possible assistance.

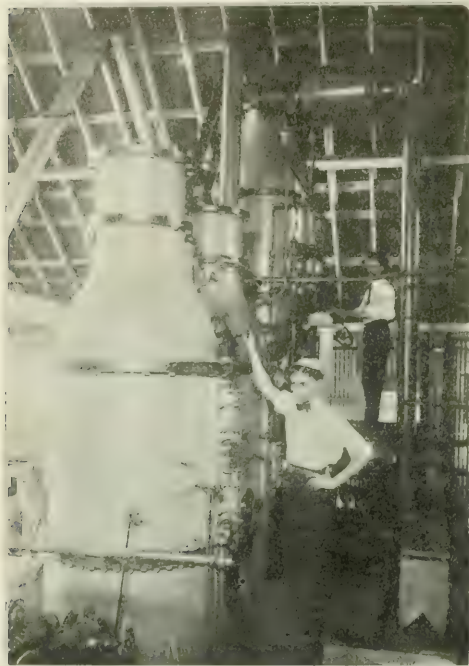


FIG. III.—EVAPORATORS AND PAN IN SUGAR HOUSE

These young men receive the same salary as other assistant chemists and for more than ten years there has not been one who failed to receive employment. An incidental but most important result has been the strengthening of the relationship between the sugar planters of Louisiana and the Louisiana State University. The students bring back to the University an intimate knowledge of the actual conditions in the various sugar houses and of the practical problems which are continually presenting themselves. The planters, on the other hand, discuss these conditions and these problems with the various officials of the Sugar School, sometimes personally, sometimes by correspondence, but always with perfect freedom.

In order to get a certain breadth of view as to the Louisiana cane sugar industry it has been the custom of the writer to visit the various plantations during the sugar season. After a good many years of personal experience, the writer has come to the definite conclusion that this personal contact between the students and teachers in the School of Chemical Engineering,

on the one hand, and the chemical plant, together with its responsible officials, on the other hand, is absolutely necessary if the school is to attain even reasonable efficiency. In each industry this contact may be obtained in a different way. In the Audubon Sugar School the practical method has just been outlined.

As these students are absent from the University in the fourth and fifth years for eight to ten weeks of the first term during the sugar season, they cannot be taught in the same classes with other students during the eight or ten weeks when they are present. They are, therefore, taught in different sections from the other students during the first term, the second term, of course, presenting no difficulties. This method placed some extra labor on the teaching staff, but it was the only logical way and has worked well in practice. There seems to be no reason why it could not be applied more generally to the articulation of courses in chemical engineering with the various industries studied. In this connection, the writer might say that he is convinced that, in the fifth year of a course in Chemical Engineering, the student should get away from generalizations and try to master reasonably well the details of some one particular industry. The confidence in his own ability which a student gains by thus narrowing his field of study, stays with him should he, by chance, find his opportunity in some other line of chemical industry.

INTRODUCTION OF AGRICULTURAL AND ELECTRICAL COURSES

As soon as the Sugar School was fairly under way, students began to come from all parts of the world and as, at the time, it was easier to secure a position as a sugar chemist than as a sugar agriculturalist, there was a tendency on the part of the student to stress Chemistry and Engineering at the expense of Agriculture. This tendency was encouraged by the unsatisfactory state of agricultural teaching twenty years ago. As the old professor of agriculture slowly began to resolve into his component parts and the professors of Agronomy, Soil Physics, Animal Industry and the like took his place, there was a notable tightening up along all lines of agricultural pedagogy. Full-term courses were offered where two or three weeks had sufficed and the increased efficiency of agricultural teaching began to appeal to students generally. But the Sugar School students found themselves in need of a very special type of tropical and subtropical agriculture, where the conditions were altogether unlike those in ordinary American agronomy. To meet this demand, it was decided in 1907 to offer such courses in Sugar Agriculture in the last three years of the Sugar School, these applying specifically to the conditions on cane plantations in Louisiana. At about the same time, Congress made it possible for the Experiment Stations to do experimental work in Mechanical Engineering. In Louisiana, this work was placed in charge of Professor E. W. Kerr, as professor of Mechanical Engineering in the Audubon Sugar School, and was concentrated on the specific problems in the sugar houses of Louisiana, such, for

instance, as evaporation, bagasse burning, boiler efficiency and the like. As new fields in Sugar Agriculture and Sugar Mechanics began to develop, it became evident that even five years was not sufficient time to give students satisfactory courses in these and in Sugar Chemistry as well, so, in 1912, a course



FIG. IV.—STUDENTS KEEPING CHEMICAL CONTROL IN THE FACTORY AT THE AUDUBON SUGAR SCHOOL

was formulated in Sugar Agriculture with Professor A. F. Kidder in charge of the special work in agriculture, the course including Chemistry and Agriculture, being distinct from Sugar Engineering which included Chemistry and Engineering. The practical work on the plantations and at Audubon Park was the same for each course. The student chooses one course or the other at the beginning of his junior year, and as there is an increased number of openings for scientific agriculturalists in sugar countries, this division has its fair share of students. It is possible that students under exceptional circumstance might find it desirable to specialize in Sugar Agriculture and Engineering, leaving out most of the work in Chemistry. Though no demand for this has yet arisen, the courses are so formulated that the demand can be met without any difficulty.

It is fair to infer from our experience in this respect that after a school of Chemical Engineering has been mainly associated with some given industry for a term of years, it would become necessary to arrange that the students have suitable latitude in elective subjects for the last year of the course. For instance, during the last year or two, many of the larger sugar mills have been changing over from the steam drive to the electric drive and it is generally believed that electrically driven machinery will largely supplant steam driven machinery in the near future. For this reason, there has arisen lately a demand for more Electrical Engineering in the sugar course, which demand we are now prepared to meet by offering as electives, special courses in that subject.

ADMISSION OF COLLEGE GRADUATES

As the value of scientifically trained men became recognized by the sugar industry throughout the world, students came to Louisiana from practically all of the sugar producing countries: Japan, China, the Philippines, Mauritius, Tahiti, Hawaii, South Africa, France, Spain, Italy, Germany, Sweden, Norway, England and every one of the South and Central American countries have sent students to the Sugar

School. In many cases these were already college graduates, and there was some difficulty in articulating their previous training with the regular Sugar Course. The first three years of the Sugar School, however, are devoted to pure science, and technology is avoided as far as possible. Students get Mathematics through Calculus, Inorganic, Organic, and Analytical Chemistry two years each of Physics, Mechanical Drawing, Mechanical Engineering, and one year of Electrical Engineering, together with English and some foreign language. As these subjects are covered in the Chemical Engineering courses at Cornell, Boston Tech., Illinois and other standard institutions, we decided to credit the first three years' work done in such institutions for the first three years of the Sugar School, without endeavoring to make a substitution of subject for subject. The last two years of the Sugar School, therefore, were made, so far as possible, of graduate nature, open to students who had had three or four years of college training and who were prepared to take the courses offered. In this class there have been graduates of various universities both in the United States and abroad. These have been matriculated as graduate students, candidates for the degree of M.S. Their courses have ranged from one to two years in length, depending upon the nature



FIG. V.—APPARATUS FOR DETERMINING THE EFFECT OF EXTENSION IN MECHANICAL LABORATORY, LOUISIANA SUGAR SCHOOL

of the preliminary training. The option of admission of a highly technical man with an undergraduate degree has been in use now for about 15 or 16 years and has worked out admirably because of the elasticity in elective subjects in the graduate courses.

There has been a decided tendency on the part of the graduates in Mechanical, Electrical and Chemical Engineering to apply for graduate courses in the Sugar School. We have arranged courses for such students and have found that they can cover nearly twice as much ground in a year as can the average undergraduate. A number of these men have gone into practical work with uniform success. In other words, the attitude of the Sugar School towards graduate students is something like this: For the mature man who is a college graduate and wants to take up this kind of work, it is fair to assume that he knows what he wants, so he is treated not as a boy but as a man and, in electing his course, he is allowed every latitude compatible with common sense. For instance, these courses hitherto have included the practical course at Audubon Park and some sugar house experience, but both these requirements would be waived in the case of the man who was already familiar with sugar house processes.

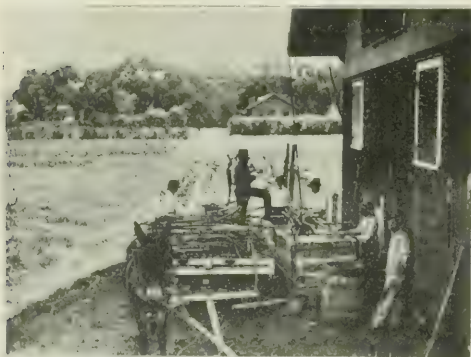


FIG. VI—DIPPING CANE IN WHALE OIL SOLUTION
EXPERIMENT IN CONTROL OF SUGAR-CANE MEALY BUG

As at present organized, then, the course of the Audubon Sugar School is five years in length and leads to the degree of B.S. The first three years are given to general scientific training similar in type to that given in most standard schools of Chemical Engineering. The technical work is given entirely in the last two years, which, therefore, include most of its distinctive features. As the method of articulating the practical and the theoretical is the result of a number of years of experiment and experience, it might not be amiss to give it in detail. At the beginning of the fourth and fifth years, the student reports to the university about the 20th of September. He stays there until the opening of the sugar season, the date of which depends somewhat upon crop conditions, but ordinarily ranges between the 18th and the 25th of October. This gives him one full academic month at the university. The sugar season in Louisiana lasts until from the 10th to the 25th of December, some smaller estates finishing earlier and a few larger ones, somewhat later. The university assumes that they all close before the end of the Christmas holidays at which date the student must again report to his

classes. This gives him one academic month before the mid-term examinations in February. He is therefore present at the university during the first and last month of the first term and is working at the sugar house during the second and third months, allowing a margin of about a week for overlapping, due to crop conditions.

FOURTH-YEAR WORK

The subjects taken by these students while at the university during these two months are of two types: The first type is strictly technical and special, as for example sugar house control, sugar machine design and sugar chemistry. Lectures in these subjects stop when the student leaves the university and begin when he returns. The second type includes general engineering and chemical subjects which are elected by other students, such as thermodynamics and machine design. The Sugar School students take half the usual number of such subjects for twice the usual number of hours per week, which requires extra sections. During the second term they report with the regular college classes in all subjects. This increases the work of the instructors for the first and fourth month and lessens it for the second and third, but as the number of class hours involved is not large, the method has worked well in practice. Laboratory subjects present, of course, no special difficulties.

During the first month of the fourth and fifth years all the students concentrate mainly on the technical chemistry and engineering of sugar house practice. As considerable planting is done during this period, they also visit the plantations under the direction of the professor of Agronomy, as occasion presents itself. The whole sugar squad is under the general charge of a special instructor in sugar technology who is generally one of the superintendents of one of the larger tropical sugar houses and is thus in immediate touch with the industry in its most recent developments. He accompanies the fourth-year sugar squad to the Sugar Experiment Station, Audubon Park, New Orleans, and remains with them during the sugar season, at the close of which period he leaves for his regular work in Cuba or elsewhere.

When these fourth-year students reach Audubon Park, they have been drilled in the routine analytical processes of sugar house laboratories and in the general mechanical principles of sugar house machinery. At Audubon Park, the university has a sugar house, cane fields, chemical laboratories—both control and research—bacteriological and entomological laboratories and a full equipment of all apparatus necessary for the investigation of any ordinary problem, chemical, mechanical or agricultural which might arise in connection with the cane sugar industry, the whole representing an investment of something over \$100,000. Under the direction of an instructor, the student squad is brought into personal contact with each of these various lines of activity, and, to the same end, the squad is visited once a week by the Dean of the Sugar School, the professor of Mechanical Engineering or the professor of Agronomy. The United States Government maintains at the Park a department for

the investigation of insects injurious to cane, and the students must keep up with the progress of these investigations. Immediately after reaching the Park, the students are put to work planting cane. This fall planting is finished in three or four days and is done by the students themselves in the most approved manner under the supervision of the director of the Sugar Experiment Station. At the end of this time the field hands begin to cut cane and deliver it to the sugar house. Thereupon the sugar squad is divided into ten sections which are assigned each to a specific station. The sugar house has a nine-roller mill grinding somewhat less than one ton of cane per hour, the juice being discharged into a cane weigher. This is Station I and the work is done by one division of the squad. From the weighing tank, the juice passes to the sulfuring and liming tanks, which make up Station II, thence to the open clarifiers, Station III, thence to the settling tanks and filter presses, Station IV, thence to the double effects, Station V. The syrup from the double effect passes to the vacuum pans, Station VI, and the grained massecuite passes to the mixer and centrifugal, Station VII. There are also bag filters, plate presses and a Sweetland press through which the juices are run for experimental purposes; these make up Station VIII. There are around the house a number of small engines and pumps; the care of these make up Station IX. To each of these stations, a small squad of students is detailed for two or three days so that every man makes the round of the stations about twice. The chemical control is Station X and rotates with the others. Samples are taken of the cane, the juice, the press cake, the bagasse, the syrup, the massecuite and the molasses and the requisite analyses made. A very elaborate system of chemical control has been instituted in as great detail as in the 2000-ton houses, specially printed blanks being provided for this purpose, the whole system being practically identical with that of the larger Cuban and Porto Rican sugar corporations. The laboratory is provided with an adding machine and also one for multiplying and dividing, so that the students may become familiar with these important labor-saving devices. Complete daily and weekly reports are made out and special stress is laid on the arithmetical side of sugar house control. The importance of this phase of chemical engineering is sometimes overlooked. It not only helps make the chemist a more valuable employee, but it also helps him to realize what he is doing and why.

From the engineering standpoint, in addition to the foregoing stations, certain squads make detailed reports on the efficiency of the various pumps, the mills and the evaporating apparatus.

From the agricultural standpoint other squads study the result of the field experiments at Audubon Park for the last twenty five years, and learn the practical methods employed in agricultural research as applied to sugar cane.

During the fourth year season, the squad is sent, two at a time, to the state sugar factory at Anapola, La., a 1500-ton house, thoroughly equipped for making

either white or 96 test sugar. Here they help in carrying out sugar house control on the large scale and under competent direction.

FIFTH-YEAR WORK

At the end of their first season, therefore, the students are fairly familiar with the technique of every part of the sugar house, though of course they are not skilled artisans. They are able to make out a complete report on the chemical control of the sugar house and, to some extent, on the chemical efficiency of the process. In the case of the students in sugar agriculture, they can also make out a report on the condition of the cane fields and their various agricultural requirements, such as fertilizers, drainage and the like. Most of the work on the purely theoretical side of both sugar chemistry and sugar engineering is given to the students on their return to the university, to which end a special equipment has been provided. For instance, there has been installed an elaborate apparatus



FIG. VII.—SHOWING RESULTS OF FERTILIZER EXPERIMENTS

for the experimental investigation of evaporation which has made possible a considerable quantity of research work along this line.

The fifth-year students, also, put in the first month at the university, concentrating on the details of various phases of sugar technology and paying special attention to speed and accuracy in their analytical work. They likewise study the principles underlying the various instruments they are to use in the chemical and mechanical control of the sugar house—as for example, the polariscope and the indicator card. When the season opens they go into actual sugar house practice at various factories over the state and stay through the sugar season. These students are treated simply as employees, are given no special favors and expect none. They draw the same salary as any other sugar chemist and hold their positions only on their merits. The Dean of the Sugar School makes an annual inspection of these factories during the sugar season and then learns back what the students are doing and what the management expects them to do. After their return to the university at the end of

the sugar season, they devote the rest of the year to the various subjects outlined in their courses.

The fourth and fifth years of the sugar school, therefore, are quite special in their nature and are open to graduates and senior students of standard schools of engineering. The student of the graduate type is classed according to his preliminary training and allowed to elect such subjects as he may be able to carry out profitably, the utmost latitude being given him.

The Audubon Sugar School is now twenty-five years old. The number of students during the past five years has been 124, 94, 65, 70, 75. The School graduates each year from 10 to 25 students. These young men have made good without exception. They are scattered all over the sugar world and occupy many of the most important positions in the sugar industry, which facts are taken to indicate that the school is founded upon correct pedagogic principles.

CODE OF ETHICS

Just one thing more might be mentioned in closing. It is somewhat difficult to discuss this and yet its extreme importance is beyond question. From the time a student enters the Audubon Sugar School until he leaves, it is the writer's custom to call frequent attention to the fact that no student can hope to learn much chemistry or mechanics or anything else of that sort at college. He merely learns where the literature is, what the problems are and how to study them for himself personally. One thing, however, he can learn at college and that is the standard of character necessary for success in Chemical Engineering. These men are not expected to stay engineers or chemists; such positions are only stepping-stones. Each man should hope to be, at some time, a superintendent or administrator and if positions of this type are to be won by merit, that merit must include absolute personal integrity. Any lapse from the highest possible code of honor will destroy the usefulness of a chemist or a superintendent. Absolute truthfulness in work and in reports, loyalty, willingness to cooperate—these things are essential to the highest success in the sugar business.

This is the code of the students in the Sugar School, insisted upon by themselves from the time they enter the university. Lapses are treated with the rude but efficient justice of student self-government and, by the time a man graduates, these standards are ground into him and are a part of his professional character. It is a matter of record in the Sugar School that in all the years of its history, there has not yet been one of its alumni to prove recreant to its personal standards, during the after years of his actual contact with the business world. The graduates of the Sugar School are more or less well-trained in the sugar industry, fair scientists or excellent as the case may be, but in all instances they are honorable men, trustworthy and loyal. They have had this record for a quarter of a century without a break. This is the one point in which the Audubon Sugar School feels it has a right to be proud.

AUDUBON SUGAR SCHOOL
LOUISIANA STATE UNIVERSITY
BATON ROUGE

THE CONCENTRATION OF SULFURIC ACID

By F. H. ARMSTRONG
Received December 26, 1916

Owing to the unusual demand for munitions and as sulfuric acid is largely used in the manufacture of these products, there has been created a great demand for high strength sulfuric acid running from 93 to 97 per cent H_2SO_4 .

In the old days the high strength sulfuric acid required was made very largely in iron and platinum stills. There are a number of other methods used for concentrating sulfuric acid but as all these give a small output and as the demand for the last year required a large tonnage, the tower method, in a large number of cases, has been resorted to by a great many chemical companies; in other cases the acid is first passed down a tower where it gets a preliminary concentration, bringing it up to 62 to 63° Bé. and thence through cast-iron pans that set in a furnace, one above the other; by the time it gets to the last pan, which is directly over the fire, it has attained the concentration of from 93 per cent to 98 per cent H_2SO_4 . In this case the gases of combustion from the furnaces pass under the pans to the tower, at which point they become mixed with the vapors from the pan; the mixed gases pass through the tower and thence through a system of scrubbers to the atmosphere.

There is quite a difference in the methods pursued in building the towers, and also the arrangements of the scrubbers for the recovery of the distillates. But the principle of concentrating in towers is the same, as practically all the engineers engaged in constructing the plants use quartz for the packing and an oil flame for generating the heat.

The writer has had considerable experience recently in supervising the operation of some concentrators. There was very little known in the South, previous to the last year, about concentrating acid to such high strength; this being true, it was largely a question of experimenting to find the best method of operating

CHEMICAL DISINTEGRATION OF QUARTZ PACKING

One of the first conditions that the writer observed was that an apparent obstruction would develop in the towers after a week to ten days' operation, necessitating shutting the plant down and washing the tower, after which the plant would usually run very satisfactorily for another week or so. During the above-mentioned washouts, the writer observed a very heavy non-gritty substance coming from the tower. It was then concluded that this substance must be silica and as silica could only come from a chemical disintegration of the quartz in the tower packing, the writer became convinced that the quartz was undergoing a chemical disintegration, most especially as there was a considerable quantity of aluminum in the acid passing over the tower.

This was finally proven to my entire satisfaction by the fact that after some weeks' operation, the plant would show all symptoms of the tower being too open and, in one case, it was found that more than one-half of the quartz originally in the tower had gone in solution and passed out. In others it was found that chan-

nels had formed through the packing, owing to the dissolution of the quartz. In view of the above, there can hardly be any disputing the fact that under the conditions prevailing in the concentrating tower there is a chemical disintegration of the packing. Before the writer had acquired the above-mentioned evidence, the question was taken up with a number of very able men, but in no case did they subscribe to the theory that there could be a chemical disintegration of the packing.

On three different occasions, one of our towers became so open that it would not concentrate beyond 63° Bé. and in each case the tower was got back to as good condition or better than it was when first built, and in one special instance the plant was brought up from 9 tons of 66° Bé. in 24 hrs. to 29.9 tons in 24 hrs. The actual time the plant was stopped to make the above stated change did not extend over 2½ hrs. The condition was remedied by simply removing the lute on top of tower and introducing a piece of ordinary light cast-iron drain pipe through the opening in tower top and passing small pieces of broken quartz through the pipe into tower. The end of the pipe was moved about as desired, thereby making it possible to place the quartz in any part of the tower. During a period of several months there was put into this tower as much quartz as was originally used to pack it, yet at the end of this period the tower did not contain any more quartz than it did when it was first started. As there was no quartz removed from the tower at any time it is quite evident that the packing was being removed by the action of heat and acid.

At one time, after the tower had been cooled off, an examination by means of an electric light let down in the tower showed that on one side the packing was gone until there was very little left over the arches. On that particular occasion it took 40 kegs of broken quartz to fill in the crevices in the tower so as to bring that side of the packing up level with the rest. One party, who was operating a plant built similar to ours, advised that he usually washed his tower out with water about four times, after which he had to shut it down and repack the tower. This man's experience bears out the theory advanced by the writer, that there was a chemical disintegration of the packing under the conditions prevailing in the concentrating tower.

PLAN AND OPERATION OF A TOWER CONCENTRATING PLANT

There is a series of symptoms present that if properly followed out will generally lead one to a proper understanding of the trouble. In order to make this plain, I will briefly describe a general lay-out of a tower concentrating plant. There is a small brick furnace into which the oil is sprayed by steam. From this furnace there is a flue leading into the side of concentrating tower. This tower has a brick lining and brick arches and is packed with about 4 ft. of small quartz, leaving about 5 ft. of space between top of tower and top of packing. The acid is fed to the tower by a syphon and boot arrangement so that there is about ½ cu. ft. sprayed over the packing about once every 30 seconds. After the boot has become nearly empty the syphon

gets air, which stops it from flowing; the boot in the meantime is being refilled from a supply tank overhead. When the boot fills to a certain point the syphon automatically starts emptying same, so we have an alternating spray. This is done to give the heat in the tower a chance to recover and the tower is supposed to concentrate better with this arrangement than when fed continuously.

The vapors and mists of acid pass from the tower into the scrubbers through an 18-in. flue, this flue being divided so that one-half of the gas goes into each scrubber. These scrubbers are merely enclosed tanks packed with fine gravel. The gravel packing is supported on brick and coke in the bottom of scrubbers, the brick being so arranged that tunnels or passages are provided for the gas to pass out through a 12-in. flue in the bottom and thence to the auxiliary scrubber packed with coke. The draught is created in the flues by either a fan or steam jets and as each plant has a certain draught pressure that gives the best results it is generally tried to keep the draught as near this pressure as possible.

In the flue between the furnace and tower there is a pyrometer tube placed, connected by wires to a dial which gives a continuous record of the temperature of the gases entering the tower. In the flue leaving the tower near the top an ordinary glass U-tube containing water indicates the suction inside the flue. There is also placed at this point a Fahrenheit thermometer, so that by observing the temperature of gas entering tower and noticing the temperature and suction in top flue, one can get a pretty good line on the working of the plant. For instance, a tower doing proper work will usually show about 1200 to 1400° F. for the gas entering, and about 280 to 290° F. with about ⅝ in. suction in the flue leaving the top of the tower. When the tower begins to become foul there will be observed an increase in the temperature of gas entering the tower and an increase in the suction pressure in the flue leaving top of tower. Also there will be observed a decrease in the temperature of the gas leaving the tower and when this temperature falls to about 250° F. it will be found that very little 66° Bé. acid is being made.

This condition is corrected by shutting down the tower and running weak acid down same until the packing becomes comparatively cool, after which it should be thoroughly washed with water running over the packing for at least 12 hrs. When the tower is again started it will be found that the temperature of gas entering it will be about 100° F. lower and the temperature of gas leaving it will be 40 to 50° higher with the suction pressure in flue reduced to about one-half to five-eighths of an inch. It is absolutely necessary to maintain a strong suction, either by steam jets or a fan, so that all vapor and distillates will be quickly taken from the tower, so as to prevent the acid from becoming too heavy and thus the oil and benzene they would condense and saturate the acid, thereby rendering the work already performed.

On the other hand, when the tower begins to become too open so that the gas goes out and the acid goes out into minute quantities the acid will pass through

without attaining a strength greater than 63 to 64° Bé. and the gases will pass out of the tower entirely too hot, going as high as 350 to 360° F.; also the suction of the flue leaving the tower will drop to almost nothing, while the temperature of the gas entering the tower will decrease from 200 to 300° F.

The above-described conditions were the ones that were corrected by introducing broken quartz through the lute at the top of the tower.

DIFFICULTY WITH AN OPEN BRICK LINING BETWEEN THE PACKING AND LEAD

The writer had a very peculiar experience on one occasion. The tower showed all symptoms of being too open. It was shut down and the top removed but the packing appeared to be in perfect condition. However, as it was quite evident that the gas was passing too freely through the tower and as we had been unable to get any 66° acid from this unit for several days previous, it was decided to remove the packing, not disturbing, however, the 18-in. brick lining between the packing and lead. After the packing had been removed and the tower repacked, the plant was started up, but with no better results than before. It is needless to say that the writer was very much concerned about the matter, as the tower would not produce 66° acid and yet there was nothing apparently wrong with the packing. However, the top was removed again and a very careful examination was made to determine, if possible, how the gas was slipping through the tower with so little resistance. It was observed that the brick wall between packing and lead was very open, there being spaces of from $\frac{1}{4}$ to $\frac{1}{2}$ in. between the bricks and as the bricks had been laid dry, with the exception of about 3 in. on the edge of the wall, it was decided that the heat was evidently coming up through the wall and not through the packing, as it should. The wall was taken down to the level of the packing (about 5 ft. from top of tower) and acid-proof cement, consisting of silicate of soda and silax, was poured down through crevices in the wall and a small amount of it appeared under the arches, proving that the theory of the heat going up through the wall was a correct one. The wall was then laid from the top of the packing up in mortar made from silicate of soda and silax. This mortar was used very liberally, making the bricks tight with it, just as would be done in building an ordinary brick wall. When this work had been finished the top was replaced and plant started up; it worked beautifully, even better than it had ever worked before.

LOSSES OF ACID IN THE CONCENTRATOR AND REGULATION OF DRAUGHT

In regard to losses of acid in the concentrator under normal conditions, when the tower was being fed with 60,000 lbs. of 60° acid in 24 hrs., the losses would amount to from 2,000 to 4,000 lbs. of 60° Bé. acid per day of 24 hrs. and there would be recovered as 66° Bé. acid about 39,000 lbs., equivalent to 46,792 lbs. of 60° Bé. acid and the balance, or 9,208 lbs., would be recovered in the distillates from scrubbers. This scrubber acid runs about 46° Bé. It is

pumped over to the sulfuric acid plant and sent down the Glover tower, where it is brought up to 60° Bé. along with the other acid passing over a Glover tower, after which it is returned to the concentrating plant again.

The losses varied greatly, according to the amount of draught that was used. When a very strong draught was being used it was found that the loss of H_2SO_4 was very much greater than was sustained when only a moderate draught was being used on plant. We, therefore, tried to get the happy medium of using just enough draught to take the distillate from the top of the tower and at same time not to have too great a loss at the exit stack.

In connection with the above, it was found that when using Lunge's method, namely, 10 cc. of $N/10$ caustic soda solution and aspirating gas through the same that the loss of SO_3 would run from 0.25 to 0.5 per cent. This test was made twice daily on each plant and was depended upon to a certain extent to determine the amount of draught which should be used, but as the tower very rapidly became choked, necessitating a constant increase of draught, the testing of the gases was of very small benefit in regulating the plant. However, if it were possible to get a tower packing that would not disintegrate, so that the opening would stay uniform, the testing of the exit gases could be used to a great advantage as a method of control.

SOUTHERN FERTILIZER AND CHEMICAL COMPANY
SAVANNAH, GEORGIA

PRINTING PLATES FROM PHENOL RESIN COMPOUNDS

By L. V. REDMAN, A. J. WEITH, F. P. BROCK

Received January 26, 1917

The growth of syndicate work in illustrated advertising, comic supplement and "filler" for our 30,000 American Newspapers, has created a need for a material which will lend itself to the rapid production of printing plates in manifold.

The plate requires to be produced rapidly and inexpensively and must be of such quality as will print clearly on the cheap sheet used by daily papers.

Such a plate is in no way intended to take the place of copper, zinc, stone or wood cuts where there is needed only one cut or at most a very few cuts of any one subject, such as in the printing of magazines, books, and catalogs. The new plate is designed to fill the need of thousands of daily papers which require the same news to print at the same time, either advertising, comic supplement, news of general interest to the country or "filler" for dailies or weeklies.

Printing plates for this work have been made from celluloid compounds and shellac by pressing the celluloid or shellac plastic into the original papier mâché mat which had previously received an impression from the zinc etching. The celluloid plate is used extensively. The shellac plate does not seem to have made its way to a commercial success. The shellac and celluloid plates will not stand the heat, pressure and moisture required for making the papier mâché mat for stereotype machines. Also the "dots" making up the screen in half-tones of celluloid are not full

and perfect. The shellac plate is brittle and requires careful handling.

It is possible that a hard rubber plate would be highly satisfactory. The time of vulcanization, high cost of materials and the fact that hard rubber at 70° C. will distort under pressure are the chief factors against such a plate.

The qualities possessed by phenol resin molding compounds make these materials highly valuable for printing plates. The heat resistance, strength in thin sheets, resistance to water, and the accuracy and speed with which they may be molded make them an excellent material for the production of printing plates in multiple. These plates may be used for direct printing on flat bed presses or may serve as a cut from which to make the papier mâché mats for stereotypes.

Practical difficulties have presented themselves in obtaining a satisfactory mold for use in making manifold plates from phenol molding compounds. If the molds be made from a high-grade steel and case-hardened, the expense is prohibitive; if the original zinc etching be used, a negative figure or picture is produced on the molded phenol sheet; and if a mold be made of the zinc or lead etchings, the pressure required for forming the phenol resin into shape destroys the sharpness of the zinc or lead cut after a few operations.

A satisfactory mold in every way can be made from the phenol molding compounds. The method of producing the mold in which is made the printing plate in manifold is as follows:

A sheet of the plastic phenol molding compound is placed on a hot plate or steam table the same as in shellac molding and is kept there until the sheet has heated through and become soft and pliable. The original zinc etching is then placed on top of the warm plastic sheet and both are placed in a hot press. Any source of heat, gas, steam or electricity, will do for the hot press. In this case steam is the most satisfactory and electricity the least desirable. The pressure is raised gradually to about 2000 lbs. per sq. in., and the compound is allowed to harden for a few minutes. Controlling bars prevent the press heads from coming too close together, and insure an accurate thickness for the mold and later also for the printing plate. Open on every side, the plastic compound is allowed to flow out around the edges. The mold is formed this way to a pre-determined thickness, generally $\frac{1}{16}$ to $\frac{1}{32}$ in.

The temperature at which the operation is carried on varies from 285 to 400° F., depending upon the quality of the material used, and the time during which the material is to be left in the press. Longer time and lower temperature give a tougher product than do the higher temperatures and shorter time. In this respect, the hardening of all phenol resins bears a very close similarity to the vulcanization of rubber.

The plastic sheet as soon as it has hardened is removed hot from the press, and the zinc or lead etching is taken off. The plastic sheet is now hard and has on its face the negative of the original zinc etching,

and in practice is known as the *mold*. On this negative cast or mold, warm fresh plastic sheet is laid, placed carefully in the press and subjected to pressure for a few minutes. As soon as the fresh sheet has hardened it is removed from the mold. This time the positive printing plate is produced, it being the reverse of the negative mold. This second molding operation re-

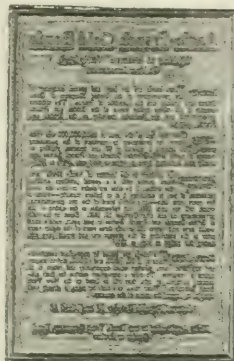
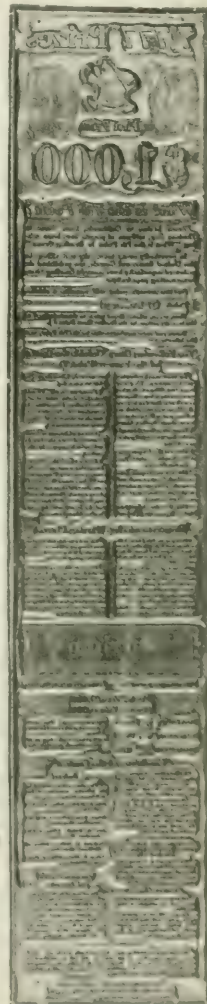


Fig. I - Printing Plate Molded already blocked



Fig. II - Printing Plate Ready for Mounting Combination of Half-tone, Line & Print

Fig. III - Boiler Plate Ready for Mounting Showing Different Types Reproduced on One Cut



quires about ten minutes for a complete cycle of operation, and may be reproduced many thousands of times with no appreciable deterioration in the original mold made from the phenol plate. From the average single column cut, about ten inches by three inches, and a satisfactory composition, great quantities may be printed. Thus, the above three hundred plates may have to be made in a single two-day run.

As the plastic sheet and mold would naturally weld together in the hot press, various methods are used to prevent the plate sticking to the negative mold or cast. A layer of oiled paper, thin metal, talc dust, etc., between the mold and cast has proven satisfactory but care must be taken when using paper or foil to see that it is not torn or trouble may result.

The use of the foil or paper produces a rounded point to the half-tone screen and produces a more desirable printing plate than the original zinc etching which generally has a protruding crown or shoulder thereby allowing ink to collect behind the point, soon blurring the plate. The smooth rounded point produced on the phenol plastic by the use of the intermediate paper or metal foil makes a plate which does not gum up and blur with the printing ink.

Half-tones have been produced from 150-mesh screen and 150 screen is the highest used in ordinary half-tone work. The ordinary newspaper cut is produced from screen not exceeding 100 mesh, as the larger dot is required for printing on coarse cheap paper.

Any form of line work can be reproduced with accuracy and is in general an easier proposition to handle than the half-tone.

Mounted plates may be molded directly upon the block of wood and come from the press blocked and ready for flat bed printing. In this form the cut cannot be unblocked. The plates are also produced in thin form ($1/16$ inch thick) and are afterwards in another operation blocked by tacking or gluing like the regular zinc cuts. Plates blocked or mounted on wooden blocks by tacking may be readily unblocked.

The weight of the molded plate is one-sixth the weight of the corresponding zinc etchings, and contributes a saving in shipping costs equal to the original cost of the plate. One square inch of plate weighs $1/9$ oz. Ready for shipping 35 sq. in. weighs 4 oz. It should be borne in mind in this case that in extensive advertising the cost of mailing or expressing the zinc cuts is often equal to the original cost of the etching.

REDMANOL CHEMICAL PRODUCTS COMPANY
636 W. 22ND STREET
CHICAGO

THE SETTING OF LITHARGE-GLYCERINE CEMENT¹

By H. E. MERWIN
Received December 26, 1916

A little litharge which had passed a 200-mesh screen was spread in a large excess of glycerine on a microscope slide under a cover-glass. After an hour indications of the crystallization of another substance around the surfaces of the litharge grains could be seen; after three hours the new substance was very apparent; and after 24 hrs. the original grains of litharge were replaced or firmly bound together by interlocking crystalline aggregates of the new substance. These aggregates consisted of radiating fibers.

Grains in a similar slide held at 80° C. for an hour were firmly cemented. The new crystals had similar optical properties in both cases.

¹ This cement is very important and not fully appreciated, e. g., it is used in very large quantities in lining the digesters in the manufacture of sulfite pulp.—EDITOR'S NOTE.

Glycerine, pure or diluted with 5 to 10 per cent of alcohol or water, heated to boiling and agitated with litharge, gave similar crystals which were much less closely aggregated. Agitation prevented to a large extent the covering of the litharge grains by the new crystals. In the best sample of material thus prepared—afterwards used for analysis—about 10 per cent by volume of unattacked litharge and 90 per cent new crystals were estimated microscopically. Analysis showed 70.8 per cent of Pb, which corresponds to 5 per cent residual PbO, and 95 per cent of the compound¹ $C_3H_5O_2 \cdot PbO$, representing the new crystals.

The crystals are apparently orthorhombic. The refractive indices are, $\alpha = 1.75$, $\beta = 1.80$, $\gamma = 1.84$, with γ parallel to the length. The crystals had been slightly attacked by the alcohol used in washing them.

After standing with glycerine for several days at ordinary temperatures the centers of the larger grains of litharge that had passed a 200-mesh sieve were still unattacked. Probably coarser grains would remain indefinitely.

GEOPHYSICAL LABORATORY
CARNEGIE INSTITUTION OF WASHINGTON
WASHINGTON, D. C.

THE USE OF A CONDENSER TO PREVENT ARCING IN BOMB CALORIMETERS

By FRED F. FLANDERS
Received January 16, 1917

Commercial lighting current of 110 volts is quite commonly used for igniting the charge in bomb calorimeters. A typical arrangement is to connect two 32-C. P. lamps in series with the fuse wire.

Objections have been raised to the use of current of such high voltage on account of the uncertain amount of heat developed by the arc formed at the instant the fuse wire burns out.²

The arc may be entirely obviated by the use of a 2 mf. condenser. This is connected across the leads running to the fuse wire and as close to the latter as possible. When protected in this manner the 110-volt current produces scarcely a visible spark when the current is broken.

The use of the condenser might also prove advantageous where a storage battery or other source of low voltage current is used, for even with voltages as low as 10 or 12 volts there is still an appreciable arc when the current is broken. Condensers satisfactory for the above use may be had of almost any electrical supply house, particularly those dealing in wireless apparatus. They are listed as flat telephone condensers, should be of about 2 mf. capacity and tested for 500 volts. A very neat one, $2 \times 4 \times 3/4$ inches, was supplied by the Clapp-Eastham Co., of Cambridge, Mass., for ninety cents.

CHEMICAL LABORATORY
MASS. COMMISSION ON MENTAL DISEASES
74 FENWOOD ROAD, BOSTON

¹ This compound was prepared by T. Morawski [*J. prakt. Chem.*, **22** (1880), 401, and Dingler's *polytech. J.*, **335**, 213] in his original studies of this cement.

² U. S. Bureau of Standards, *Circular* **11**, p. 7. Issue of May 15, 1911. *THIS JOURNAL*, **9** (1917), 106. Under (6), Firing current.

ADDRESSES

DEVELOPMENT OF CHEMICAL INDUSTRIES IN SOUTHERN CALIFORNIA SINCE JANUARY 1, 1916¹

By ARTHUR W. KINNEY

Industrial Commissioner, Los Angeles Chamber of Commerce

An eminent authority says that the measure of a country's appreciation of the value of chemistry in its material development and the extent to which it utilizes this science in its industries, generally measure quite accurately the industrial progress and prosperity of that country.

The year 1916 has been the most notable year in the history of Southern California in the amount invested in chemical manufacturing enterprises and in the number of new products exploited. Millions of dollars have been expended in modern plants and more than twenty new products have been developed, samples of which are on display at the industrial bureau of the Chamber of Commerce.

Very few of the people of this region appreciate the opportunities and possibilities which prevail here with regard to an important chemical industry. The great European war, which has curtailed and in many instances completely shut off the old supply of chemicals heretofore imported, has caused an enormous awakening throughout our nation, and has been productive of a large amount of chemical research and investigation. The reason for this is apparent, in view of the statement that the volume of trade and manufacture in the United States at the present time, which is directly dependent on the needs of the chemist, is about \$7,000,000,000 per annum. As the months roll by it is being demonstrated that American chemical manufacturers have the brains and ability to produce nearly all substances which have heretofore been imported. In view of the authoritative statement that in California there exists a wider diversity of the crude chemical materials of nature than in any similar area of the world, it is not strange that this section is playing such a prominent part in the exploitation of new materials and is doing its full share in the building up of a great American chemical industry.

In this article we shall dwell only upon those Southern California enterprises which have commenced operation since January 1, 1916.

During the year the Hercules Powder Company has come into the field and invested \$1,500,000 at Chula Vista, below San Diego City proper. The improvements consist of barges and harvesters, two of the latter costing \$45,000 and \$60,000, respectively; a pier 2300 feet long, a floating machine shop, 156 tanks holding 50,000 gallons each and 9 holding 400,000 gallons each. There are housings for an intricate mass of machinery, engines, electrical equipment, laboratories, evaporators, separators, presses, conveyors, etc. Potassium, iodine and acetone are taken out of solution by processes known only to the chemists, of which there are sixteen. Power is supplied by six batteries of Edgemoor boilers, with a capacity of 2700 horse power. The plant covers an area of several acres.

At the harbor district of Los Angeles five good-sized kelp products concerns have begun operations during the present year—the National Kelp Potash Company, Oceanic Engineering Company, Pacific Products Company and International Potash Properties Company of Long Beach, and the Diamond Match Company at Wilmington. The product of the latter company is used by the great plants of the Diamond Match Company of national fame. After considerable investigation the Department of Agriculture has decided to locate and operate at Summerland, Santa Barbara County, an experimental kelp products plant which will have a capacity of 200 tons of kelp per day.

This institution will cost approximately \$175,000, and will give the potash industry a thorough tryout.

POTASH INDUSTRIES

The American Trona Corporation, of which Baron A. de Rapp is president, has completed during the year two costly refineries, one at Trona, Seales Lake, San Bernardino County, where the raw material is obtained, and the other at Los Angeles Harbor, where the concentrated salts are to be refined.

The buildings at Seales Lake, extending a distance of one-third of a mile, are of fireproof construction and include laboratories, engineers' building, auxiliary building, evaporator building, machine shops, power plant equipped with four 500-horse-power Babcock & Wilcox boilers, spray pond, restaurant, offices, sleeping quarters, physicians' quarters with hospital and operating-room and cottages for married employees. A supply of fresh water is brought from the mountains sixteen miles distant.

The buildings of the plant at Los Angeles Harbor are also of fireproof construction and include a refinery building, office building, laboratory, warehouse, machine shop and power plant containing two 500-horse-power Babcock & Wilcox boilers.

The American Trona Company is now shipping potassium chloride from the Seales Lake plant. Other probable products from this and the harbor plants are caustic potash, permanganate of potash, bicarbonate of potash, borax, sodium carbonate, chloride and sulfate.

Another large chemical enterprise which will handle similar products is that of the Solvay Process Company, an \$18,000,000 corporation, now erecting a modern plant at Borosolvay, Seales Lake. The buildings of this concern include a power plant, evaporator building, machine shop, crystallization building, warehouses, clubhouse, commissary and cottages. The Solvay Process Company is the discoverer of the process for manufacturing caustic soda and now operates large chemical plants at Syracuse, N. Y., and other cities.

Other sources of potash exploited during the year have been the plant of the Riverside Portland Cement Company and various Southern California beet-sugar factories. From the first-mentioned source many thousand dollars' worth were obtained as a by-product.

At San Diego the Lower California Chemical Company is erecting the first unit of a plant which will be devoted to the making of orcein dyes, using as a raw material the orchilla weed, a moss found growing in vast quantities along the western coast of Lower California. It is claimed that these dyes can be produced cheaper than the imported article and are equal, if not superior, to the same.

DYESTUFFS

Another dyestuff enterprise of the year is the Internal Dye Products Company, which has recently equipped a new plant at Vernon. This company is backed by Los Angeles men and will engage in the manufacture of aniline dyes, using as raw materials the by-products of the local oil refineries and gas plants.

At Corona, Riverside County, the Citrus By-Products Company, a cooperative organization composed of various members of the California Fruit Growers' Association, has begun an active operation manufacturing citric acid from cull lemons. Having used this year over 2000 tons of the latter, the present source of this commodity has been Italy, where it comes because the industry consumes from one-third to the whole of the lemon crop.

During the year three new concerns have gone into the manufacture of strontium nitrate. The chemical is largely employed in the manufacture of red fire and is used by manufacturers

¹ Reprinted from the Los Angeles Sunday Times, December 17, 1916.

of fireworks and railway signals. The raw material comes from San Bernardino and Imperial Counties. Prior to the war practically all this commodity was imported from Europe. The new companies in operation are F. G. Mortimer Company, at Vernon; Long Beach Chemical Company, and Southern Reduction Company, both at Long Beach. The latter concern also operates a new plant at Vernon, where it is making a high-grade of chloride of lime and chlorine. Another new enterprise at Vernon is the California Chemical Company, which is now erecting a plant for the manufacture of orchard sprays.

The Linde Air Products Company, which operates factories in twenty or more American cities, has just completed in Los Angeles a modern plant for the manufacture of oxygen gas.

During the year the Grand Canyon Lime and Cement Company has equipped and placed in operation a complete establishment for the manufacture of hydrated lime.

The Industrial Bureau has been advised of the erection of a factory at Escondido which will handle eucalyptus lumber from the large groves in that vicinity. One of the important by-products will be eucalyptus oil, now largely used in manufacturing pharmaceutical preparations.

OTHER NEW PRODUCTS

Other new products of the year are molybdc acid salts, made by the Rose Chemical Company and American Alloy and Chemical Company, tungstic acid by the Tungsten Mines Company, and oxide of antimony by the Western Metals Company. In addition to the foregoing there have been made in limited quantities molybdc oxide, ammonium molybdate, ferro-tungsten, ferro-manganese, ferro-vanadium, ferro-molybdenum and strontium hydrate. Crude sulfur from Nevada has found a ready sale among our local manufacturers.

Of more than passing importance has been the exhaustive investigation of the Rittman refining process made by the Independent Oil Producers' Agency and the statement made that while fairly good results have been obtained, the installation of a small plant more closely adapted to California requirements is being considered.

This has been a remarkable year in chemical development, made so largely through the incentive of high prices, and the things accomplished must be gratifying indeed to our business men and chemists. We have here raw materials of great variety; we have by-products almost without number. Adequate research work and the solving of the problem of keeping down the manufacturing costs of production should enable us to convert these raw products into commodities that will eventually bring hundreds of millions of dollars to this region.

LOS ANGELES, CALIFORNIA

INITIATION OF EXPLOSIONS¹

By WALTER ARTHUR
Received February 2, 1917

Just when gunpowder was first known is a matter of most vague conjecture, but its use was recorded many centuries ago. Its advent into the world brought most marvelous changes into political matters, and at present, is playing the most important rôle in the greatest of all human activity. Accompanying the use of powder and explosives, and closely allied with their development, is another and most important problem—the initiation of the burning or explosion. Powder and explosives afford us a convenient means of doing work, if the energy represented can be made use of at a desired moment and in a manner perfectly safe to those using them. The character of the explosion is dependent upon the efficiency of the method of ignition. Hence the importance of the question of initiation.

Until quite recent times, black powders or kindred mixtures were the only explosives in use; the energy contained was liberated by the burning of the mixture. This required only the

minutest flame to start the ignition, as the particles of the various components were extremely finely divided, and a very small amount of heat was sufficient to raise them to the ignition point. The method of ignition was to fill with powder a small opening which led into the powder chamber, and by means of a flame or spark, ignite this powder train from the outside. This was the old method of the match locks and flint locks. Most of the old cannons we see in our parks and public places were of this type.

PRIMERS

In 1799, Howard discovered the substance we know as mercury fulminate. Its ability to fire gunpowder gave rise about the year 1815 to the development of the percussion cap. This is the beginning of what might be termed internal ignition in contradistinction to the earlier method which we may style external ignition.

The percussion cap may be briefly described as a small metal capsule containing a small amount of mercury fulminate, or mercury fulminate mixture, or other mixture with similar properties. This was used by placing it over the ends of a small tube which lead to the powder chamber. When struck a sharp blow, the mixture detonated, giving rise to considerable heat, thus igniting the powder. This method of ignition for firearms was in common use until very recent times and is occasionally seen to-day. The significance of this invention was as great as the discovery of guncotton or smokeless powder. It made the ordinary firearms much more effective by relieving the gunner of any anxiety as to whether he had powder in his pan. It permitted of ready use and made the arm independent of the weather. The combining of the projectile, powder charge and priming charge into one cartridge, has made our breech-loading firearms and machine guns possible.

There are a number of methods of internal ignition; all of them are much alike. In some substances, as in light ammunition, where a cartridge case with a thin head can be used, the priming mixture is placed in the rim of the head. This rim is struck a sharp blow by the firing pin where it is desired to ignite the powder; hence the so-called "rim fire." In most instances the priming mixture is placed in a small cup and inserted in a chamber in the head of the cartridge case, the firing of the priming charge being done by crushing the priming mixture between the cup bottom and the anvil. Many manufacturers of such ammunition place the anvil in the cup, but others make the anvil a part of the cartridge case, the result of the explosion of the primer pellet being a flame of considerable length and intense heat. The primer cup, being held securely in its chamber, allows no escape of flame except through a vent into the powder charge.

The length and heat of the primer flame will determine very largely the character of explosion in the cartridge case. If the flame be short and the temperature not very high, only a portion of the powder may be burned before the projectile leaves the muzzle of the gun. This, of course, lowers the pressure behind the projectile; as a result, a lower velocity of the projectile is obtained. On the other hand, if the primer flame be long and the temperature high, all of the powder may be fired.

The number of mixtures proposed for use in percussion caps and primers is legion; four of these are as follows:

21.9% Sulfur (flowers)	53% Potassium Chlorate
30.8% Antimony Sulfide	25% Lead Sulfoxyanide
47.2% Potassium Chlorate	17% Antimony Sulfide
35.01% Ground Glass	5% Trinitrotoluene
28.01% Mercury Fulminate	51.2% Potassium Chlorate
14.00% Potassium Chlorate	25.5% Antimony Sulfide
1.97% Shellac	8.9% Sulfur (flowers)
21.00% Antimony Sulfide	12.4% Ground Glass
	2.0% Shellac

It will be seen that either potassium chlorate or mercury fulminate is to be found in each of them.

In order to increase the sensitiveness of the primer, an abra-

¹ Presented before the January Meeting of the Philadelphia Section of the American Chemical Society, January 18, 1917.

sive, such as ground glass, is added. The glass, due to the sharp edges and hardness of its particles, cuts into the particles of fulminate or potassium chlorate, and assists in their breaking when the mixture is crushed under the firing pin, and as the firing of the primer is a result of the breaking of the crystals of the potassium chlorate or fulminate, the sensitiveness is thus very much increased.

MANUFACTURING PROBLEMS

The difficulties encountered in the manufacture and loading of primer mixtures are many. Owing to the extreme sensitiveness of such mixtures to friction or blows, they are usually mixed in the wet condition, and dried after loading into the caps.

In order to secure perfectly uniform results, it is necessary to have a thorough mixture of the various components. In using such materials as potassium chlorate or antimony sulfide, a great deal of difficulty is encountered in getting the proper granulation. Very coarse materials, about 100 mesh, give very poor results; the flame is short and the sensitiveness is poor. The best results come from materials of about 200 mesh; here sensitiveness and flame length are good. The difficulties in using such fine mixtures comes in the mixing. These excessively fine materials are very difficult to mix thoroughly owing to the tendency to collect in small pellets which resist the usual mixing. One of these very small pellets is often sufficient to cause a misfire if it gets into the primer cups.

Another difficulty, comparatively simple in its nature, yet disastrous in its results, comes from overloading the cups. Each cup is designed to hold a certain charge. Sometimes, in careless filling, the maximum charge is exceeded. The anvil is forced in under great pressure, the result being that the pellet of priming material is so hard that the firing pin cannot break it; the result is a misfire.

MODERN EXPLOSIVES

We shall turn now to another class of explosives which require the use of a primer to liberate their energy. In the year 1864, Alfred Nobel, a Swedish engineer, used mercury fulminate for the purpose of filling priming caps to initiate the explosion of nitroglycerine and dynamite. This discovery forms one of the greatest advances of the last century—an advance to which we owe the development of the whole modern technique of explosives, and such giant accomplishments as the building of the Panama Canal. Although discovered some twenty years previous, it remained but little more than a scientific curiosity until a convenient detonator was devised. These detonators or dynamite caps are of two types—that which is fired by burning of a slow fuse, and that fired electrically. They consist of small copper capsules partially filled with mercury fulminate, or a mixture of mercury fulminate and potassium chlorate. The detonating cap to be fired by a slow fuse is exactly as described above, the fulminate being fired by the burning powder at the end of the fuse. The detonating caps fired electrically are as just described, except immediately above the charge of mercury fulminated is a small charge of gunecotton which is fired by the heat from a short resistance wire. The electric current necessary for such work depends upon the number of charges to be fired. These detonators are made up in various sizes and strengths, and are numbered from 1 to 10.

Designation No.	1	2	3	4	5	6	7	8	9	10
Charge in grams	0.3	0.4	0.54	0.65	0.8	1.0	1.5	2.0	2.5	3.0

By the use of electric detonators, a great many charges may be fired simultaneously, thus accomplishing what would otherwise be impossible. This method also allows all persons to retire to a safe distance before the explosion occurs. It also affords a means of detonating quantities of nitroglycerine deep down in the earth, as in oil well shooting.

SUBSTITUTES FOR MERCURY FULMINATE

Recently a great part of the mercury fulminate in these detonators has been replaced by picric acid, trinitrotoluene, or tetranitromethylamine. The strong initial effect is thereby increased; in this way 0.5 g. of mercury fulminate has been made to detonate a charge which required 3.0 g. of mercury fulminate in the earlier caps.

The use of priming substances for high explosives in modern warfare is at present of much interest. The methods of application are much the same as in commercial explosives, the only difference being in the use of a time element in many cases. The initial primers are provided with firing pins which are actuated either by the sudden movement of the projectile in the gun or by the striking of the shell against some resisting body. Since the space in high explosive shells through which a firing pin might move is quite limited, a very sensitive priming mixture is used. Mixtures of mercury fulminate, potassium chlorate, a strong reducing agent, and often an abrasive such as ground glass are used. In order to protect these primers against abrasion and atmospheric agencies, shields or caps of paper or metal are provided. The whole of it must be so arranged that a light blow of the firing pin measuring only a few inches will suffice to bring about the necessary explosion of the primer. The explosion of the primer detonates a greater charge of mercury fulminate which communicates its detonating influence to the body of the main explosive. Quite often a booster charge is added between the fulminate and the explosive, and in this way the detonating action is built up.

In armor-piercing shells it is desirable that the explosion take place after the shell has penetrated the armor. In this case the action is such that the primer is fired as a result of impact with the shell against the armor plate, this in turn igniting a train of powder so arranged that the main detonating mass will be exploded at the correct moment. Owing to the fact that these shells travel at a great velocity, only the briefest delay is required between the action of the primer and the detonator.

In high explosive shells where the entire action is to be instantaneous, the delay action is omitted, the explosion of the priming charge, detonator and boosting charge taking place in most rapid succession.

In the case of shrapnel shells where an adjustable time action is required, movable trains of powder are interposed between the primer and the main charge, the primer being fired from the set back in the gun. Shells of this type are often provided with two primers—one to be used with the time action, another one to function on impact.

There are various types of cannon primers which we cannot discuss at this time; most of them differ from the small arms primers in size and mechanical details. Some of them are exploded by friction instead of a blow.

MIXING

Some of the difficulties encountered in the manufacture of the various priming mixtures might be of interest at this time. The first thing that naturally attracts attention is the mixing of these compositions, as they must be sensitive to blows and friction. The handling and loading is attended with much danger. As the presence of some liquid in the mixture acts as a sort of cushion between the various particles, these mixtures are usually made up with water or alcohol. After the mixture has been put into place, the liquid is dried out. Some firms handle these mixtures dry, but it is always attended by considerable danger: even in the wet condition, the mixture must, or should be done by hand. Great care must be exercised during the mixing lest some portion become too dry and the friction from the rubbing start an explosion. The mixing table and the room must be kept thoroughly clean.

Attendant upon the danger from explosion is the danger from poisoning when mercury fulminate is used in the mixture or loaded separately. Not only is mercury fulminate a poison when taken internally, but the dust from it produces dermatitis and skin eruptions.

FIRING PINS

It is interesting to note that the functioning of artillery primers made with a shallow layer of a friction mixture backed by mercury fulminate, is dependent upon the character of the blow. If a light blow is delivered, the fulminate only burns; if a severe blow is delivered, the fulminate is exploded. The character of the point of the firing pin has a great deal to do with the sensitiveness of primers of this type. If a blunt point be used, a much heavier blow is required than if a sharp firing pin be used. If a long taper point be used, much less disturbance of the mixture is produced than if a short taper point be used. A round point also gives less disturbance to the mixture than a triangular or a square point. The maximum effect should be produced by a short taper sharp square point.

THEORY OF EXPLOSIONS

The question has often arisen, "Why does a mixture of potassium chlorate and some easily oxidizable agent explode when struck a sharp blow?" This is not easily answered. The explosion depends, of course, upon the fact that crystals of potassium chlorate are broken or fractured in the presence of some substance that unites with the oxygen very readily. If a substance, like red phosphorus, be in contact with the broken crystals, an explosion of great brisance occurs. If some substance like sulfur is present, which unites with oxygen much less readily, an explosion occurs which is less active and the report therefrom is much less dull. In fact, potassium chlorate and red phosphorus are so active that they can scarcely be mixed without an explosion, while potassium chlorate and sulfur will admit of quite considerable mixing. If potassium chlorate and sugar be mixed we get merely a burning—so slow is the exchange of oxygen.

We may picture in our minds a crystal of potassium chlorate as made up of centers called potassium, chlorine and oxygen all arranged in some perfectly definite manner and held together by lines of force of some kind. When a crystal is broken, some of these lines of force between the oxygen and the other elements are severed, and for the moment are free. If phosphorus be present, which is always on the lookout for its friend oxygen, it immediately seizes upon the opportunity to add another member to its household. The warmth of friendship produces sufficient heat to warm up the neighboring oxygen communities to a state of activity, hence heat, flame and general rearrangement of affairs!

The question is asked, "What happens when a crystal is broken when no phosphorus or oxidizable substance is present?" Of course, this question cannot be answered at present; our knowledge of the molecular arrangement is too scanty. If crystals of mercury fulminate and a few other like substances be broken rather quickly even when unattended by an oxidizing substance, a most severe explosion occurs. But why? This is just as difficult as the other questions. The answer may be made that crystals of mercury fulminate are unstable. This explains nothing. Perhaps some of the recent work of Bragg in crystal structure may eventually give us some information.

The question has often been asked, "What properties of mercury fulminate enable it to act as a detonator, and in what way is the primary explosion related to the principal explosion?" The chief characteristic of mercury fulminate which makes it valuable as a detonating agent, is the ease with which it can be exploded by simple and ordinary means and the wonderful pressure developed therefrom, which brings about the explosive decomposition of the explosive mass. A large number of chem-

icals are violent explosives and many exceed mercury fulminate in explosive power but are less suitable or are not suitable at all as detonators. Some are too sensitive to shock or friction; some are too insensitive. Some may cause the explosive wave in the main explosive mass to proceed too slowly. Mercury fulminate occupies the middle position. A great number of investigators have attempted to account for the initiating effect of detonating compounds. Abel advanced the theory of synchronism of molecular vibrations between the primary and secondary explosives. This theory is supported by the fact that many substances, as diazo-benzene, nitrate and nitrogen chloride, could be used only in large quantities, if at all, as a detonator of explosives. While mercury fulminate in small quantities was sufficient to produce a detonation, Abel ascribed this exceptional behavior to a resonance phenomenon, which he described as a molecular vibration which brought the molecules of the explosive to be detonated, into a synchronous vibration, thence to detonation. L. Wöhler made a thorough investigation of the Abel theory and came to the conclusion that it was not sufficient to account for the phenomenon. No theory advanced so far seems wholly satisfactory.

It was found by Abel that the most violent exploding compounds, nitrogen chloride and iodide, are practically without detonating action on nitroglycerine and gun cotton. Only once could he cause detonating action with 3.25 g. of nitrogen chloride, while 0.32 g. of mercury fulminate was sufficient to produce the detonating action. This remarkable difference is explained by Wöhler, by the enormous pressure which mercury fulminate shows in contrast to that of nitrogen chloride, and, in addition, calls attention to the fact that, although the gases evolved by the explosion of the two compounds are very nearly equal, the heats evolved are only 312 calories per kilo for nitrogen chloride as against 411 calories for mercury fulminate. Wöhler attaches the greatest significance to the fact that the loading density of mercury fulminate is far beyond that of nitrogen chloride.

In spite of the fact that nitrogen chloride has a smaller calorie number and a lower loading density, it is likely that nitrogen chloride produces a greater instantaneous pressure than mercury fulminate. Judging from the shattering effects produced upon glass and similar bodies, nitrogen chloride greatly exceeds mercury fulminate in brisance. If we take into consideration the difference in loading density and heat evolved, we find that difference is not sufficient to account for the tenfold difference in effect.

It is common practice to manufacture detonators which are intended for explosives that are brought to explosion with difficulty with a booster charge of a like or similar substance, such as trinitrotoluene or tetranitromethylaniline. This supports rather than opposes Abel's theory.

In the year 1883, Berthelot offered the theory that the detonation of a brisant explosive was to be considered as a sudden wave-like decomposition, propagating through the whole mass, brought about by the kinetic energy of the detonator. According to modern views, however, neither the pressure as such, nor the violent changes brought about by it, is sufficient to account for the detonating waves of a secondary explosive. Another author of recent date agrees with this view that it is the adiabatic heating of the medium in contact with the priming substance, caused by the great pressure which initiates the exceedingly high velocity of the detonating waves.

The action of a blow of a hammer is often explained upon the assumption that the heat, into which the energy of the hammer is transformed on being suddenly brought to rest, heats the portion of the explosive struck to a temperature at which a sudden increase of the velocity of decomposition leads to an explosive velocity. It is quite well known that very sudden heating of an explosive leads to an explosion.

How then can the detonation of an explosive be carried over an intervening air space? The thermal hypothesis will not account for this. This is explained by the compression and rarefaction of the surrounding air. Since the force of such waves decreases as the square of the distance, this theory is not sufficient. From what has been said, it can be seen to be a very complex subject, and how many theories fail when all the facts are taken into consideration.

DETONATORS

For many years mercury fulminate has held its place as a detonating substance as superior to all others. Of recent years, however, its place has been threatened by other compounds which bid fair to displace it. One of the most promising of these is lead azide; lead azide is a salt of hydronitric acid whose

constitution is expressed thus: $\begin{array}{c} \text{N} \\ \diagup \quad \diagdown \\ \text{N} \end{array} \text{NH}$. Some investigators

unite it thus: $\text{N} \equiv \text{N} = \text{N} - \text{H}$. This acid forms a great number of salts, as mercury azide, silver azide and sodium azide.

The heavy azides, such as lead azides, are prepared by treating a solution of sodium azide with a soluble metallic salt, such as lead acetate, the sodium azide being prepared from nitrous oxide and sodium amide.

Large crystals of lead azide and mercuric azide have been found to be very sensitive to mechanical shock, the sensitiveness increasing with the size of the crystals. Even the breaking of a single large crystal is said to bring about explosion. Crystals as large as 3 mm. in length, when dry, often explode when brushed with a feather. If a hot saturated solution be allowed to cool slowly, large crystals sometimes form, which detonate under water. The formation of such crystals must be avoided. This property is scarcely obtainable with the fulminates.

Mercury fulminate and lead azide differ very greatly in flash point—lead azide flashing about 330° , mercury fulminate flashing about 180° . Lead azide in fine crystals appears to be less sensitive to blow than mercury fulminate. It is very stable when stored at high temperatures, such as 50°C .; it is, however, decomposed by strong sunlight. The action of lead azide upon metals is slight, while fulminate is quite active.

Mercury fulminate may be dead-pressed, while lead azide increases its brisance and explosive power with pressure. If detonator caps be loaded with lead azide and a booster charge, much less lead azide is necessary to produce the desired detonation. The sensitiveness of fulminate to mechanical shocks is much lessened by the presence of as much as 1 per cent moisture, while lead azide is not much lessened by this small amount. This particular property is extremely valuable in case of storage of detonating caps in humid atmosphere.

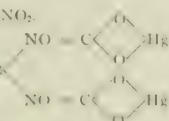
Many other substances have been proposed as detonating agents. Trinitro-resorcine or lead styphnate [$\text{C}_7\text{H}(\text{NO}_2)_3 \cdot \text{O}_2\text{Pb}$] has been found to be an excellent explosive. Hexamethylamine tri-peroxide-diamine [$\text{N}(\text{CH}_3\text{O} \cdot \text{OCH}_2)_3\text{N}$] is said to exceed mercury fulminate 4 or 5 times in priming power.

A number of others may be mentioned as:

Nitrogen tetra sulfide, N_2S_4

Diazo benzol nitrate, $\text{C}_6\text{H}_5\text{NO}_2 \cdot \text{NO}_2$

Basic mercury nitro-methane, Hg



Perechlorate of tri-mercuric chloride, $\text{ClO}_4\text{Hg}_3\text{Cl}_3 \cdot \text{O} = \text{C} = \text{COH}$

Dr. Alfred Stettbacher, in *Zeitschrift für das gesamte Schuss- und Sprengstoffwesen*, of Oct. 1 and Dec. 1, 1914, has presented a most splendid résumé of recent developments in this field, from which paper I have drawn freely.

WATER-METERS IN THEIR SANITARY RELATIONS:

By HENRY LEFEMANN

Received September 30, 1916

The management of an American city is the despair of the efficiency expert. Ex-President Taft expressed the view that in two respects the promise of better things that had been seen in the formation of the United States under the Constitution had seriously failed of fulfillment: procedures in courts and the administration of American cities. The administration of civil and criminal law in most parts of this country is legalized robbery, and the business and engineering administration of cities is chiefly remarkable for stupidity and dishonesty. I come from a city that has been widely advertised as "corrupt and contented," and daily experience compels me to admit the substantial accuracy of the phrase. In spite of the development of the science of city-planning, miles of small streets are allowed to be laid out, and while the street prism is being excavated for water and gas supply and for telephone conduits, no provision is made for electric light and power wires. High-tension currents are permitted to be carried on hideous poles through residential districts, involving danger to persons and property, and subjecting the service to frequent interruptions from storms. Situated with an enormous supply of fresh water at its boundaries, which, by the construction of simple storage reservoirs, could have been rendered safe for all uses, it was for many years one of the worst typhoid nests in the world. Now, after spending many millions for installing a plant for purification of these supplies, its "Solons" are debating the problem of meeting a greatly increased demand, and instead of seeking rational means of preventing waste, are looking towards an expensive enlargement of the plant.

I am presenting this paper, however, not to inveigh against any particular municipal administration, but to call attention to a relation between engineering and chemistry that I think is often overlooked. I have long felt that the main sanitary problems of municipal administration are essentially engineering ones, and that undue emphasis is given to the purely chemical data. There is, of course, no phase of municipal sanitation more important than water supply. Water, by the very necessities of our existence, is largely consumed now, and it must be furnished freely and continuously in a perfectly safe condition. We are, unfortunately, accustomed to regard it as without price; we think it should be "as free as air," but this cannot be expected in municipal life, and the sooner the citizen realizes that water should be paid for like food, clothing and transportation, the better for all of us. Indeed, it would be well if the community could be brought to feel that water of high purity is a luxury and should command a good price.

The interrelation between chemistry and engineering becomes still more intimate by the growth of the modern practices of sewage disposal. It has become necessary not only to secure an abundant supply of good water, but to return it to reasonable purity after it has been used. The time is rapidly passing when a community may take as it pleases from the upper reaches of a stream, and throw into the lower reaches its drainage. From two points of view comes, therefore, the need for preventing water-waste, and thus the question of a controlled distribution is brought vividly to the notice of the sanitarian.

Such control may be obtained in two ways. By an intermittent distribution, the places supplied being provided with storage tanks, thus limiting the amount of water available during the 24 hours, or by measuring the water delivered to each residence and charging for it with a minimum rate. The storage tank method with intermittent pumping is used in many foreign cities, and has some features to recommend it, but with the lavish use of water among Americans, very large tanks would be

Presented at the 100th Meeting of the American Chemical Society, New York City, September 1-5, 1916.

needed. The meter-system is preferable. The mechanical problems in regard to water-meters are solved and many forms that are accurate, inexpensive and durable are available.

I have residential experience in but two cities, Philadelphia and Atlantic City, but it happens that these present a decided contrast in the matter of water-supply, and serve well to illustrate the point that I wish to discuss.

Philadelphia has been notoriously wasteful of water. This is not due to any tendency to excessive cleanliness. Although about the middle of the 19th century it was often praised by visitors for the conditions of its streets, yet it rapidly fell from grace in this respect, and except as to an incomprehensible and reprehensible practice of frequently washing the sidewalks, it shows, at present, a good deal of general neglect in street management. Many years ago, an English visitor—Tupper, I think—said that "the carriage-ways are always dirty and the footways always clean." At the present time, owing to lack of system for control of the distribution, the consumption is about 300 gals. per person per day; an enormous amount, surely indicative of great waste. Metering is almost non-existent. A few householders have discovered that by installing meters a considerable saving of water rent may be secured, but this is merely the outcome of the ridiculously low meter rates. For some years, indeed, the city ordinances forbade the installation of a meter in a private house, and left it practically optional to large establishments. The mass of consumers are on a flat rate, that is, based on what they may, not on what they do use. How any person charged with the administration of a municipality in any capacity can be so indifferent to business methods as to favor such a method would seem to be beyond human comprehension, but it is after all a "strictly business" matter. Large manufacturing establishments and certain private individuals are interested in maintaining conditions which permit them to use water unrestrictedly, while paying less than their proper share of the expense of the supply, and as these persons exert a good deal of support to the dominant political party, especially in the matter of campaign contributions, a subservient administration ignores the just method.

Turning to Atlantic City—which offers an interesting contrast to Philadelphia, in this as in some other respects—we find according to the 1915 report of the Water Department, that nearly the entire consumption is metered, and that during the months in which the visitors are comparatively few (October to May) the consumption is about 150 gals. per person per day. It must, however, not be overlooked that many hotels have an independent supply from artesian wells, and that the city has almost no industries that are large water users. On the other hand, during the dull season, it is especially the large hotels that are running at restricted output, and bathing is a special feature of the resort. This is largely sea-bathing, yet even this necessitates the use of fresh water both for rinsing the person and for the laundry of bathing suits. Most of the large renting establishments now have running fresh water in every room. The fact that residents are required to pay for the water used does not seem to cause any undue restraint in the ordinary uses, though, of course, it tends to the installation of good plumbing and to keeping this in repair.

The consumption per person in Philadelphia is somewhat difficult to determine, and in any case, regard must be had to the fact that the city is spread over a wide area, and contains a very large number of industrial establishments that are heavy water users. Private sources of supply are not numerous. As a rule, both the subsoil and deep water obtainable within the city limits is unfit for drinking and manufacturing purposes. The pumping data show that frequently the consumption is about 300 gals. per person per day, as noted above, but this figure is based on what is termed by engineers "plunger displacement" and is generally regarded as too high. Moreover,

it does not consider leakage in the street distribution system, which is probably rather high. House leakage, especially in the flushing apparatus, is very high.

It is hardly necessary to present any statistics of water waste in American cities for nearly every one is aware of it, but as a brief illustration I give the results of an investigation made a few years ago by John C. Trautwine, Jr., who was for several years chief of the Bureau of Water of the City of Philadelphia. A block of the characteristic two-story, small-street dwellings was utilized.

Number of dwellings (7 roomed).....	142
Total number of openings.....	782
Number leaking slightly.....	22
Number running continually.....	32
Gallons delivered in 24 hours.....	119,800
Gallons wasted by leakage.....	103,600
Gallons per capita: Delivered.....	222
Actually used.....	30
Wasted.....	192

A large portion of the waste is brought about by a small proportion of users, so that a restriction by metering would affect mostly those who are indifferent to the welfare of others.

As I remarked above, the problem of waste-prevention has assumed an additional interest by reason of the necessity of sewage purification. All communities, and even occupiers of isolated country houses, now recognize that the effluent water must be brought to a fair condition of organic purity, at least, and that the greater the dilution of this effluent the greater the cost and difficulty of treatment.

In the discussion of this subject, the main opposition to measured supply comes from the owners of manufacturing establishments and from a limited number of well-meaning, but misguided people, who believe that some harm will be done if any restriction should be put on the use of water. Their slogan is that "water should be free as air" and that everybody should be encouraged to be clean. A careful examination of the houses in which the worst leakages occur would probably show no greater degree of cleanliness than in those in which the plumbing is kept in repair and the water used with judgment.

The truth is, however, that the same line of argument that is used to prevent the introduction of meters may be used to justify free distribution of food and beverages and free amusement. Moreover, all the data available show that all reasonable requirements may be met by the system of assigning a minimum allowance, and changing a flat rate, imposing additional charges only by those who exceed this. Careful investigations in American cities have shown that 7 cu. ft. (somewhat over 50 U. S. gallons) per person, per day, will meet all necessities in a high-class home in a large city. In Philadelphia, at present, a minimum charge of \$8.00 per year allows the use of 200,000 gals., but this is much too large, and it is proposed to raise the price and reduce the allowance so that \$12.00 will be charged for 90,000 gals. per year, which in a household of five persons will give about 7 cu. ft. per person per day.

Briefly, then, my thesis is that in view of the importance of pure water the enormous amount now required, and the necessity of purification of sewage, the sanitary engineer and chemist should use every effort to have public water supplies managed with rigid prevention of wastes and reckless use, and that this cannot be done without complete metering of the supply. Consumers should be taught that principles of conservation of resources, as well as proper management of filtration and sewage-disposal plants, require such a system, and further that the installation of meters with the provision of a minimum charge does not interfere with the use of water as freely as health and comfort require. Municipal supplies must depend almost entirely on surface waters. Here and there, artesian and subsoil sources may be available, but these exceptions are of no practical importance. I am still of the opinion that I expressed

many years ago in a paper before the Pennsylvania State Board of Health, that unpurified surface-water is always unfit for drinking, and that, as concerning it, analyses—bacteriological and chemical—are academic. The object of science is, of course, the discovery of truth, and from this point of view, any addition to knowledge, whether the discovery of a new marking on Mars or the properties of the circle in non-Euclidian space, must be appreciated, but the sanitarian deals with the purely utilitarian phase of science. I think there is no more important problem before the people of the United States than the conservation of the water supply, and it is the duty of informed persons to insist with all possible energy upon the necessity in economy in the use of water, for maintaining the quality of the original material and for reducing the cost of the subsequent purification of the effluent. For these reasons, I regard the water-meter as a most important sanitary agent.

1839 N. 17TH STREET
PHILADELPHIA

ADVANTAGES OF SOFTENED WATER IN LAUNDRY WORK¹

By J. H. RYAN

Received November 8, 1916

My topic to-day is what advantage softened water has over hard water, the saving not only to the laundryman, but also to the customer, and what the possibilities are for the equipment of a modern laundry with an efficient water-softening plant.

The laundries of this country in 1914 transacted business amounting to \$142,503,350, and there was paid for labor \$71,764,059; the amount invested in machinery, equipments, buildings, etc., was \$98,055,000. These figures give some idea of the magnitude of the laundry business, and yet, as a matter of fact, it is still in its infancy. The majority of the laundries in this country are devoting most of their time to the laundering of the provincial stiff collar and shirt, but this portion of the business is by far the smallest part of the work that the average American home has to offer. For example, one man in Michigan decided he would enter the family wash field and in less than one year increased his business over \$1400 per week. When the American laundry is properly equipped and makes the proper effort to obtain this class of work, the field is practically unlimited.

It might be well for us to consider for a moment the class of work, also the difficulties that the laundrymen have to contend with. Laundry is cosmopolitan in its service. There is, of course, a wide range in the quality of the fabrics treated. Not many years ago fabrics manufactured in this and other countries were heavier, very much stronger and would therefore stand more grief in the laundry. This class of goods is seldom ever used now; it has been replaced with thin delicate fabrics which are "loaded," sometimes to the extent of from 10 to 70 per cent in order to make them heavy and apparently more durable. Aside from this, every conceivable color known comes to us from day to day, which, in treatment, must receive the utmost care. Hence, the problem is a very different one from that of twenty years ago. The question that the laundrymen are trying to solve is how to do this class of work for American homes with the least wear and tear and at the lowest possible cost.

For more than a quarter of a century I have been in the laundry business. About half of that time I was connected with a laundry that used hard water exclusively. I can best illustrate the point I am trying to make by giving you a little personal experience I had more than twenty years ago. In those days we heard very little about water analysis, or at least the laundry men knew very little about it. All they knew about washing

was this: if they used plenty of caustic soda or soda ash in the soap and a plentiful supply of bleach, their clothes would come out of the machine clean, but very often they were in serious difficulties and did not know just why; neither did they know just how to work their way out of their troubles. The story I am about to tell you will demonstrate beyond any question of doubt, the value of water softening in a laundry and the danger of using hard water.

The laundryman I worked for was troubled a great deal with a yellow or brown cast in his work. His collars always had yellow seams. He insisted that it was the iron in the water that was causing this trouble and at a considerable expense he installed a filter, but this did not do away with his difficulty. At that time, and even now, a great many of the laundrymen use chloride of lime and soda for bleaching purposes; soda is used to soften the bleach, in other words to prevent it from destroying the soap. It mattered very little how much of this bleach was used, there would still be yellow seams and edges on the collars. About this time I read somewhere that oxalic acid was a good bleacher, so I made up my mind that I would do a little experimenting on my own account. I took some collars home and prepared a solution of oxalic acid and water; in this solution I placed the collars, rinsed them, and immediately the yellow seams vanished but a green tint remained and I had considerable difficulty in washing out the effects of the acid. After the proprietor had inspected the work, he asked me one day how I did it and I told him I had a new bleach; he thought so favorably of the work I was doing that he offered to form a stock company, if I would turn over the formula to them so they could manufacture it.

About this time I became a little negligent about washing the green tint out of the collars, so one day when I had an extra large amount of collars delivered to my home and did the necessary work, the foreman and the proprietor made up their minds I was using sulfuric acid; they proceeded to experiment, sent out for a bottle of sulfuric acid, filled a wooden pail three-quarters full of water and poured in the acid until they thought the solution was sufficiently strong to do the work. They then rinsed in this solution a nightshirt which had a decided yellow tint; the third time the garment went into the pail the boss found himself hanging onto two sleeves, the rest of the nightshirt resting quietly and unattached in the pail; but it had the green tint the same as I had left in the collars; after this operation was over I told them of my secret bleach and when they used oxalic acid in their rinsing and blueing water in sufficient quantities the yellow edges would disappear.

This particular laundryman never knew just why or how the acid was taking care of the yellow seams, neither did he know just what was making the yellow seams; it was the result of attempting to break hard water in the machine by using an excessive amount of alkali.

It is not necessary for me to go into detail in attempting to bring to your minds the great havoc the laundrymen make when he attempts to break hard water in the machine, especially when it is loaded with clothes. You might ask me if there is any danger in using soft water when the water is treated as a water softener. The facts are that the danger is identical with that of the hard water, so far as the use of acid is concerned; the minute the alkalinity is raised above a given desirable point, and then the acid remedy will have to be applied.

There are three water softener systems that are generally used in the laundries of this country. The permanent, the continuous, and the non-pipe systems. The permanent system is seldom used, so it leaves the field open practically speaking to the continuous and non-pipe systems.

About twelve years ago we had what was known as the all-Feederale system of water softening. The essence of treatment

¹ Read at the 52nd Meeting of the American Chemical Society, Urbana, Champaign, Illinois, April 28 to 31, 1916.

was purely caustic soda; we used this system for about three years and always had trouble whenever we reduced the hardness below 8 grains, because we would always have an excessive amount of alkalinity in the water so that it would take a large amount of acid to neutralize it before we were able to blue or destroy the yellow color that would appear in the goods after they were ironed. The four-pipe system, as I understand it, uses a caustic soda treatment, but they do not attempt to rinse or blue their clothes in softened water; hence the necessity of the four-pipe system. I am very much opposed to the system of washing in soft water and then rinsing in hard, because it destroys all the visible effects of soft-water washing, *i. e.*, that soft velvety feeling that clothes possess when washed and rinsed in soft water. Our water in Kalamazoo is 21 grains and is quite hard—about 3 lbs. of solids to every 1000 gallons of water. It is impossible to wash clothes in our water and reduce the hardness below 3.5 and 4 grains with any degree of safety, for just as soon as the hardness is decreased below that point there is trouble, due to an excess of alkalinity.

We have had splendid results with our water softening system. It has been in operation now for a number of years and we have never had a particle of trouble in our washroom; on the contrary the results have been unusually satisfactory. We use a continuous water softener. The treatment is 280 lbs. of building lime and 40 lbs. of soda ash to every 100,000 gals. of water. Under this treatment our water tests hardness 4, alkalinity 5 and causticity 3.5 grains per U. S. gallon.

We have not used any chloride of lime or oxalic acid since we installed our water softening plant. We use a little acetic for our blue. We have always claimed that the secret of good washing was pure clear soft water and I believe we have demonstrated this beyond any question of doubt. We believe we are doing more family washing than any other city in America twice our size and we attribute this largely to the method of treating our water and our washing methods in general.

SAVINGS MADE BY USE OF SOFT WATER

As an experiment we washed recently 100 shirts in raw hard water with 3 lbs. of neutral soap; we washed this same number of colored shirts in the same machine with the same amount of soft water with 1 lb. and 6 oz. of the same soap. We washed 95 lbs. of family washing in raw hard water with 2½ lbs. of neutral soap; we repeated the same operation and with the same weight of clothes and the same amount of soft water as hard water with 1¼ lbs. of soap. All the soft water used tested 4 grains. This is not all the saving, however; the bleach is reduced to a minimum and no acid is required for the purpose of neutralizing alkalinity left in water or getting proper color. If we did not have a water softener, we would use about 1400 lbs. of neutral soap per week. The present market value of neutral soap is about \$0.07, which would make our soap bill \$98 a week. Our saving is thus about \$50 per week.

The laundries using chloride of lime and oxalic acid are finding them a very expensive commodity at present. To my mind the present abnormal condition of the market is one of the best things that has happened to many laundrymen for a number of years, because it has taught them that laundries using the proper kind of water softener can and do get along without the use of those chemicals and do better work. After all, what the laundry business needs more than any other one thing is plenty of pure clean soft water, and when a laundry will install a system of water softening that will produce this kind of water, a large share of its troubles will cease and the customers will be happier for they will receive their clothes clean, clear and soft. White goods will be white, soft, and last longer than when washed under any other process known to the writer.

STREAM INSPECTION IN CONNECTION WITH THE OPERATION OF SEWAGE TREATMENT WORKS

By C. B. HOOVER

The treatment of the sewage of municipalities is made necessary in order that the natural advantages of our streams may be conserved. These natural advantages consist in the opportunities which our streams furnish as sources of supply for public water works and power purposes, for recreational activities, and as an important factor in adding beauty to the land.

The discharge of sewage into a stream of water may convert it into a foul open sewer, or, it may have no appreciable effect upon the stream, the result in any case being governed largely by the composition of the sewage, the dilution which the stream affords, and the prevailing temperature. There may be found to-day almost any combination of these three factors and in fact in most of our larger inland towns and cities, a wide range of combination of these three factors may be observed within a period of one year, *i. e.*, a given volume of sewage will encounter in the stream a widely varying dilution, and, in turn, the mixture of sewage and stream water will be subjected to widely varying rates of oxidation, due to changes in temperature during the year.

The object of sewage treatment is to prevent harmful stream pollution and broadly speaking, this means the prevention of the discharge of pathogenic bacteria into the stream, or, the prevention of a nuisance in the stream, or both. When the problem is simply one of eliminating pathogenic bacteria, chemical sterilization is practiced and stream inspection will reveal but little that cannot be ascertained through an inspection and analysis of the effluent of the works.

When the problem is one of the prevention of a nuisance, the desirability of stream inspection will increase as the dilution afforded by the stream decreases. The minimum dilution by the stream may be such that stream inspection will be unnecessary because a satisfactory stream condition may be safely assumed from the results of tests and analyses of the effluent of the works; furthermore, the minimum dilution may be such that assumptions of this character cannot be relied upon and the only way to check the adequacy of the treatment of the sewage is to inspect thoroughly the stream into which the treated sewage is discharged. If the stream is polluted from other sources, the results of stream inspection will not be a very reliable index of the adequacy of the treatment of the sewage which is discharged into the stream either above or below the other points of pollution.

It is thus evident that stream inspection, in order to be of value, must be comprehensive and must be made both above and below the point of discharge of the effluent of the treatment works. The absence of definite standards of purity for polluted streams would seem to indicate a difficulty as to what should be looked for in stream inspection. Where the polluted stream passes through a sparsely settled district where land values are low, the standard of purity need not be as high as where the stream passes through a thickly settled agricultural district where land values are high and where a foul-smelling and unsightly stream would seriously reduce the value of riparian properties. The keeping of a stream in a non-offensive condition might be all that would be required in the first case and if the effluent from the works will not develop an offensive odor after a two days' incubation in a closed container at 37° C., it may be safely assumed that such an effluent when discharged into a stream will not produce an offensive odor regardless of the dilution which the stream may afford, and under these circumstances, comprehensive stream inspection would hardly be necessary.

Presented at the 53rd Meeting of the American Chemical Society, September 28 to 30, 1916.

Where circumstances demand much better stream conditions and where the dilution at best is slight and where the volume of sewage is often greatly in excess of the stream flow, comprehensive stream inspection is a necessity in order to determine the adequacy of the treatment of the sewage.

At Columbus, Ohio, a situation of this kind must be dealt with and the difficulty of the problem may be appreciated from the fact that the volume of treated sewage (18 to 25 million gallons) which is discharged daily into the Scioto River is often, during the dry, hot summer months, four times that of the daily volume of flow of the stream. The critical period with respect to the maintenance of satisfactory river conditions is from April 1 to December 1, this being the period of higher temperatures and small dilutions. The routine of river inspection during this period consists of an inspection trip once a week from a point about two miles above to a point about twenty-five miles below the effluent outfall of the treatment works. There are two inspection stations above and five below the works and at each of these stations the following observations, tests, and analyses are made:

- 1—Temperature of the water of the stream.
- 2—Dissolved oxygen content of stream water. From this value and the temperature of the water, the percentage of saturation is calculated.
- 3—A sample of the water is taken to the laboratory and the dissolved oxygen consumed (called by some the oxygen demand) test is made.
- 4—The methylene blue test is made on a sample of the water having its *in situ* dissolved oxygen content.
- 5—The odor test (48 hours at 37° C.) is made on a sample of the water having its *in situ* dissolved oxygen content.
- 6—The chlorine value is determined on a sample taken to the laboratory.
- 7—The presence or absence of odor from the stream is noted.
- 8—The presence or absence of color (particularly black) is noted.
- 9—The presence or absence of floating sewage solids or sludge is noted.
- 10—The stream bed is dragged to disclose the presence or absence of sludge deposits.

The collection of this data every week for 8 months of the year during the past 5 years has given the City of Columbus a very complete record of the condition of the Scioto River above and below the treatment works and has aided materially in the enlargement of capacity and improvements in the treatment, which have been accomplished and are being planned.

The interpretation of this river data is often simple, but sometimes very confusing. Chlorine values can often be used to approximate roughly the stream flow and thus to indicate the dilution which the stream is supplying. Chlorine values in connection with dissolved oxygen consumed values have in several instances indicated that the stream was suffering from sludge deposits. This condition has been found above the works near storm sewer outlets, and a week or more after the storm flow had ceased, the chlorine content below the outlet would be the same as that above the outlet, but the dissolved oxygen consumed value would be very much higher below than above. The chlorine value indicated an absence of recent pollution and the much higher dissolved oxygen value indicated that the stream was suffering from sludge deposits, the presence of which was also verified.

When an incompletely oxidized sewage effluent is discharged into a stream of water there are two possible sources of oxygen loss in the stream. The effluent rarely is more than 70 per cent saturated with dissolved oxygen and if the water of the stream has a higher saturation than the effluent, there will be a loss of oxygen when they become thoroughly mixed and the loss will be more noticeable as the dilution decreases. The second loss

results from the absorption of dissolved oxygen by the unoxidized material in the effluent and this loss will also be more noticeable as the dilution decreases. The stream water supply of dissolved oxygen is constantly being replenished by absorption of oxygen from the air. When there is a very low or negative dilution, the oxygen may be absorbed by the sewage more rapidly than it can be replenished and this results in the establishing of offensive anaerobic putrefaction; this condition may continue for several miles down the stream; then dissolved oxygen will begin to appear in the stream and the oxygen content will continue to increase to the point of saturation, if no additional pollution occurs. After the point of minimum oxygen content has been passed and an increase in the oxygen content is noted, the stream may be said to have thrown off its burden and from that point on it is convalescent and in due time will recover its original condition of cleanliness.

Just how far oxygen depletion in a stream should be permitted to go has never been definitely settled and it does not seem probable that a standard for general application will or should be adopted unless it should happen to be in the nature of an absolute minimum requirement. It seems more probable that every case will become a law unto itself, the standard being evolved on the basis of local conditions and public sentiment.

In interpreting river inspection data, especially where the stream is pretty heavily burdened with sewage, no single test will give a satisfactory diagnosis of the stream condition, and in fact, single tests of either methylene blue or per cent of saturation with dissolved oxygen very often give very erroneous ideas as to the relative condition of the stream from one station to another. The stream at one point near the source of pollution may show a fair percentage of saturation and a fair stability value and at a point farther down-stream the saturation and stability value may be very much lower; these lower values would apparently indicate a worse river condition, but the dissolved oxygen consumed test may give a value much lower at this point than at the point farther up-stream, and, when the results of the three tests are considered it becomes apparent that the per cent of saturation and stability values often mask a great deal of potential pollution, which can be revealed only by the dissolved oxygen consumed test.

It has been found at Columbus that when the stream is heavily burdened with sewage the inspection must be very comprehensive in order to diagnose accurately or correctly the condition of the stream.

DIVISION OF SEWAGE DISPOSAL
CITY OF COLUMBUS, OHIO

SOME REMARKS ON THE BIOCHEMICAL TREATMENT OF SEWAGE, WITH ESPECIAL REFERENCE TO THE ACTIVATED SLUDGE METHOD¹

By GEORGE T. HAMMOND²

The discoveries of Pasteur and others, in the field of biology, led to the recognition of the necessity of sewage treatment, not only to prevent a nuisance, but also as a protection to the community from disease.

At quite an early period the filtration of sewage was proposed and undertaken in England, but the real nature of purification by this means was not understood. It was supposed that the effect of the filter medium was physical and mechanical, a kind of straining out of suspended matter, and it was not until the discoveries above mentioned and experiments had been made that the real nature of the filtration process became understood.

¹ Read before the First Meeting of the American Chemical Society, New York, September 10, 1915.

² Engineer of design and construction, the American Filtration Institute, Philadelphia, Pa.

Report, *Transactions of the American Chemical Society*, 1916.

Meanwhile, various methods were suggested and tried for the treatment of sewage with chemicals. The object at first appears to have been the destruction of the putrescible matters, which was soon found to be impracticable; then the removal of them by means of chemicals effecting a separation of the organic matters from the liquid, and a precipitation thereof as sludge, which could be removed and disposed of separately.

It was also thought that the chemicals might be employed to destroy the biological activities (discovered by Pasteur) or the "germs," as these at first were called, and that this was the most important object to attain; as the study of biochemistry advanced, the absurdity of this object became apparent, until at length no further attempt at sterilization, than disinfection, is thought by most authorities, to be desirable in sewage treatment. It is now well known and recognized that the so-called germs, or as we now call them more correctly, the bacteria, are our allies and agents in sewage treatment, and the only varieties of them we fear and desire to destroy are the pathogenic bacteria: these have their natural habitat in living animal tissue, or in animal organs, and, therefore, are dangerous, but, being adapted especially to life conditions within a narrow range of temperature, are readily destroyed.

Besides various forms of filter beds, sewage application to land under cultivation was employed before the biological processes of oxidation, etc., were understood. Experience had demonstrated their success and usefulness. Of these, the most interesting instances are the extensive farms of Paris and Berlin.

While much was done abroad in the early days of sewage disposal study, especially in England, it was in our own country that the most important experimental results were accomplished, and the honor of carrying the work onward to success belongs, very largely, to the Commonwealth of Massachusetts, and to the Lawrence Experiment Station.

As a result, we now recognize that the object to be aimed at in sewage treatment is biochemical oxidation of the unstable organic materials contained in the sewage, and we employ methods and processes, which make use of bacterial life. If we now use chemical precipitation, we expect that the effluent finally will reach stability by means of natural biological agents, and, as at Worcester, either prepare it for dilution in a river containing myriads of bacteria, or discharge it upon filter beds, removing previously as much suspended matter as possible, to be treated in a more intensified form. We have found that the removal of solids from the sewage, as soon as practicable, prevents their becoming dissolved and saves the expense of removing the organic material after it has disseminated through a vast quantity of water, to handle which is attended with a cost in proportion to its amount and the contained pollution. Such matters as we are able to remove by screens or tanks decreases the burden on filter beds, or on the oxygen content of waterways, into which the sewage may be discharged, where the method employed is dilution.

Following the information published by the Massachusetts State Board of Health, it has become the principal object of sanitary engineers, in designing sewage treatment and disposal plants, to bring together in the most suitable and efficient manner the decomposable materials, the oxidizing bacteria and an abundant air supply for the bacteria. All forms of sewage disposal on land, in the method known as broad irrigation or sewage farming, all filtration methods, such as the sand filter, the percolating or sprinkling filter, called in England a "bacteria bed," the contact filter, etc., no less than the various forms or methods of treatment using compressed air forced into sewage in a tank, or a filter bed, depend upon this fundamental principle, which is also nature's principle, by means of which brooks, streams, rivers, ponds, and indeed all natural waters, are purified. This principle, in short, consists of the biochemical oxidation of the decomposable materials present in foul water or sewage.

Since the discovery of oxidizing bacteria, there has been a continuous evolution or progress in the growth of scientific knowledge on this subject, to the investigation of which some of the foremost scientists have given freely their best efforts.

METHODS OF BACTERIAL OXIDATION

The various methods may be briefly referred to as *Broad Irrigation*, or sewage farming, which, on account of the small amount of sewage that can be applied per acre per year, is not now in much favor. As already mentioned, Paris and Berlin still employ the method, although the latter has at Wilmersdorf a large percolating filter plant. *Sand filtration*, instances of which may be seen at Saratoga, N. Y., and Worcester, Mass., which latter has 70 acres of sand filter beds. *Contact beds*, or *contact filters*, as employed at Manchester, in England, and at many places in Europe and America. *Sprinkling*, or *percolating filters*, which may be seen at Salford and Birmingham in England, Wilmersdorf in Germany, Baltimore in this country, and many other places, both in Europe and America, which are doubtless the most efficient sewage treatment plants in operation at present.

These plants all depend for their treatment upon the cultivation of bacteria on the surfaces of media of various forms, over which the sewage is applied, after having, to a greater or less extent, received some preparatory treatment by means of screens, tanks, etc.

The most recent method of sewage treatment is by means of compressed air discharged into it in a tank. This has been denominated the "activated sludge method."

Aeration of sewage in a tank by means of compressed air is in reality only a reversal of the method by filtration. In the former the bacteria are not only afforded their necessary oxygen by compressed air, but they are moved up and down through the liquid and brought into contact with it until the entire liquid is caused to have the greatest possible number of these agents of oxidation within it, and until they have by their life processes converted the unstable organic contents into a stable condition.

In the filter the same identical result is secured by applying the sewage to a bed of sand or of broken stone, the particles of which are surrounded with films formed of bacterial and other growths, over which the sewage percolates in the presence of abundant atmospheric air. The liquid in passing through the filter flows over the surfaces of the medium, and the more vasicular character of the latter, the better.

Mr. Wilkinson, of Manchester, England, has given us a graphic presentation of the relation of the ordinary filtration to the activated sludge process:

"On starting up a new filter, the sewage shows but little change after passing through, but, as time goes on, a growth shows itself in the body of the filter, in what may be termed the stationary framework, and colonies of bacteria accumulate there, which attack the sewage and effect putrefaction, or oxidation, of the organic matter.

"These bacteria being mainly aerobic, an ample supply of air is necessary, in order that they may thrive, hence the necessity for adequate ventilation of the underdrainage. * * * Let us take a given volume of the stationary framework from a ripe filter, and carefully remove the coating, or growth, throughout the material. We shall then have a certain volume of what may be termed sludge, rich in aerobic bacteria, which may be referred to as the activated sludge of this particular process. In the new process (activated sludge), the active sludge is circulated throughout the sewage in the presence of air, as against the present-day practice of passing sewage in thin films over active sludge retained on a stationary framework, as in the case of percolators.

"The real problem then, is as follows: To ascertain the most economical method of applying air to sewage with maintenance

of complete circulation of the activated sludge, without any formation of dead banks of material. The problem may now be said to resolve itself into one of reproducing in a tank the changes which take place in a percolating filter. We have our tank, which represents the walls and floor of the filter; we have our colonies of bacteria and the air necessary to support their life; and what we require to do is to provide means for supporting an even distribution of this life throughout the body of the tank, other than by allowing the bacteria to adhere to a stationary framework, such as stone, slate, or clinker material. Compressed air will both insure sufficient agitation and effect the desired results as regards preserving uniform contact and even distribution in the liquid. * * * "

Experimenters had been investigating the treatment of sewage by forced aeration for many years, but the honor of naming the process was reserved for an English chemist. In a happy moment of inspiration, Dr. Gilbert Fowler, of Manchester, England, bestowed upon it the name "Activated Sludge." As is well known, the process antedates the name. Dr. Fowler saw the work of Clark at Lawrence in 1912, and has given the latter credit for his share in the development of the process.

The method itself was, in fact, the offspring of many fathers. It would scarcely be worth while in a brief paper like this to attempt the determination of the question of parentage. It will serve our purpose to call attention to the fact, that previous to the experimental work of Colonel (now General) William M. Black and Professor Earle B. Phelps (a member of this society), at the Brooklyn Twenty-Sixth Ward Sewage Works in 1910, there had not been demonstrated anywhere a practical method of sewage treatment by the direct application of compressed air. The elaborate experiments made by these investigators with various forms of tanks of sufficient size to make the tests on a working rather than a laboratory scale, were described fully in a report made by them to the Board of Estimate and Apportionment of the City of New York, dated February 16, 1911. As stated in the report, it was found possible to reduce the demand of sewage for oxygen 33 per cent to 50 per cent in a retention period of about 3 hrs., with the application of about two volumes of air per volume of sewage and by larger volumes of air and longer application, to obtain complete stability. As the cost of the process appeared to be low, about \$2.00 per million gallons of sewage for the air, this method seemed to be a very attractive means of treating sewage. It was, however, recommended that further and larger experiments be conducted, or that the old sewage treatment plant at the Twenty-sixth Ward Works be equipped for using the method in a full size trial. As the latter measure was found to be impracticable, on account of the expense of equipping the old plant for the new method, it was determined to establish an experiment station for the study of sewage treatment at this location, to try out this and other methods of treatment, and \$50,000 was provided by resolution of the Board of Estimate and Apportionment, dated April 18, 1912, to carry out the work, which was placed in the charge of the Bureau of Sewers, of Brooklyn.

The experimental work of this plant began in 1913, and has continued up to the present. The results to last fall, so far as aeration and activation methods were concerned, were presented to this society in a paper read by Mr. E. J. Fort, Chief Engineer of Sewers, Brooklyn, at the meeting held at Urbana, Ill. Since that time the work has continued along those lines, but varied somewhat from the experiments described by Mr. Fort. It is not our intention to go over the ground already so ably covered, especially as the final report of the work of the Experimental Station will soon be available.

As this paper is presented by an engineer, it will be excusable if the chemical side of the subject is left for the chemist.

AERATION METHOD FROM THE ENGINEER'S VIEWPOINT

From the engineer's point of view, the most interesting question to be considered relates to the availability of the method for employment in the treatment of sewage preparatory to disposal. The engineer's problem and the chemist's are, no doubt, the same whenever the technical side of sanitation is to be considered; but, ordinarily, the engineer has also a duty to perform that perhaps is less scientific, but scarcely less important in effect, for he is charged with the design and installation of sanitary structures to meet the pressing needs of rapidly growing towns and cities, the tax papers of which are usually overburdened already with public expenditures. These structures must not only be designed and built, but also maintained at a considerable yearly cost, a mistake or failure in which is little short of a public calamity. The engineer's problem, in short, is quite as much related to municipal affairs and the limitations imposed by financial and political conditions as to the technical problems.

The engineer is taught by his daily practice to recognize that the sewage treatment and disposal system which experience and experiment demonstrate to be the most reliable, economical and simple in operation, which, without offense or nuisance, will insure an effluent satisfactory and suitable at all times for discharge under local disposal conditions, is the most available for the purpose.

This is a conservative view and, if always adhered to strictly, there would, perhaps, be few rank failures; but, on the other hand, there would be but slow progress in the science of sanitation. Had we been content with the early methods of treatment, we might, perhaps, have perfected some of them to a much greater degree, but we would not have made much advance in our profession. While we ought to be conservative, we ought also to have our eyes open for new things, in order that we may give our clients the benefit of new ideas and inventions.

So much has been published about the principal activated sludge plants, that it would be scarcely necessary to give a particular description or account of either of them. The writer visited nearly all of them during the winter and spring of the present year, and has been in communication with them all very recently.

The method certainly produces a clear sparkling effluent, without smell or nuisance. The ground required for installing a plant is probably the least for any method of treatment, and the tanks are less costly than filter beds that would produce an effluent of equal stability. The removal of bacteria effected, as observed, in the effluent is remarkably high. The sludge contains constituents that make it of value for use in the manufacture of fertilizer. So far the picture is rosy. But there are many difficulties that make dark shadows in this fine prospect, and while it is true that progress is being made toward their solution, they must be recognized and given due weight under the present condition of the art.

The amount of sludge which must be disposed of easily stands first among these problems. This varies from 2,000 to 4,000 gallons, or even more, per 1,000,000 gallons, with a water content of from 90 to 96 per cent. This sludge is highly putrescible unless dewatered, which is an expensive operation. Success in dealing with the problem is reported by Mr. Hutton, from Milwaukee, but the details and cost data are not yet available. None of the other plants report that they have solved the difficulty, although discussing remarkably new methods in by a few experiments.

At the Armour & Co. plant at the Chicago Stock Yards, experiments are still under way with dewatering methods, and their conclusions are reported as not final. It seems, however, at the present time, that a battery of methods, flow settling tanks, which decrease moisture in sludge and permit

followed by a Worthington, or similar, press, is the best method up to the present. The sludge, after pressing, is dried by a direct or an indirect heat drier to 10 per cent moisture, which is necessary, in order that the material may be used in making fertilizer. The cost of this method is such that the commercial value of the product must be considerable, in order to make the treatment available. If means of transporting the dried product to market are costly, or fail at a critical moment, serious trouble may arise.

The only other methods mentioned are drying on sand, or Imhoff sludge beds, or discharging wet sludge upon land by various means.

One does not feel like asserting that the requirements of sludge disposal have as yet been successfully supplied at a cost that mere sludge disposal will stand. The value of the dry material as a fertilizer base is, however, considerable, if markets are available, and transportation sufficiently easy from the plant to the factory.

"Our further analyses of the sludge for fertilizer value," writes Mr. Noble, of Armour & Co., "shows it will run between 4.5 and 5 units of ammonia, the value of it being, therefore, about what we have previously estimated, namely, \$9.00 to \$10.00 per ton in the dried state." These figures, it will be observed, refer to the sludge derived from the stockyard sewage, and will probably not be equalled with ordinary domestic sewage.

It is quite probable that this difficulty can be overcome to a considerable extent by means directed to the removal of sludge-producing material from sewage previous to the treatment, as for instance, by screens or tanks. So far no complete data are obtainable on this point, but experiments seem to justify the expectation of success. Experiments are needed to show how fine such a screen should be, for if it removes too much suspended matter, the process may be seriously interfered with. So far as the writer can speak from experience, the Imhoff tank is not likely to prove as successful as the screen in this preliminary treatment, as the tank takes out too much of the best size material in suspension for the activation process. But this is not stated as having been proved conclusively, and more data are needed on the point. If an Imhoff tank is used, the surplus activated sludge might be reduced to the condition of Imhoff sludge, by being introduced into the digestion chamber, as suggested to the writer by Mr. Leslie C. Frank sometime since.

While the conditions at Milwaukee are rather unique and favorable to the activated sludge method, as well as to the transportation of the dewatered sludge, it is doubtful if other cities less favorably situated will feel justified in going to the expense of installing extensive plants for dewatering sludge. The combination of a commercial venture with sewage disposal need not necessarily prove a failure, but the chances against its success do not make the project seem attractive.

A recent communication from Mr. Hatton states: "After elaborate experiments on the dewatering of sludge and sludge drying, we find that there are very few problems connected therewith that have not already been solved in industrial establishments where material of like character must be treated. Either of two kinds of presses reduce the moisture from 99 per cent to 75 per cent, and there is no difficulty by either the direct or indirect dryer to reduce this moisture from 75 per cent to 10 per cent or lower."

This statement is of great interest and it seems very promising. It seems to the writer, however, that in most places the problem will always be, how to minimize the formation of surplus sludge, and how to get rid of what does form without dewatering it in a plant especially provided for this purpose. If it cost more per ton to dewater than the sludge will sell for, or the net value obtainable therefor, then even though the

value figures at \$9.00 to \$10.00 per ton, few will care to undertake such a venture, or at least go further than what would be the fair cost of sludge disposal by other means.

PARTIAL DRYING OF SLUDGE

Dewatering sludge is a matter of difficulty and expense and cannot but add a burden to the maintenance of a plant. This may be provided for in large plants, if the value of the sludge recovered warrants; but in small plants it would probably lead to a nuisance and would not be usually undertaken where the sewage amounts to less than 10,000,000 gals. per day. To install the necessary plant would be expensive, and the cost of maintenance out of proportion to the possible benefit. In great cities like Milwaukee, Chicago, Cleveland, etc., where transportation can readily be secured to a fertilizer factory, it may succeed, but in smaller places its success is doubtful, and unless new methods by which it may be cheaply and efficiently accomplished are found, it probably will seldom be undertaken. It is well recognized that the problem of dewatering is mainly one of proper design of plant and of cost. The apparatus for use in this process has long been known and used in the various trades. But the application of such apparatus to the sludge problem is as yet undeveloped, and in the stage of experiment. It is quite possible that the best method available has not yet been discovered.

The Schaefer-ter-Meer centrifugal sludge dryer, used on a large scale at Frankfurt-on-the-Main, and at Hannover, in Germany, has been thoroughly developed as a sludge-drying machine, which can handle with success large volumes of sludge and dry it sufficiently to burn in an incinerator plant. This machine was experimented with at our Jamaica Sewage Disposal Plant, and tests show that operating on sludge containing 91.5 per cent of moisture, from a lime precipitation tank, it effected a removal to 64.2 per cent moisture, and operated continuously while effecting this removal. The cost of this method, as shown by the tests, was rather high, but the tests were really not a complete exhibition of what these machines can do.

The Dickson method of sludge dewatering, which employs brewers' yeast to effect a separation of water and sludge, also offers a possible means of success, and has the advantage of a fully developed system by means of which the dewatering and drying can be carried from the commencement to the completion of the process, without extra handling between the various steps. The dried sludge leaves the apparatus in bags ready for shipment to the fertilizer factory, or may even be made a complete fertilizer ready for market as it leaves the plant.

So far the cost of these methods has not been determined for activated sludge, but the writer believes it will not be lower than the cost for drying ordinary sludge.

It is quite possible that the sludge may be destroyed by a septic process where the amount of it is not great enough to make dewatering an attractive measure. But little study has been done in this direction and much is desirable.

As the sludge tends to break up and dissolve with overaeration and in doing so diminishes in volume, this gives promise of still another method that so far has received but little study.

We have found at the Brooklyn Experiment Station that by means of long-continued aeration, activated sludge may be broken up and reduced to 10 per cent or less, of its original volume. The problem is to get rid of the water during this reduction, so as to decrease the volume to be aerated. That this may be done seems fairly possible.

Taking the surplus activated sludge as a special problem, it would seem that we should be able to design a plant to reduce its putrescible contents by means of biological agencies. If we may treat the sewage by "activation," why may we not also find such a means of treating the sludge? Since we have found that long-continued aeration will reduce it to a very small vol-

ume, cannot we find means of doing this without excessive cost for air?

We observe that after a short aeration period with activated sludge, clarification of the sewage takes place, and that out of a million gallons we have a net amount of 2000 to 4000 gals. of sludge, which we must dispose of separately, and this is about 99 per cent water. Clearly we can afford to aerate this small volume for a long time, if necessary, to effect its reduction to a form which will not cause a nuisance. Experiment shows that about half of this volume is free water which can be removed by an hour's tankage, and that 24 hours' aeration of the sludge will separate a large part of its remaining water, and the bacteria will keep on working for us.

Thus we are continually treating a diminishing quantity of sludge, and the problem of plant design seems the principal problem.

AERATION PROCESS

Another matter that is receiving the most careful attention is the aeration process. Mr. G. L. Noble, of Armour & Co., writes: "We are attempting, by experimental work, to decrease the period of aeration by the introducing of pure cultures of organisms from activated sludge, which appear to be especially active in producing nitrification. Our work, however, along this line is only in its infancy, and we have no data to report, * * * ; we have found that the action of the organism is inhibited by sewage warmer than about 95° F." This shows the trend that experimentation is now taking, and suggests great possibilities; also that we have yet very much to learn about the method.

In the matter of design of activated sludge plants, much might be said about what we have still to learn. The shape, depth, size and arrangement of tanks is as yet in the study period, and this remark applies also to the best method of supplying the air to the sewage in the tanks.

The earliest experiments, those made successfully by Messrs. Black and Phelps, at Brooklyn, in 1910, out of which it is quite possible that the entire activated sludge invention, directly or indirectly, developed, employed perforated pipe grids; similar methods were used elsewhere, until in England, Messrs. Arden and Lockett used a porous material in their experiments with success. Following this, similar material came into use in this country, and this, while still employed extensively, has probably achieved no greater success than pipe grids. In the writer's work, both methods were employed, but the pipe grid proved much the best on the average.

In conclusion, it may be said that while a great deal remains to be learned about the problems which we have referred to, as well as others, and many difficulties must be overcome, the activated sludge method seems very promising; and while it may not prove as cheap as other methods of sewage treatment, there are many conditions which will favor its use. A word of caution should be added, that the method is still in the stage of experiment and in using it one should frankly admit that there is much to be learned about it before full confidence is justified.

215 MONTAGUE STREET
BROOKLYN, NEW YORK

RE-AERATION AS A FACTOR IN THE SELF-PURIFICATION OF STREAMS

By EDGAR B. PHIPPS

Received December 2, 1916

In the administrative control of stream pollution, the economic principle of maximum utilization of a resource may usually be applied to divide streams into two major groups, depending upon whether or not they must be used as sources of domestic water supply. In the class of water supply streams,

permissible pollution is limited in bacterial terms, with secondary reference to organic matter *per se*, and to such special impurities as acidity, iron or harmful mineral compounds. In the case of streams which are not used as sources of domestic water supply, or where self-purification intervenes to such an extent that permissible pollution is not limited by water supply standards, nuisance conditions become of controlling importance. Physical effects, visible floating material, discoloration, oily scums and deposits upon the bottom and side of the channel, and chemical changes resulting in the depletion of the dissolved oxygen and consequent odors as well as destruction of fish life, all may contribute to the general condition of nuisance. Each kind of effect has its specific remedy and a properly designed treatment plant is one which accomplishes the specific improvement required without involving additional and unnecessary expense in dealing with non-essentials. In fact sewage treatment may be overdone. Consider a stream providing ample dilution but with a sluggish flow. Removal of settleable solids by a tank is obviously required. Now if zealous authorities insist upon the addition of a trickling filter and stop there then conditions in the stream are made actually worse because of the additional settleable solids discharged, whereas the additional reduction in oxygen demand is of no advantage with the ample dilution present.

Of the various types of sewage treatment, those involving oxidation of organic matter are at present by far the most expensive, and in our endeavor to protect streams against nuisance conditions every effort should be made to utilize the maximum oxidizing power of the stream itself. A stream will oxidize sewage according to its own oxygen resources which are of two kinds, initial dissolved oxygen and oxygen obtained through reaeration. It has usually been assumed in discussions of nuisance conditions that the dilution ratio is the essential criterion of safety but this assumption has led to unfavorable results and a simple computation with the data of modern sewage chemistry will serve to show its fallacy.

The oxygen demand of the sewage of the District of Columbia has a summer value of about 300 p. p. m. The normal sewage flow is at a rate of about 0.25 sec.-ft. per 1000 population. The summer value of the dissolved oxygen in the Potomac above the city is approximately 8 parts. Allowing a depletion of oxygen down to 4 parts, a minimum value for non-nuisance conditions, there is required a dilution of 1 : 75 or nearly 19 sec.-ft. per 1000 population to satisfy this oxygen demand by mere dilution. Experience has shown that in open river conditions and with reasonably pure diluting water a stream flow of 6 sec.-ft. per 1000 is ample for the prevention of nuisance, and the Chicago Drainage Canal was designed upon a basis of 3.3 sec.-ft. In the case of the rivers with 6 sec.-ft. per 1000 it is evident that over two-thirds the total oxygen requirements are satisfied by reaeration. In a canal purposely designed to avoid any interference with smooth hydraulic flow, reaeration is at a minimum and it is not surprising that results are unlike those obtained in rivers under like dilution conditions. In so far as disposal of sewage by dilution in a running stream is a process of true purification and not merely one of destructive of stream values, it depends upon self-purification of the stream in which reaeration is an essential factor. Curiously this important matter has received little or no scientific attention.

BASIC PRINCIPLES OF REAERATION

In the present discussion of reaeration as a factor in the self-purification of streams, certain underlying assumptions will be stated and discussed for the purpose of establishing the present status of our information and the proper direction of future study.

1. Pure water exposed to the air at a given temperature, will dissolve atmospheric oxygen up to a maximum amount, this value being known as the saturation value.

The solubility of a gas in water is proportional to the gas pressure. Since the oxygen pressure in the air is approximately one-fifth an atmosphere, the true solubility of oxygen in water exposed to pure oxygen at atmospheric pressure, is about five times as great as the so-called saturation value. In the presence of green plant life, exposure to nearly pure oxygen is frequently observed and oxygen values of several hundred per cent of saturation are frequently recorded. A correct knowledge of the true physical relation existing is quite necessary to the understanding of the apparently abnormal results which have often in the past been ascribed to faulty chemical analysis. The solubility of oxygen is also a temperature function. Tables of saturation values are to be found in any standard work on water analysis. Approximately 10 parts by weight of oxygen will dissolve in 1,000,000 parts of water at 16° C. and the solubility increases roughly by about 2 per cent per Centigrade degree decrease in temperature and *vice versa*.

2—Self-purification in a polluted stream is the result of the biochemical oxidation of organic matter and requires oxygen for its consummation. The more concentrated the organic matter the greater the rate of oxygen depletion.

American sewages have a biological oxygen demand of from 200 to 400 p. p. m. This means that if diluted with saturated water at 16° C. they would exhaust the oxygen supply of that water in dilution ratios of one part of sewage in from 20 to 40 parts of water. With greater dilutions corresponding partial oxygen depletion will result.

3—A stream saturated with oxygen will withdraw no more oxygen from the atmosphere. If partially depleted it absorbs additional atmospheric oxygen and the rate of such absorption or re-aeration while dependent upon many other factors is directly proportional to the state of depletion.

4—Under any given condition of pollution and re-aeration, a point of maximum oxygen depletion is reached, somewhere down-stream, at which the rate of depletion and the rate of re-aeration are equal. This will be termed the critical point since it determines the maximum effect of the pollution.

Above the critical point the oxygen content of the stream is diminishing, below it is increasing. The location of this point is evidently conditioned by the time of passage or by distance in hours rather than in miles. It is also a temperature function since depletion is accelerated by higher temperatures. As the velocity of stream flow is usually at its minimum during the hottest months, the critical point moves up-stream rapidly with increasing temperatures.

5—The condition of the stream at the critical point, representing a balance between rate of depletion and rate of re-aeration, is, at constant temperature, a function only of pollution and of re-aeration.

6—The capacity of a stream to dispose of sewage within any specified limits of nuisance is obviously measured by the condition of the stream at the critical point. Since it is at a minimum at maximum temperature and minimum stream flow, it becomes under fixed temperature and flow conditions a function of re-aeration only:

7—The capacity of a stream for re-aeration under extreme conditions of high temperature and low stream flow, therefore, measures its capacity to receive and dispose of sewage by self-purification within any prescribed limits of stream depreciation or nuisance.

In the past, although the relation of dissolved oxygen to the condition of a stream, as well as the fact of re-aeration, have been fully recognized, the relations set forth in the above principles have been partially or wholly overlooked because of imperfect ideas of the rôle of oxidation.

Mr. Hering evidently voiced the best opinion of the day when he wrote in 1887,¹ "Oxidation and total destruction of sewage

by decomposition was for a long time thought to be the main cause for the clarification of polluted rivers. To-day it is known to be but a minor cause, compared with dilution and subsidence."

Observation made upon the old Michigan Canal showed that the sewage which, with a dilution in water of 1 cu. ft. per sec. per 1000 population, and after flowing 30 miles in about as many hours, was quite offensive, became inoffensive after discharge into the Desplaines and later into the Kankakee River and with dilution increased to about 3 ft. It was erroneously concluded that the same inoffensive condition would have been obtained throughout by a primary dilution in 3 sec.-ft. per 1000 inhabitants.

IMPORTANCE OF OXIDATION DATA

Such a conclusion followed logically from the assumption of the minor importance of oxidation and the latter was apparently justified by the chemical methods of the times. Oxidation was measured in terms of nitrogen rather than oxygen and it is only within the past few years that the chemist has been in possession of methods which correctly record the progress of the oxidizing reaction.

In 1906, Hering and Fuller reported upon this matter further, and stated,¹ "The disposal of sewage by dilution depends upon the amount of oxygen in the diluting water being sufficient to prevent putrefaction of the organic matter in the sewage as the latter undergoes bacterial decomposition." Their recommendations were based upon results obtained in Massachusetts upon flowing streams, and were to the effect that a dilution of not less than 3.33 sec.-ft. per 1000 population would be necessary, after the elimination of trades wastes. Throughout the discussion emphasis is laid upon the oxygen initially present in the dilution water.

The application of observational data, obtained upon running and comparative shallow streams where conditions are ideal for re-aeration, to deep canals with sluggish flow and minimum re-aeration conditions cannot but lead to unsatisfactory results. A large part of the residual oxygen found in streams of the former type can now be shown to have been derived from natural re-aeration. If it be assumed that such residual oxygen was initially present and had not been utilized by the sewage, the capacity of the sewage to consume oxygen is thereby underestimated and the application of the data to streams of the second type with deficient re-aeration will lead to insufficient dilution and a condition of nuisance not anticipated.

As early as 1900, Palmer² found the dissolved oxygen at the lower end of the sanitary canal in August to be 5.88 per cent of saturation, increasing to 70 per cent after passing the dam. Wisner³ reported in 1911 the frequent absence of oxygen for many miles above the lower dam at Lockport with a dilution of about 3.3 sec.-ft. per 1000. Passage over the dam increased the dissolved oxygen to about 19 per cent of saturation. The relative importance of dilution and re-aeration will be appreciated if it be noted that simple passage over the dam had the effect of a 25 per cent increase in saturated dilution water, or was equivalent to raising the dilution from 3.3 to 4.1 sec.-ft. per 1000.

Numerous other examples of the same sort are to be found in the literature but enough have been given to illustrate the point.

The problem of the moment deals not so much with present conditions as with the future. It is of the utmost importance to determine the future effect of gradually increasing pollution upon any given stream. In connection with purification treatments it is highly desirable to know what degree of stream improvement may be anticipated from any specified degree of purification in order that the cost of various treatments may be properly balanced against the benefits to be expected. Finally there frequently arises the problem of the effect of a very large

¹ Fuller, "Sewage Disposal," 1913, 252.

² Report on Streams' Examination, Sanitary District of Chicago, 1903, 95A.

³ Quoted by Fuller, "Sewage Disposal," 1913, 214.

¹ Quoted from Fuller, "Sewage Disposal," 1913, 227.

pollution of a hitherto unpolluted or slightly polluted area, following the location, for example, of new intercepting lines and discharge points. The essential elements of the specific and the general solution are as follows: Determination of the extent of pollution at a given point, measured in terms of the new sewage chemistry which deals with oxygen relations, and of the degree of self-purification and amount of residual oxygen at some lower point, together with temperature and hydraulic data, furnish the basic facts. The oxygen requirement and rate of oxygen depletion are then known. The condition of the lower station in the same terms is calculable. The actual condition compared with the calculated gives the re-aeration factor for the stretch. This must be determined for the same stretch over a considerable period of time in order properly to include the variations in hydraulic conditions. In particular the re-aeration is a function of depth, velocity of flow and degree of turbulence. Similar data may be obtained at the same time over other typical stretches and the relation of the re-aeration factor to other physical and hydraulic conditions noted. From such a comprehensive study there will be obtained eventually the necessary data for the determination of the re-aeration constant of the stream in question under various physical conditions. Then the result of increasing or decreasing pollution, always measured in proper terms of oxygen demand, will be readily calculable. Repetition of the study upon another stream will give similar data for that stream and also permit some study of the effect of stream type upon re-aeration. With accumulating data of this sort it is not unreasonable to anticipate that the fundamental constants will ultimately be derived with which the capacity of any stream to receive and dispose of sewage within stated nuisance limits may be determined in advance. Such constants will furnish the only rational basis upon which to estimate the effect of increasing or decreasing pollution, or the degree of purification necessary or desirable in any case. As these matters have been shown to be of primary importance in any application of the principle of conservation to streams, the importance of work of this character is obvious.

In the foregoing discussion it will be noted that no reference has been made to either of two distinct phases of the pollution problem, the matter of dangerous bacteria and that of sludge deposits. Both are separate and distinct problems capable of solution independently of the problem of oxygen supply and leading to nuisance of distinct character. The presence or absence of these factors does not influence the methods or conclusions of this discussion, although the matter of deposits does enter the analytical problem.

TURBULENCE OF STREAMS A FACTOR

An important conclusion of this discussion will be touched upon briefly in passing. Re-aeration is conditioned among other things by the degree of turbulence of the stream. In quiescent water a diffusion gradient is established which practically stops re-aeration. The effect of dams and rapids in increasing aeration is not so much dependent upon the momentary exposure of the water but is largely due to the mixing action whereby the diffusion gradient is broken up and re-aeration permitted to proceed. In artificial canals turbulence is avoided as largely as possible. The effect of a single dam upon de-aerated water has already been shown to be equivalent to a large increase in initial dilution. Where dilution is for any reason limited, the capacity of sluggish and non-turbulent streams can be greatly augmented by providing for artificial turbulence at certain points in their course. Such turbulence need not be of the character of a fall, nor need it cause a loss of head. A number of mere overflows or "boils" will be found more efficient than a single large fall.

The determination of the re-aeration coefficient of a stream has been undertaken for the first time in connection with the investigation of the Ohio River now being made by the U. S. Public Health Service under the direction of P. A. Surgeon Wade H. Frost. The actual analytical problem is exceedingly complex and the mathematical reduction and analysis of the results is both complicated and laborious. The work has progressed to a point at which it is obvious that results of value and consistent with the theory here stated have been obtained.

SUMMARY

In the development of the maximum economic use of a stream, its capacity to dispose of sewage and waste within any specified degree of depreciation or nuisance is a factor of first importance.

This capacity is limited by stream conditions and is a function of the capacity for re-aeration.

For this reason the dilution unit is an improper one for a discussion of nuisance and self-purification and results obtained upon one stream, expressed in such units, are not applicable to another.

Re-aeration is capable of experimental determination not only in single instances, but in terms of general applicability.

Its determination in such general terms involves laborious work of a hydraulic and analytical nature. A beginning has been made along this line in the Ohio River Investigation by the U. S. Public Health Service.

25TH AND E STREETS
WASHINGTON, D. C.

CURRENT INDUSTRIAL NEWS

THE GERMAN NITROGEN INDUSTRY AND THE FUTURE OF GERMAN AGRICULTURE¹

During the last ten years German agriculture has succeeded in increasing the yield of the land to an extraordinary extent, and in this connection a comparison with France is of interest.

Thirty years ago the yield per hectare in France was about the same as in Germany. Since then the yield in France has risen about 0.1, whereas Germany has nearly doubled her yield as indicated below:

WHEAT YIELD PER ACRE IN 100 KILOS		
Yearly Average	1881-86	1911-13
Germany	13.8	22.3
France	17.0	13.6
Russia	7	6.9

This excellent result is partly due to Farmers' Associations, Agricultural Schools and the employment of modern methods.

¹ Extract from the *Frankfurter Handelsblatt*, May 29, 1916.

but chiefly to the ever-increasing quantities of fertilizers used. The following is a comparison of the amounts of fertilizers used per hectare during the last few years:

	Potash	Nitrate of Soda
Germany	17.08 kg.	8.10 kg.
France	0.806 kg.	4.10 kg.

Germany has always been well provided with potash, but up to about 10 years ago had to rely almost entirely on imports of nitrate of soda for her nitrogen. The following table shows the increase in the imports of nitrate and in this connection it should be mentioned that about 10 to 15 per cent of these quantities have been used for industrial purposes.

GERMAN CONSUMPTION OF NITRATE OF SODA (METRIC TONS)									
1880	1885	1890	1900	1905	1911	1912	1913	1914	1915
58,000	170,000	250,000	340,000	410,000	510,000	500,000	500,000	500,000	441,000

Gradually, however, the German Chemical Industry has been building up a substitute for nitrate in the form of sulfate of ammonia. At the beginning of this century the production in

Germany was still small and imports amounted to about 48,000 tons per annum. Since 1906, however, things have changed and Germany has exported larger quantities than she has imported.

The development of our consumption of sulfate of ammonia is shown by the following table:

	Imports	Exports	Excess of Imports over Exports	Excess of Exports over Imports	Product from Coke Ovens, etc.	Total Consumption
1888.....	35,000		15,000			
1900.....	23,000	2,000	21,000		104,000	125,000
1909.....	58,000	59,000		1,000	281,000	280,000
1910.....	31,000	93,000		62,000	313,000	251,000
1911.....	24,000	74,000		50,000	418,000	368,000
1913.....	35,000	76,000		41,000	501,000	460,000

The increase in the use of sulfate of ammonia has, therefore, been extraordinarily rapid. In the year 1913, 460,000 tons of ammonia were used as against 750,000 tons of nitrate of soda. Taking the manurial value of sulfate compared with nitrate as 4 to 3, the 460,000 tons are equal to 610,000 tons of nitrate, so that the two competitors were running each other pretty close already in 1913.

In 1914 synthetic sulfate of ammonia first entered the lists as a competitor of nitrate of soda on a practical scale. Theoretically, the possibility of producing ammonia by purely chemical means had long been known, and the well-known Norwegian method was first of all developed, the German chemical trade being largely interested.

The difficulties in introducing this process into Germany on account of the lack of water power forced the Badische Aniline and Soda Works to develop a process of their own. In conjunction with Professor Haber they proceeded to do this, putting all their energy into the Haber process and giving up their Norwegian interests.

At the beginning of the war, the Badische were producing on a scale large enough for one single works, but yet not sufficiently large to compensate for the loss of nitrate of soda. In the first year of the war there was accordingly a considerable shortage of fertilizers for agricultural purposes. But our chemical industry quickly came to the rescue, and should the blockade of Germany be prolonged, we shall soon be in a position to deliver more nitrogen for agricultural purposes than formerly consumed in peace times.

The following particulars give an idea of the extraordinary rapidity with which the Haber process has developed. The capacity rose from 30,000 tons in 1913 to 60,000 tons in 1914, and about the middle of 1915 the output of the original works was about 150,000 tons. For 1916 the production is reckoned at 300,000 tons. It is no secret that the Badische Company has lately put up further large plants in another part of Germany, so that its producing capacity for 1917 will no doubt be considerably in excess of 1916.

Assuming that the Haber production in the near future will reach 500,000 tons, this process alone will represent the production of an amount of nitrogen nearly equal to the amount of nitrate of soda we used to import. In passing, it may be mentioned that such a production at a price of \$60.00 per ton would represent an annual turnover of 30 million dollars for this one firm.

In addition further large quantities of nitrogen have been produced with state aid in the form of cyanamid, with the aid of which German agricultural needs can easily be met. Furthermore the whole tendency in the coal industry has been towards the increase of by-product ovens. Up to the time when the war broke out, about one-fifth of our coal was coked, but the war has forced resort to coking to a far greater extent than before. Everything points to the conclusion that in the near future the direct combustion of coal will be recognized as altogether uneconomic and disappear, and its place be taken by by-product processes. This of course means increased recovery

of ammonia from coal. Assuming that only double the quantity of coal hitherto used is employed for the recovery of ammonia, the increase in sulfate of ammonia production amounts to 450,000 tons. Based on the above the following comparison between 1913 and 1917 can be made:

Sulfate of Ammonia.....	460,000 tons =	92,000 tons Nitrogen
Norwegian Nitrate of Lime.....	35,000 tons =	4,500 tons Nitrogen
Cyanamid.....	30,000 tons =	6,000 tons Nitrogen
Ammonia-Haber Process.....	20,000 tons =	4,000 tons Nitrogen
Total.....		106,500 tons Nitrogen
plus Nitrate of Soda.....	750,000 tons =	116,000 tons Nitrogen
Grand Total.....		222,500 tons Nitrogen

Sulfate of Ammonia.....	700,000 tons =	140,000 tons Nitrogen
Norwegian Nitrate of Lime.....		
Cyanamid.....	400,000 tons =	80,000 tons Nitrogen
Ammonia-Haber Process.....	500,000 tons =	100,000 tons Nitrogen
Total.....		320,000 tons Nitrogen
Nitrate of Soda.....		None

If these statements are only approximately correct our own production will already next year be greater than our consumption before the war including the amount of nitrate of soda imported. In case of need, therefore, we can altogether do without the importation of nitrate of soda for agricultural purposes. This does not mean, however, that the import of nitrate of soda is either unnecessary or undesirable. Nitrate will remain very much wanted for certain purposes and agriculture will be glad to make use of it as long as prices remain competitive, especially in view of the amount of German capital invested in the Chili nitrate industry. If our home production of nitrogen can be supplemented by nitrate of soda, so much the better, for our experts are agreed that we cannot give our agriculture enough nitrogen. The dire necessity the war has brought upon us, forcing us to help ourselves in all sorts of ways, has in this respect added a valuable gift for the future in that these new sources of nitrogen will enable us to increase our agricultural production.

All sorts of possibilities are involved. It would be thoroughly in keeping with the character and accomplishments of the German Chemical Industry to proceed with the production of combined fertilizers after having successfully solved the problem of the synthetic production of ammonia. These new fertilizers may perhaps some day drive out the old material in the same way that synthetic indigo drove out the natural product.

It is not impossible that Germany may become the great exporter of nitrogenous fertilizers. The most important point, however, is the increase in the productivity of our land. The economy of 9,000,000 pounds per annum on nitrate of soda imports cannot be compared in importance with the saving in our imports of wheat and foodstuffs which would be effected by means of increased fertilizing.

FORMATION OF TOLUENE BY ACTION OF ALUMINUM CHLORIDE

According to *Chem. Soc. Abstracts*, F. Fisher and H. Niggemann [*Ber.*, 49 (1916), 1475] have studied the conditions for the most productive degradation of xylene to toluene by the action of aluminum chloride. The best temperature is found to be that of boiling xylene, while 2 to 4 per cent of aluminum chloride is quite sufficient and 2 hours long enough for the purpose. Under these circumstances, xylene gives an approximate 12 per cent yield of toluene and also benzene and polymethylated benzenes. Benzene is decomposed by the energetic action of aluminum chloride but without producing more than traces of toluene. Experiments with xylene-benzene mixtures have also been carried out with the hope of transferring a methyl group from the one to the other, but this ingenious idea has not yet led to definite results.—A. McMILLAN.

CONDENSER-TUBE REPAIRS

A method of mending condenser tubes is described in a recent issue of the *Electrical World*, and it is said to have effected considerable saving. The method consists in cutting out the section containing the break and inserting a new one which is joined with the other sections by an inner sleeve or ferrule about $2\frac{1}{2}$ in. long. The latter is composed of a piece of tubing about half as thick as the condenser tube and has a diameter that will make it fit tightly in the sections to be joined. Both the ferrule and the ends of the section to be joined are thoroughly tinned and sweated together. Special care must be taken to cut the ends square so that they will meet and make a practically continuous tube. Any solder adhering to the outside of the joint should be wiped off or removed by emery cloth so that the tube can be inserted with tube plates in the regular manner. To save delay in making repairs, usually several ferrules are prepared and tinned in advance.—M.

INDIAN SAFFLOWER OILSEEDS

In an article in the *Indian Trade Journal*, Mr. J. P. Gore points out that there are two varieties of Indian Safflower—*Carthamus tinctoria* and *Carthamus oxycantha*, the first being cultivated in different parts of India while the latter grows as a weed in the Punjab. The seeds of the former are small and flat, somewhat resembling linseed. They contain 6 per cent moisture and on extraction with ether yield 28.02 per cent of a pale yellow oil. There is also a considerable amount of woody fiber in the seed. The fully extracted meal gave the following analysis: Moisture, 9.30 per cent; albuminoids, 13.50 per cent; carbohydrates, 22.80 per cent; fibrous matter, 51.70; and ash, 3.70 per cent. The oil is described as being a good drying oil and might be used in the manufacture of soft soap. The author considers that this oil is worth more attention for manufacture of varnishes. It is at present used in the Northwest Frontier Provinces for the manufacture of varnished wax cloth.—M.

A NEW HYDROCARBON

A new hydrocarbon, to which the name Spinacidene has been given, was described in a paper read by Mr. R. Chaston Chapman at a recent meeting of the Chemical Society, London. The author explained that a sample of cod-liver oil submitted to him for analysis gave a value indicating the presence of 89 per cent mineral, with 11 per cent of some fish oil, but, owing to the large amount of unsaponifiable matter and bromine absorbed, he determined to investigate the matter further. The oil was found to have been obtained from the livers of certain members of the sub-family *Spinacidae*, of the *Celacea*, and the product yielded about 90 per cent of the new hydrocarbon. The compound is described as being colorless and mobile, and on warming gave odor of the lemon terpenes. It is optically active and on exposure it becomes viscous. The ultimate analysis seemed to suggest the formula $C_{24}H_{32}$ and the molecular refractivity indicated presence of three double bonds.—M.

PLASTIC CELLULOID

A simple method for rendering celluloid plastic is described in the *British Medical Journal* of a recent date, so that it can be molded into any shape for application in the tissues in certain parts of the body for certain conditions. The celluloid is placed in ether solution and, in a few hours, it swells slightly and becomes soft as a jelly. It is then taken out of the solution and molded into any shape and set aside to dry. The celluloid regains its original thickness and general appearance, but retains its new shape. As ether is a powerful bactericide, it will effectively sterilize the mold and make it ready for insertion.—M.

CHROMITE

Crude chromite ore, so important in modern steel metallurgy, says *Engineer*, 123 (1917), 59, has generally to be dressed to make it suitable for sale. It has usually to be broken up by hand or mechanically to a suitable size so that it can be hand-picked. The output should contain about 50 per cent of chromium sesquioxide. Chromite is obtained in large quantities from New Caledonia in the South Pacific. There is a large output from Rhodesia, and Greece exports chromiferous ores in considerable quantities. There are large deposits of low-grade ore in both Germany and Austria. Great Britain and France have to import all the chromite they require. North America has a small output, about 2000 tons annually, but has also to import. There are many chromite mines in the Ural district, mainly along the outcrops of the rivers Kameuka and Top Kaja, which have yielded as much as 20,000 to 30,000 tons annually. The mineral is also found in some of the areas from which platinum is recovered. In Japan, outcrops have been found but there is no output as the quantities available appear to be too limited to encourage enterprise.—M.

CALCIUM CARBIDE INDUSTRY

According to the *Times Engineering Supplement*, No. 507, p. 16, the importations of calcium carbide into the United Kingdom for 1916 were, approximately, 24,000 tons as compared with 26,000 tons in 1915 and about 28,000 tons in 1914. The decrease is not due to any falling off in the consumption, but there seems to have been a considerable shrinkage in the demands of private users, owing to the closing down of country houses, etc. This falling off was made up by the extensive demand for carbide in the manufacture of war appliances by means of oxy-acetylene welding. A gradual increase in the use of small light miners' lamps burning acetylene took place in this country during the past year following the lead given by the United States. The employment of these lamps has been shown to be very advantageous in increasing the output of minerals and providing better illumination. The supplies of cyanamide made from carbide greatly decreased during the past year owing to the large proportion of cyanamide being used for the preparation of nitrate of ammonia and nitric acid.—M.

A NEW CELLULOID CEMENT

The *Oil and Color Trade Journal*, 51 (1917), 416, quoting from a Swiss contemporary, gives an account of a new and valuable celluloid cement for gluing leather splits together so as to form solid slabs of plates of leather. As is well known, celluloid solutions possess the drawback of being much too sticky. If a celluloid solution is prepared in acetone or other solvent, it is impossible to obtain a substance of sufficient liquidity with more than 16 to 18 parts by weight per 100 parts by weight of acetone, as, if the proportions of celluloid be increased, then the resulting liquid will not penetrate between the fibres of the material and the parts will not adhere. In order to secure a highly liquid solution containing a greater percentage of celluloid, the following process must be observed: Chemically pure acetone, celluloid and oxalic acid are placed in a hermetically closing iron receptacle. The amounts are: acetone 10 kilos, celluloid 20 to 30 kilos, oxalic acid 0.5 to 2 kilos. After hermetically closing the receptacle, the ingredients are thoroughly mixed by suitable stirring gear at normal temperature. This is continued either incessantly or at intervals for a period of 12 to 14 hours. The product obtained can be used at once or kept for an indefinite period in the hermetically closed receptacle. This adhesive must correspond to the absorptive capacity of the material. If too thin, it must be suitably thickened and pressure may be used to force it into the material, if necessary. It is insoluble in water, it is highly valuable for fastening leather, and will be of special use in driving-belt factories.—M.

METAL POWDERS AND SPANGLES

Vigorous efforts, says the *Times Engineering Supplement*, No. 506, have been made to capture certain of the industries which once were wholly in German hands, and, even in cases where the trade did not exist before the war, steps have been taken to assist firms who are willing to embark in the new manufacture. It is stated that in 1913 not a single pound of bronze powder was made in France although the annual consumption of imported metallic powders attained a total value of over \$2,304,000. This was the more remarkable because the industry was first started in France at the close of the 18th century. The restarting of this trade is associated with the manufacture of spangles which has existed in the Department of the Oise since 1850. These spangles are stamped out of extremely thin sheets of metal, chiefly alloys of copper, but at times silver and gold spangles are produced from very thin leaves of the precious metals. The uses of the different kinds of spangles are too numerous to mention. A very important one, in the case of thin brass spangles, is for the brushes of dynamos, but they are mainly employed in decoration. The fragments, chippings and metallic laminae which result from the manufacture are now being employed successfully for the preparation of various kinds of bronze powders, the tints and shades of which are produced in a wide range of colors. A process has, moreover, been devised for imparting a high polish to the powders thus prepared.—M.

CHINESE GAMBIER

Reports from Hong Kong, says the *Oil and Color Trade Journal*, 51 (1917), 502, state that an increased trade is now being done in "cunao," or Chinese Gambier in South China, and the amount of trade passing through Hong Kong runs to about 30,000 short tons per annum. For many generations past, the Chinese have used this product for dye and preservative purposes and, now that aniline dyes have disappeared from the Hong Kong market, this gambier is coming into more general use. The dye is got by crushing and soaking the roots of a plant known as cunao, the resulting liquor being drawn off and concentrated. Two qualities reach Hong Kong. The second-grade quality is the product of Indo-China and is employed for the first dyeing of the material, while the actual Chinese product is used for the finishing dye on account of the deep brown gloss it imparts. The dye is of a brown color, is highly astringent, goes excellently with various mordants and is extensively used in China for dyeing silks, etc. The coarser quality is the chief component of a mixture used for fishing nets, sails and the like to prevent them rotting away. It has all the merits of gambier but is much cheaper. It is exported in the form of a paste but is said to lose its finer qualities if kept too long. If properly packed and further concentrated, there seems to be no reason why the product should not keep indefinitely.—M.

DISPOSAL OF WASTE TIN AND SCRAP

According to a contemporary, the borough of Hornsey, England, has put down a furnace for dealing with waste tin and scrap. It is heated by the destructor flue gases and is arranged in such a way that the work can be carried out without increasing the staff. The results of the first three months justify the experiment as the annual receipts for 194 tons should amount to 293 pounds 5s. 6d. It will be noted that, notwithstanding the difficulty of disposing of waste metal, the destructor yard has been kept clear of accumulation and, it may be said, that the trade has been secured with an increase of about 40 per cent upon the returns received from pre-war German trading and this by a simple process involving no material encroachment upon the yard space or additions to the working staff and a comparatively nominal capital outlay.—M.

THE GERMAN LIGNITE INDUSTRY

According to a report in *Engineering*, 103 (1917), 104, the German lignite industry has fared well during the war and better than ever in 1916. This industry has gained considerable importance, notwithstanding the development in coal mining and, although it comprises some 300 installations, these are controlled by comparatively few companies, some of which are large concerns with substantial capital. The shortage in the production of coal since the war broke out, some 28 per cent for the first year and about 10 per cent for the second year of the war, caused an immense increase in the demand for lignite and, as the following figures show, the production in spite of the shortage of labor was larger in 1915 than in 1913:

YEAR	PRODUCTION IN TONS	
	Raw Lignite	Briquette
1913.....	87,000,000	21,400,000
1914.....	84,000,000	21,400,000
1915.....	88,400,000	23,500,000

The year 1916 is expected to show a further rise. From a financial point of view, the results of the lignite industry during the war have proved satisfactory in spite of increased expenditure. The aggregate profits of the 20 leading lignite concerns show but a slight decline for 1914-15, as compared with 1913-14, and in 1915-16 the result surpassed 1913-14. For 1913-14, the average dividend was 10.4 per cent, while for 1915-16 it was 10.8 per cent, and is likely to be higher for the present year. The war seems to have opened up new markets and lignite has now become a factor of some moment in various chemical industries and deposits of the substance are eagerly sought after. The rises have increased considerably as is shown by the fact that the German Petrol Company which is going in for tar production from lignite, paid 185 per cent for shares in the Rositz Lignite Company, which shares were below par before the war.—M.

FLAX-GROWING INDUSTRY

In the January issue of the *Times Trade Supplement*, the possibility of a revival of the flax-growing industry in Great Britain is the subject of an article by Dr. J. V. Eyre. The writer states that the experience of the last three seasons has shown that high-class flax-crops can be raised in the British Isles, and Belgian experts have declared the crops to be generally equal to those raised in their own country. The main difficulty since war broke out has been to obtain labor at harvest time to pull the crop. To meet this difficulty, engineers and others have been engaged for a long time on the design of a machine to effect the pulling satisfactorily and several machines are now under construction or are in the experimental stage in both Canada and Ireland.—M.

OILSEED CROPS

According to the *Chemical Trade Journal*, 60 (1917, 7), the first forecast of winter oilseeds (rape, mustard, and linseed) crop issued by the Department of Statistics, India, states that the total estimated area under rape and mustard reported up to date is 3,888,080 acres. This is 19 per cent above the area at this time last year. The total area under linseed is estimated at 2,627,080 acres or 3 per cent below the area for last year. The latest information published by the Imperial and Continental Office of Agriculture, Rome, shows that the estimate of the linseed crop of 1916 in the United States is 1,400,000 bushels, or 10 per cent above the 1,260,000 bushels and 10 per cent above the previous year. For the Canadian crop of linseed, the estimate is 115,000 bushels and 194,000 tons compared with 100,000 bushels and 100,000 tons in the previous year. From agricultural sources, it appears that in the Argentine, the cultivation of the linseed crop is extensively based on account of short cotton and the yield is estimated to be only 250,000 tons compared with 100,000 tons for 1915. At Buenos Aires, the linseed crop is reported to be poor both in quantity and quality.—M.

BRITISH OIL TRADE IN 1916

The *London Chamber of Commerce Review* for 1916 states that a marked feature during the year under review has been the continued demand for oils of every grade and more particularly the higher grades of lubricating oils. Owing to increased freights and extra cost of insurance, prices throughout the year maintained a very high level. In early spring conditions were very stringent, supplies being at a premium, and even the common oils brought as much as the best oils in normal times, while some grades were almost unobtainable. Easier conditions prevailed later, but towards the end of the year the market again hardened and, at the time of writing, there is every indication of a rise in prices and a shortage of supplies. It is generally agreed that for some time after the war a return to normal will be impossible. Stocks have been depleted by the abnormal demands and the difficulty of securing freights from the other side of the Atlantic has increased and will not disappear as soon as hostilities cease. The question of future supplies is at present one of great anxiety to importers. There are no indications of any lessening of the demands by ordinary users from which it may be argued that, during the new year, business will be extremely brisk with high prices ruling all around.—M.

THE EXTRACTION OF SUMACH

According to an article in *Leather World*, 9 (1917), 76, when using sumach, it should be remembered that this material is very liable to loss through faulty extraction. Of all the common tanning materials, sumach is the one in which the tannin is most easily destroyed. This loss or destruction may take place if the sumach is not extracted at the correct temperature. Many tanners think that, in order to get the whole of the tannin from sumach, it is necessary to boil it, but this is quite wrong as, by boiling the substance, 20 to 30 per cent of the tannin may be destroyed. The correct temperature for extraction is between 120 and 140° F.; if the temperature is raised above this, some may be destroyed. The sumach should be mashed with water at this temperature but, after the extraction of the tannin, the solution should not be kept for any length of time before being used. A sumach infusion ferments more quickly than that of any other tanning material and, if allowed to stand for some days, a large proportion of the tannin is lost. Contrast this with mimosa bark, the liquors of which can be kept almost indefinitely without appreciable loss. Sumach should, therefore, not be extracted before it is required for use. By observing these points, considerable economy in the use of sumach may be exercised.—M.

FRENCH COLOR INDUSTRY

The *Dyer and Calico Printer* says that a long discussion between the chemists and the pharmacutists in the pages of *La Revue des Produits Chimiques* reveals the fact that the French artificial color industry is handicapped by ancient enactments, the first of which became law in 1777. These date from the time when chemistry was ranked with astrology or even black magic, and the result is that, in the words of our contemporary, the administration officially ignores chemistry and the chemist. The authorities know only the engineer, the physician and the pharmacist. If, therefore, a French works wishes to put synthetic medicine on the market, it must "interest a pharmaceutical chemist in the manufacture of these products." The law seems to enact that a pharmaceutical chemist shall alone make medicine and must be on the staff of the color works. Certainly, he need not be resident at the works and may conduct his department from some other town, but he must accept pay for the use of his name. This adds to the cost of production and it is easy to see that it is an unnecessary drawback to the French color industry in its competition with imported products.—M.

CRANE AND HOIST MOTORS

The British Thomson-Houston Co., London, have designed a new type of motor for intermittent service, special attention being given to the need for avoiding breakdowns. The machine is described as being of the totally enclosed reversible series, wound commutating pole type and has been standardized for ratings up to 50 H. P., these ratings being based on continuous operation for 30 minutes at full load with a temperature rise not exceeding 55° C. The machines are of the 4-pole type. The magnet frame is of cast steel made in two parts, the top half carrying the brush holders and being provided with lugs to support the assembled motor, while the bottom half has a strong foot drilled for holding-down bolts. The fact that the drillings for the holes can be made at any place along the feet is an advantage. The armature core and commutator are assembled on a sleeve, a form of construction which permits the removal and insertion of a shaft without the necessity for disturbing the armature windings or the commutator. The armature windings are composed of former wound coils inserted in open slots. A valuable feature is that the shaft extensions are arranged to permit the spur gear of the brake to be mounted on either end of the shaft.—M.

A NEW POCKET-LAMP

A pocket-lamp without a battery is a recent Hungarian invention. An engineer of Budapest transforms muscular energy into electrical energy producing light. In shape and intensity of light, it equals the ordinary torch-lamp. The thumb moves a small lever outside the case, which on being depressed and released, springs back into its original position. This movement is transmitted through a ratchet and pawl to a set of pinion gears which drive a small dynamo, the field of which is fitted with a permanent magnet. It is necessary to keep on moving the lever with the thumb as long as light is required, but the energy stored up in the spring is sufficient to maintain light for a few minutes after the movement of the lever has ceased. When the design is carried out in a heavier form as a hand-lamp, the lever is actuated by squeezing two parallel handles attached to the case, one of which is fixed and the other movable. The principle, says the *English Mechanic*, 105 (1917), 4, might also be applied to other purposes, as to ignition dynamos for blasting.—M.

RUSSIAN PLATINUM MINES

Some time ago H. M. Consul at Ekaterinburg reported that the annual sale by auction of the gold and platinum mines in the Urals was to take place at the Ekaterinburg Mines Department on February 6. In all 600 mines were to be put up for sale, the majority being situated, as is usually the case, in the Orenburg Government. As a rule, these mines are bought up with the idea of reselling them abroad at an enhanced price. H. M. Consul, however, in a later report, states that the government authorities have decided that, until further notice, all platinum mineral is to be held and sales refrained from, in view of the proposed requisition of platinum by the government.—M.

MAGNETOS

When war broke out, says *Engineering*, 103 (1917), 84, there was only one British firm manufacturing magnetos, its output being under 100 per week. Practically every magneto which went on motor vehicles, motor boats and aircraft of Great Britain came from Germany or America. To-day there are twelve or more British firms making magnetos. Their entire output, which reaches a total of over 165,000 magnetos, has been made for war purposes, being used on aeroplanes, sea-planes, airships, motor-lorries, motor-ambulances, motor cycles, "tanks," big-gun tractors, motor boats, wireless sets, searchlight sets, lighting sets and other contrivances where magnetos are required.—M.

CHEMISTRY IN WARTIME¹By RICHARD B. PILCHER²

Owing to the conditions of modern warfare, chemists have been more than ever in request. To give a full account of their work, if it were possible, would be imprudent, but it is well to place on record a statement confined to what it is permissible to relate, giving some indication of the importance of the profession of chemistry to the nation in these times.

The Government has secured the guidance of chemists and other men of science to assist in the investigation of suggestions and inventions, and to bring their knowledge and experience to bear on measures and devices of offence and defence, while apart from those acting in an advisory capacity, chemists have been called for service in the field as well as in the factory. In such times there is a demand for the solution of problems of an unusual character which can be entrusted only to men of the highest scientific training, with initiative and foresight.

So much had we come to rely on foreign sources of supply for many of our needs that means had to be found for dealing promptly and efficiently with difficulties, some of which, unless overcome, threatened serious disaster. The chemists of the country had not been found wanting.

The laboratories of our universities and colleges have become small factories for the preparation of drugs and medicaments, and many institutions have been trusted with the examination of materials used in the manufacture of explosives. The measures taken in this emergency secured uniformity in method and the standardisation of processes which would otherwise have been difficult to attain. Under the supervision of their professors, students unfit for service with the colours have been helping the country, and at the same time gaining useful experience.

Several hundred chemists have been engaged for assistance in the laboratories and in the works of Government and controlled establishments supplying armaments, munitions, and other materials of war. Many of these have found an opportunity of helping the country through the registers maintained by the Institute of Chemistry and other societies for this purpose. In cases where the number of men having technical experience in some branches was limited, the authorities have made arrangements for probationary training, so that their services should be available when required in new factories.

The staffs of the chemical departments of Woolwich Arsenal and other Government factories have been considerably augmented, as also that of the Government Laboratory, which, as the recently published report shows, has been largely responsible for the examination of foodstuffs and many other requirements of the Expeditionary Forces.

In previous wars the authorities have considered officers of the R. A. M. C. sufficiently trained for all necessary military duties involving chemical knowledge, but in the present conflict, with an unprecedented demand for medical men, qualified chemists have volunteered in such numbers as to give practical force to the suggestion that they should be engaged for the purification and examination of water supplies and for dealing with matters of hygiene requiring chemical knowledge. As a result many have been appointed to commissions and engaged for scientific work, not only with the R. A. M. C., but also with the A. S. C. and A. O. D., and other units. Attached to various forces at home, with the armies on the Continent and in Africa, chemists have thus rendered valuable service.

In consequence of methods of offence initiated by the enemy, such as the employment of poisonous gases, there arose a further demand for men with training in chemistry for service in the field. For the duties involved the authorities deemed it expedient to enlist men with such training rather than entrust

them to men without any scientific knowledge, and the unit thus formed is a fighting force. With the assistance of the universities and technical colleges and the various bodies interested in chemistry, an entirely new force was brought into existence. The officers were mainly selected from chemists who already held commissions, while sergeants and corporals with knowledge of chemistry were transferred from other units. That they did their work well is shown by the despatches of Lord French and Sir Douglas Haig.

From the experience gained in the campaign it is clearly advisable that the State should have control of such an organization of professional chemists as to ensure at any time their efficient service in the many requirements of the naval, military and air forces. In addition to competent chemical advisers of undoubted standing, the following appear to be essential: Chemists to control the manufacture of munitions, explosives, metals, leather, rubber, oils, gases, food, drugs; chemists for the analysis of all such materials and for research; chemists, on active service, to assist in the control of water supplies, in the detection of poison in streams, in the analysis of water and food, in the disposal of sewage, and in other hygienic matters; chemists, both at home and in active service, to assist in devising safeguards against enemy contrivances of a scientific nature, and methods of offence to meet the same, as well as for the instruction of troops in such matters.

It has been called a "chemists' war" and an "engineers' war." Many regard it largely as a conflict between the men of science of the countries engaged. Our chemists have not been dismayed at that, but it is impossible to foresee to what limits beyond accepted tenets the enemy is prepared to go in the application of science to warfare, and we cannot reproach ourselves with having set an example of frightfulness.

To sum the matter up, chemists have met the situation with a spirit of true patriotism, and have been promptly organized for the service required of them. It is not too much to hope that, as the discoveries of science have been applied to the destruction of humanity, they may be devoted more and more to the furtherance of the arts of peace, to the uplifting of civilisation, and the pacification of the world.

During the war, in spite of the shortage of labour, considerable additions have been made to the large manufacturing concerns throughout the country in the extension of factories, both for the production of things hitherto obtained from abroad and for the requirements of the war.

One important lesson which on no account must be lost sight of is that the country must be self-supporting in all such requirements.

The chemists engaged in connection with the production of materials of war include a large number who were previously occupied in works which have passed under Government control. Most of these were members of the Institute or graduates in science, and many were teachers, who thus obtained an insight into operations on a manufacturing scale. If they return to teaching, this experience will have broadened their views, but many will no doubt prefer to remain in industry. Of those with the forces, probably the majority will return to their former work. In any case, many good British chemists should be available for the furtherance of British industry.

RESTRICTION ON MAGNESIA

The British Minister of Munitions, in a notice that under the Defence of the Realm Act, is published in *Official Gazette*, restricts the production and use of magnesium and magnesia products for and in connection with the construction or repair of any building, other than temporary, or any flooring or decking, or the manufacture of any manufacturing or non-conducting material, except under and in accordance with the terms of a permit granted by the Minister of Munitions.—M.

¹ Proceedings of the Institute of Chemistry 51917), copied from the *Chemical Trade Journal and Chemical Engineer*, 60 (Feb. 24, 1917), 163.

² Registrar and Secretary of the Institute of Chemistry.

ALUMINUM PRICES

The selling price of aluminum ingots of ordinary commercial purity, 98 to 99 per cent, has been fixed in Great Britain by the Ministry of Munitions at \$1080 per ton, carriage paid to consumers' works. The maximum price of remelted aluminum scrap or swarf ingots of 98 to 99 per cent purity has been fixed at \$1008 per ton, carriage paid to consumers' works. This maximum price must not be exceeded but a lower one may be fixed by agreement between seller and buyer based upon the metallic aluminum content. These prices take effect from February 1, and permits will be granted for such dealings in the above-mentioned materials as are in accordance with the above prices which are subject to alteration at any time by the Minister of Munitions.—M.

NEW COMPANIES IN JAPAN

According to reports from H. M. Commercial Attaché at Yokohama, the following are among the latest industrial developments in Japan: A company with capital 2,500,000 yen (\$1,250,000), has just been formed at Tokio for the purpose of refining zinc by electrolysis and for mining and smelting other metals. A glass factory is being erected at Yokohama with a capital of \$1,500,000 and it is expected that operations will be started in March, and orders have already been placed with this company for large quantities of bottles. Another company with a capital of \$500,000 proposes to erect in the suburbs of Tokio a factory for the manufacture of plate glass. A mining concession for silica is said to have been obtained by the latter company in the Shizuoka Prefecture. With a view to working an oilfield in the Yamagata district, a company with a capital of \$1,500,000 has been formed, while another with a capital of \$3,000,000 proposes to take over and work a number of oil concessions at Kwiokawa, Akita Prefecture. As a result of the experiments made in the manufacture of soda ash in Nagoya, a joint stock company with a capital of \$500,000 has been formed to manufacture this product and land has been acquired at Na-

goya harbor to erect factories. An electrochemical company with a capital of \$500,000 will build factories at the river Arakawa for the manufacture of bleaching powder, etc.—M.

BRITISH BOARD OF TRADE

During the month January 15–February 15, the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.

ADVERTISING NOVELTIES:	Enamelled iron shades for electric lights
Knives, cheap, to retail at 10c. each	Eyelets for boots
Mirrors, small, covered with celluloid	Fezzes, felt
Pencils	Gum Arabic
Beech boards for brushes (good quality)	Gedda, amber sorts
Bells, metal, toy	Hose pipes, 2 1/4 and 3 in.
Bottles, glass, straw-colored	Isinglass
Bootlaces, leather and mohair	Latex cups
Buckles, brace, brass	
Candles	
Cord-wire	
Cases, cast-iron, for electrical fuse-boards and switch-gear	
CHEMICALS:	
Amorphous phosphorus	MACHINERY AND PLANT FOR:
Alphanaphthol	Making boot lace tags
Alphanaphthylamine	Making gelatine
Aniline oil	Making capsules
Dimethylaniline	Grinding safety razor blades
Metaphenylenediamine	Making glass flasks
Metatololenediamine	Conversion of starch into dextrine
Naphthionate of Soda	Making candles
Nitrobenzene	Stamping out leather, cloth and rubber washers
Orthotoluidine	Gelatine, shredding plant
Saltpetre (refined, granulated)	Electric baling presses
Sulfanilic acid	Hydraulic baling presses
Caustic Soda, 100 tons 95 per cent	Paste, to give a polish to rough twine
Epsom Salts, druggists' quality	Push-buttons
Glauber's Salts of Soda	Rosin, American, 1000 tons
Dextrinous substances (powder)	Studs, press, also two-piece
Dyes, cheap, for ink making	Tanks, wagon, for distributing oil
Egg-beaters, Dover pattern	Wheels, chilled iron
	Wheels, tracing
	Wire, galvanized, 4 mm. thick
	Wire nails, assorted 7/4 in. by 18
	B. W. G. to 5 in. by 8 B. W. G.
	Wood (ash) rims for sieves
	Zinc, sheet, suitable for lining packing cases

—M.

SCIENTIFIC SOCIETIES

CALENDAR OF MEETINGS

American Chemical Society: Spring meeting, Kansas City, Mo., and Lawrence, Kan., April 10–14, 1917. Annual meeting, Boston, September 10–16, 1917.

American Electrochemical Society: Thirty-first General Meeting, Detroit, May 2–5, 1917. Fall meeting, Pittsburgh, October 4–5, 1917.

American Institute of Mining Engineers: Annual meeting, St. Louis, October 8–13, 1917.

American Iron and Steel Institute: New York, May 25–26, 1917.

American Society for Testing Materials: Atlantic City, June 26–30, 1917.

NINETEENTH ANNUAL MEETING AMERICAN CERAMIC SOCIETY, NEW YORK CITY, MARCH 5 TO 8, 1917

The Nineteenth Annual Meeting of the American Ceramic Society was held March 5 to 8, 1917, at New York City with headquarters at the Astor Hotel. All the sessions were held at the Astor Hotel except the one of Tuesday afternoon, March 6, which took place at the Metropolitan Museum of Fine Arts, and was followed by a tour of the Museum. The annual business session of the Society was held on Monday morning, March 5, and was followed by the Presidential Address by Mr. Lawrence E. Barringer, of the General Electric Company, Schenectady, N. Y. On Thursday, March 8, an excursion was made to Perth Amboy, N. J., and vicinity, to visit the Atlantic Terra Cotta Company, Didier-March Company, and the Fords Porcelain Works.

PROGRAM OF PAPERS

HEAVY CLAY WARES: THEIR MANUFACTURE AND TESTING

- Study of Effect of Variation of Pressure in the Forming of Dust Pressed Tiles. F. K. FENCE.
The Advantages of Clay Storage and a Description of a Successful Installation. F. A. RIDDLE.
Notes on the Manufacture of Promenade Tile. M. W. BLAIR.
Notes on the Flow of Clay through Hollow-Ware Dies. G. D. MORRIS.
Humidity: Its Control and Relation to Drying Clay Wares. W. A. DENMEAD.

- The Effect of the Size of Grog in Fire Clay Bodies. F. A. KIRKPATRICK.

- The Relation between the Fusion Point and Composition of Refractory Clays. R. J. MONTGOMERY AND C. E. FULTON.
Volume Changes of Some Quartzites and Commercial Silica Bricks on Heating. D. W. ROSS.
Note on the Fine Grinding of Refractory Materials before Testing. R. J. MONTGOMERY.

- Relation of Fusing Point of Ash to Availability of Coal for Burning Ceramic Wares. R. R. HICE.
An Attempted Heat Balance on a Continuous Kiln. C. B. HARROP.
Making Paving Brick from Blast Furnace Slag. J. B. SHAW.
The Principles of Construction of Bucket Elevators. G. D. MORRIS.
Modification of Load Test on Fire Brick. J. B. SHAW.

RAW MATERIALS, MINERALS, THEIR OCCURRENCE, REFINING AND TESTING

- Notes on the Use of Sulfuric Acid in the Sedimentation of Kaolins. H. G. SCHURECHT.
Notes on Kaolin Refining. I. E. SPERAT.
American Clays for Floating Enamels. J. B. SHAW.
The Relation of Salt to Clay in the Purification of Clays. H. G. SCHURECHT.

- A Study of Some American Refractory Bond Clays. A. V. BLEININGER AND G. A. LOOMIS.

Clay and Shale Deposits in the Vicinity of Toronto. E. W. KNAPP.

Apatite: A Substitute for Bone Ash. N. B. DAVIS.

An Instrument for the Measurement of Plasticity. W. E. EMLY.

Discussion on Standard Methods of Clay Testing. Led by A. V. BLEININGER.

A Method of Measuring the Time of Set of Calcined Gypsum. W. E. EMLY.

GLASS AND ENAMEL INDUSTRIES

Glass Sands: Their Origin, Mode of Occurrence and Properties. C. R. FETTER.

The Physical Chemistry of the Fining of Glass. R. M. HOWE.

Glass Tank-Furnace Operation. R. L. FRINK.

History of Albaster Glass. A. SILVERMAN.

Discussion: In What Chemical Condition Does Manganese Exist in Glass when Used as a Decolorizer, and What Factors of Furnace Conditions Affect It? Led by R. L. FRINK.

Enamel Surfaces under the Microscope. E. P. POSTE

GLAZES AND COLORS

The Cost of Raw Lead Glazes. H. F. STALEY AND L. HEWITT.

Chrome-Tin Colors at Cone 9. R. H. MINTON.

A Synthetic Production of Sulfate Blisters in Whiteware Glazes. C. F. BINNS.

A Study of Three-Component Nonmative Systems in Raw Lead Glazes.. H. F. STALEY AND W. G. WHITFORD.

The Crawling of Malt Glazes. C. F. BINNS AND M. E. SAUNDERS.

Bristol Glazes, Compounded on the Eutectic Basis. Second Paper.

A. S. WATTS.

The Control of Fusibility in Fritted Glazes. H. F. STALEY AND R. J. RILEY.

Report of Practical Application of Bristol Glazes Compounded on the Eutectic Basis. A. S. WATTS.

BODIES AND THEIR PROPERTIES

Notes on Flint and the Preparation of Porcelain Bodies. G. H. BROWN AND C. F. GEIGER.

The Interchange of Quartz and Flint in Pottery Bodies. C. F. BINNS AND W. I. SUTTON.

A Deformation Study of $MgO-Al_2O_3-SiO_2$ Mixtures. A. S. WATTS.

A Deformation Study of $BaO-Al_2O_3-SiO_2$ Mixtures. A. S. WATTS.

Latent Heat of Fusion of Lime and Magnesia. E. W. WASHBURN.

A New Principle in Heat Measurement. W. C. HARTER.

Note on the Temperature-Porosity-Volume Changes of Some Porcelain Bodies. G. A. LOOMIS.

Note on the Production of Special Refractories, Marquardt Porcelain and Magnesium Aluminate. F. H. RIDDLE.

SESSION AT THE METROPOLITAN MUSEUM

Ancient Greek Pottery. MISS RICHTER of the Museum Staff.

An Attempted Reproduction of Ancient Oriental Glazed Pottery.

CHARLES F. BINNS AND NELLIE I. WELSH.

Chinese Porcelains. MR. BOSCH REITZ, of the Museum Staff.

An Indigenous American Artist, and His Medium. EDWARD ORTON, JR.

View of the Ancient Greek Pottery and the Chinese Porcelains in the Museum Galleries. Conducted by MISS RICHTER and MR. REITZ.

SPRING MEETING AMERICAN CHEMICAL SOCIETY, KANSAS CITY, APRIL 10 TO 14, 1917

The Fifty-fourth Meeting of the American Chemical Society will be held in Kansas City, Tuesday, April 10th, to Saturday, April 14th, inclusive. The Society and hotel headquarters will be at the Hotel Muehlbach, corner of 12th and Broadway Streets.

DIVISIONAL PROGRAMS: The usual meetings will be held by all of the Divisions, with the following special programs: The *Physical and Inorganic*, and *Organic Divisions* will hold a Joint Meeting, Thursday morning, April 12; the *Division of Industrial Chemists and Chemical Engineers* will hold a Symposium on the Chemistry and Metallurgy of Zinc, Thursday, April 12.

EXCURSIONS: Interesting excursions are being arranged covering trips to the following industries: Packing houses, flour mills and other foodstuffs manufacturing, zinc smelters, acids, cement, paper, soap and structural steel factories, and serum laboratories, and probably also a petroleum refinery. A trip will also be made to Lawrence to visit the University of Kansas.

CHAIRMEN OF THE LOCAL COMMITTEES

Lecturer: W. A. WHITAKER, University of Kansas, Lawrence, Kansas.

President: R. H. HUBBARD, Richmond Baker Grocery Company, Kansas City, Missouri.

Reception and Registration: L. E. SAYRE, University of Kansas, Lawrence, Kansas.

Smoker: G. H. CLAY, Procter and Gamble, Kansas City, Kansas.

Banquet: R. CROSS, Kansas City Testing Laboratories, Kansas City, Missouri.

Publicity: F. B. DAINIS, University of Kansas, Lawrence, Kansas.

Excursions: C. F. GUSTAFSON, Manual Training High School, Kansas City, Missouri.

Entertainment of Ladies: Mrs. F. B. DAINIS, 1224 Louisiana Street, Lawrence, Kansas.

PROVISIONAL PROGRAM

TUESDAY, APRIL 10. *Evening*, Dinner to the Council and Council Meeting.

WEDNESDAY, APRIL 11. *Morning*, Opening Session. *Afternoon*, Public Session: "Petroleum and Natural Gas." *Evening*, Smoker.

THURSDAY, APRIL 12. *Morning and Afternoon*, Division Meetings. *Evening*, Banquet.

FRIDAY, APRIL 13. *Morning*, Division Meetings. *Afternoon*, Excursions. *Evening*, Open.

SATURDAY, APRIL 14. *Morning*, Excursions.

PAPERS FOR THE MEETING: All titles for papers should be in the Secretary's hands on or before March 27th; or in the hands of the secretaries of divisions on or before March 25th, with the exception that titles of papers should reach the Secretary of the Division of Industrial Chemists and Chemical Engineers on or before March 21st.

The Division of Industrial Chemists and Chemical Engineers have voted that the titles of all papers shall be sent to the Secretary of the Division, which title should be accompanied by an abstract, in time to have the abstract passed upon before the paper is put on the program; that any title sent without an abstract shall not be printed in the program, and that the time limit for the presentation shall be five minutes, unless special arrangements are made with the Secretary of the Division.

By vote of the Council no papers may be presented at the meeting, titles for which are not printed on the final program.

ADDRESSES OF THE DIVISIONAL SECRETARIES

Agricultural and Food Chemistry: Glen F. Mason, H. J. Heinz Co., Pittsburgh, Pa.

Biological Chemistry: I. K. Phelps, Bureau of Chemistry, Washington, D. C.

Fertilizer Chemistry: F. B. Carpenter, Virginia-Carolina Chemical Co., Richmond, Va.

Industrial Chemists and Chemical Engineers: S. H. Salisbury, Jr., Northampton, Pa.

Organic Chemistry: H. L. Fisher, Columbia University, New York City.

Pharmaceutical Chemistry: George D. Bad, Chemistry Building, University of Illinois, Urbana, Ill.

Physical and Inorganic Chemistry: Earl V. Millard, Institute of Technology, Boston, Mass.

Water, Sewage and Sanitation: H. P. Corson, U. S. Public Health Service, Grove City, Pa.

LADIES' ENTERTAINMENT: The Committee headed by Mrs. E. B. Dainis is actively at work arranging a program for the pleasure of visiting ladies. Ladies may come to the meeting with the assurance that everything will be done for their comfort and pleasure. Details will be found in the final program.

FINAL PROGRAM: The final program will be sent to all members signifying their intention of attending the meeting, to the secretaries of sections, to the Council, and to all members making special request thereof by postal card or attached to the Secretary's office.

OBITUARY—FREDERICK ROWLAND HAZARD

Industry and society lost a commanding figure in the recent death of Mr. F. R. Hazard of Syracuse. He will long be known as a member of the group of men who brought the heavy guns for the manufacture of munitions to the United States.

Born in Peter Dale, P. I., Mr. Hazard received his early schooling in Providence, R. I., and was graduated from Brown University in 1881. Two years later he was employed at this

father's woolen mills at Peace Dale, and then spent a year or more in Europe studying the ammonia soda process. Equipped with knowledge so acquired, Mr. Hazard came to the newly-established plant of The Solvay Process Company, at Syracuse, the first alkali plant built in the United States. In the manufacture of alkali, Mr. Hazard had found a field which was to be the chief interest of his business life. As Assistant Treasurer, Treasurer, and for the past nineteen years as President, he participated in the management which, through its initiative, foresight and energy, not only instituted alkali manufacture in this country, but made this country absolutely independent of European supply.

As an executive, Mr. Hazard possessed unusual attainments. In addition to natural gifts of the first order for executive and financial management, he had a complete and detailed understanding of the ammonia soda process. This minute knowledge of the business made him an executive of unflinching judgment in matters of manufacturing policy as well as in the fields of finance and organization. There is one striking feature of Mr. Hazard's administration that needs particular mention. By sheer force of character he created an "atmosphere" in the multiple organizations of which he was the leader that is best described as "wholesome." Not only by his example of simple and right living did he set a standard of individual conduct, but by his simple and right methods of *thinking*, by his unswerving justice and "squareness," he set a standard of business ethics which affected every man in the organization.

Since Mr. Hazard's advent to the Presidency of The Solvay Process Company, the interests of the Company have been greatly extended, and through its associated companies, it has rendered a service of the very first importance in conserving the coal supply of the country through the application of the retort coke oven. It is not too much to say that the example set by the Solvay interests under Mr. Hazard's presidency, in developing the coal by-product industry, is the prime reason for our nearly perfected independence of Europe in the matter of coal-tar intermediates, dyes and explosives.

Besides being President of The Solvay Process Company,

Mr. Hazard was President of Split Rock Cable Road Co., President Solvay Collieries Co., Treasurer Tully Pipe Line Co., Treasurer Semet-Solvay Co., and Treasurer By-Products Coke Corporation. Naturally, Mr. Hazard's business interests reached out beyond the companies that received the greater part of his attention. He was officer or director in several banking institutions, and his breadth of mind and understanding made his counsel always of value. He was President of the Syracuse Trust Co. at the time of his death and at various times had been Trustee in Onondaga County Savings Bank, Director in Commercial Bank, and Director in First National Bank.

From his connections and from inclination, Mr. Hazard was always interested in affairs chemical. The Syracuse Section of the American Chemical Society has had occasion many times to be thankful for his generous help, notably at the holding of the joint meeting of the Ithaca, Rochester and Syracuse Sections. For several years past, Mr. Hazard had been President of the Manufacturing Chemists' Association.

Keeping step with his business vision and accomplishments, Mr. Hazard's place in the social structure of the community was one of pre-eminence. His name is linked inseparably with the success of the Y. M. C. A. and the Y. W. C. A. activities in Syracuse; with the hospitals and free dispensary; with the Boy Scouts; with the Associated Charities; with the work of the Moral Survey Committee, and with the fight against the loan shark evil. He had been President of the Onondaga Provident Loan Association since its inception. He was also Past President of the Y. M. C. A. Chamber of Commerce, Syracuse Athletic Association, Syracuse Music Festival Association, and of Solvay Village.

An account of Mr. Hazard's character would not be complete without a reference to the constant thought he gave to the well-being of the Company's employees, and indeed to all men and women who toil. He was untiring in his efforts to make plant conditions and home conditions safer, better and happier. He worked as well as gave, and society lost in Mr. Hazard a character of rare genius in constructive philanthropy.

J. D. PENNOCK

NOTES AND CORRESPONDENCE

DUREX BARIUM PLANT BURNED

Editor of the Journal of Industrial and Engineering Chemistry:

We regret to announce that on Thursday night, March 8th, our plant at Sweetwater, Tennessee was practically destroyed by fire, and at the present writing we are unable to say when we will be able to supply barium carbonate, sodium sulfide and depilatory. Fortunately the Long Island City, N. Y., plant of Toch Brothers will be able to handle all existing blanc fixé and barium chloride contracts. We are trying to make arrangements through other sources to manufacture part of our products. This fire, of course, does not interfere with our raw material supply.

Owing to the fact that the Durex Chemical Corporation had every possible facility for fighting fires and had both the night force and the day force thoroughly trained, it is well to point out to other chemical manufacturers that every precaution be taken against incendiary fires at the present time. Two weeks ago one of the bridges connecting two of the buildings of the Durex plant caught fire during the day, but the men were so well trained that inside of five minutes the fire was extinguished. The present fire took place at 12.30 in the morning, and the time clock of the watchman showed that he had been at the place where the fire originated ten minutes before. In less than 30 minutes the barium carbonate plant and the barium sulfide plant No. 1 were beyond control. In less than a half hour all the smokestacks collapsed.

Mr. Henry M. Toch, the President of the Durex Chemical Corporation, is at present of the opinion that the corporation should build a plant in Chattanooga and another one in Long Island City.

320 5TH AVE., NEW YORK
March 15, 1917

DUREX CHEMICAL CORPORATION
Per MAXIMILIAN TOCH

TWO LETTERS ON CORROSION OF INGOT IRON CONTAINING COBALT, NICKEL, OR COPPER

Editor of the Journal of Industrial and Engineering Chemistry:

The authors of the paper published under the above title, *THIS JOURNAL*, 9 (1917), 125, have very freely discussed the resistance to corrosion of a pure commercial open-hearth iron manufactured by the American Rolling Mill Company of Middletown, Ohio, and sold under the brand-name of American Ingot Iron and have attempted to contrast the corrosion resistance of this product with certain alloys built upon it as a base, containing cobalt, nickel and copper.

The authors' conclusions are based mainly on exposure and loss in weight tests of small test pieces prepared in the laboratory. American Ingot Iron was melted up in small crucibles in an electric furnace and treated with degasifiers and certain alloying constituents and small castings about 1.25 inches in diameter were made from which small discs were turned, etc., etc. These little discs, about the size of a half dollar were suspended by silk threads or by other means and put out on a roof. After cor-

roding for what is termed a sufficient length of time, the samples were treated with ammonium citrate to remove adherent rust and weighed. The loss in weight is recorded and tabulated, and upon these tabulations some very sweeping conclusions are based. In fact, eleven separate conclusions are appended to this paper, which, if justified by the experimental evidence, ought to settle the much debated question of the relative corrosion of pure iron and some of its alloys for all time to come. As a matter of fact, however, the conclusions are not justified nor are the results in accord with those obtained on samples obtained from sheets of similar analysis manufactured on the large open-hearth scale of operation, as the authors themselves point out.

General Conclusion III, p. 135, states that alloys formed by the addition of 0.25 to 0.30 per cent of copper, nickel and cobalt to American Ingot Iron are more resistant to atmospheric corrosion than the pure American Ingot Iron from which the alloys were prepared. The manufacturers of American Ingot Iron have for many years been interested in studying the properties of all possible alloys built on a pure iron base. The scientific research department of this company is well known to be second to no other anywhere in the iron and steel industry in respect to personnel, laboratories, equipment and plant experimentation facilities. It is a comparatively easy and cheap procedure to make up series of alloys in small laboratory crucibles but the research department of the American Rolling Mill Company has long since discovered that corrosion tests made on such samples are simply unconvincing and misleading. A careful inspection of the results recorded in this paper furnishes abundant evidence, if any were needed, of the truth of this statement. The differences in the corrosion factors derived from duplicate samples of the same heat show a wider variation in many cases than is shown between the samples of the various alloys. To select a few instances only, Sample H, 207 (a), a 0.50 per cent nickel alloy, showed a corrosion loss factor of 510, while its duplicate, H, 207 (c), showed a loss of 910. A 0.125 per cent cobalt alloy, 34204 (a) sample cut from a commercial sheet showed a corrosion loss of 1180, while its twin cut from the same sheet showed a loss of 292, a greater difference than is shown between any of the average differences between the competing types that were under test. Since sweeping conclusions are in order, why is it not fair to conclude that one sample out of any given heat is excellent in corrosion resistance and another very bad indeed, or, perhaps, even better, why not conclude that all such tests are misleading and, therefore, worse than none at all?

Based on very similar methods of testing, E. A. and L. T. Richardson¹ have concluded that the addition of copper to pure iron has a very slight influence on corrosion resistance, while the present authors conclude rather vaguely that "it seems to be conducive to reducing the corrosion of American Ingot Iron under atmospheric conditions."

No one has been more concerned than the manufacturers of American Ingot Iron to discover whether the alloys of cobalt, copper and nickel, as well as many other elements, with pure iron were superior to a carefully standardized and guaranteed purity of iron itself. Not only atmospheric corrosion, which is rarely encountered by uncoated sheet iron in service, but all the multiform and variable conditions of service exposure have been studied. Not wishing to make this discussion too long, it may be stated that although premature publication of results has been carefully avoided, the conditions noted in more than a thousand full size commercial sheets do not agree with the conclusion of the authors who seem to have been a little troubled by this tendency themselves. Having arranged cooperation with the American Rolling Mill Company after supplying the cobalt material, they received a number of full size cobalt alloy

sheets made on the big scale of operation usual in open-hearth practice. The authors, however, did not receive any nickel or copper alloy sheets. It is difficult to understand, therefore, how they can discuss the corrosion of Ingot Iron containing nickel or copper, since they did not have any such material in their tests. After Ingot Iron has been melted in a crucible and had other constituents added to it, it is no longer American Ingot Iron. They state:

"The samples, Nos. 34175 to 44009, prepared by the American Rolling Mill Company, so far as this series alone is concerned, do not tend to bear out the conclusions from the series prepared at the laboratory. From these samples alone it would seem that additions of small amounts of cobalt, up to one per cent, have very little effect on corrosion, and that the addition of nickel to about 0.7 per cent was harmful."

In conclusion, I desire to give expression to a fact that is very often overlooked. Independent investigators, with a zeal which may be altogether proper, can publish results of tests and draw sweeping conclusions without any particular sense of duty or responsibility to anybody except themselves by so doing. A great manufacturing company, however, believing in and proud of the excellence of its products which are mainly the fruit of organized research work, has to be very certain indeed that it is right before it urges upon consumers the purchase of new products, possibly at an increased price, and which in any case must be ready to stand the test of service and make good not only under atmospheric corrosion, but under the thousand and one conditions that all-round service must meet.

WASHINGTON, D. C.

February 1, 1917.

A. S. CUSHMAN

Editor of the Journal of Industrial and Engineering Chemistry:

In his comments on the paper by Mr. Blake and myself as printed in *THIS JOURNAL*, 9 (1917), 125, Mr. Cushman makes a point of "coöperation" with the American Rolling Mill Co. We received their products for our tests in exchange for a considerable batch of very pure metallic cobalt. Beyond that, I recall no coöperation being contemplated for the four series of observations on small samples which were made for the Canadian Bureau of Mines, primarily for the purpose of studying the effect of additions of metallic cobalt. Further independent publications were contemplated regarding the observations on the rolling mill sheets (Series V), concerning which there was considerable correspondence regarding coöperation. This was in 1913, about four years ago, but nothing has since been done by either party about coöperative research, except that each supplied the other with analyses of materials submitted. This has been acknowledged in the text. I take this opportunity again to thank the American Rolling Mill Company and in particular, Dr. Beck, Director of their Research Department, for many courtesies in connection with our exchange of materials. The present paper is not intended to cover Series V, *i. e.*, observations on the rolling mill sheets. We state: "It will take at least another year for these sheets to corrode through to destruction, before which time no final conclusions can be drawn." It is contemplated that our observations on these sheets should form a complete and independent paper to be published more or less simultaneously with those of the American Rolling Mill Company on the same or similar sheets.

In his last paragraph, Mr. Cushman undertakes to lecture "Independent investigators" in general, and presumably ourselves in particular, for lack of "sense of duty and responsibility" in contradiction to his "coöperation" in supplying samples. I have served and am at the moment serving in directly and sensitive official in several capacities, but I have found it better that than collect the "sense of duty and responsibility" from my pocket book than that of some friends and neighbors. But for such space and time have already been taken according to the personal

¹ Paper before American Electrochemical Society, September 29, 1916.

aspect introduced by Mr. Cushman into the discussion. I shall pass to the consideration of the paragraphs referring to technical questions.

Mr. Cushman remarks, "as a matter of fact, however, the conclusions are not justified nor are the results in accord with those obtained on samples obtained from sheets of similar analysis manufactured on the large open-hearth scale of operation as the authors themselves point out." We pointed out no such thing! In the first place, we cut no samples from the sheets. All samples were cut from bars. The remark probably refers to Conclusion IV, following Series II. Mr. Cushman failed to note that this conclusion was from a preliminary series of measurements on samples which were unannealed. We carefully limit that conclusion by the phrase "so far as this series alone is concerned," namely, Series II, and because the samples of this series were unannealed, it was regarded as preliminary, and another full series of alloys was prepared.

The next series of measurements (Series III) were made on annealed samples, from which most of the general conclusions were drawn. This series indicates that the samples prepared by the addition of small percentages of copper, nickel and cobalt (from 0.25 to 3.0 per cent) to American Ingot Iron, as described in the text of the paper, are more resistant to atmospheric corrosion than the original American Ingot Iron, which was used as a base for the preparation of the alloys, and which was used as a standard of comparison.

Mr. Cushman remarks: "It is a comparatively easy and cheap procedure to make up series of alloys in small laboratory crucibles, but the research department of the American Rolling Mill Company has long since discovered that corrosion tests made on such samples are simply unconvincing and misleading." We have in mind, as well as Mr. Cushman, that accelerated corrosion tests, such as are frequently made on small scale samples, are often unconvincing and misleading. I do not regard that these tests, extending over 9 or 10 months under actual atmospheric conditions, may be classed as accelerated tests, nor do I admit that the general results will differ from those on large sized sheets similarly submitted to corrosion action. This point may properly be the subject of discussion and variance of opinion, but I particularly take exception to Mr. Cushman's discussion of this point, which seems characteristic of his attitude throughout. I quote from him: "A careful inspection of the results recorded in this paper furnishes abundant evidence, if any were needed, of the truth of this statement. The difference in the corrosion factor, derived from duplicate samples of the same heat, show a wider variation in many cases than is shown between the samples of the various alloys. To select a few instances only; Samples H 207 (a), etc., etc....." Mr. Cushman calls attention to a pair of measurements for Sample H 207 (a) of magnitude 910 and 510, respectively, namely, with an average deviation of individual measurements from their mean of about 28 per cent. For the other sample, to which he calls attention, he has quoted the figures 1190 and 292, these being the extreme corrosion losses for the sample, and indeed for any sample. These figures show an average deviation from their mean of approximately 60 per cent. Mr. Cushman prefaces his remarks with respect to these figures by the phrase "to select a few instances only."

With respect to the above, in Series I, there are pairs or triplets of measurements on 19 alloys. Disregarding the two samples to which Mr. Cushman has called attention, and one other, the average deviation of individual measurements from their mean for the entire series is approximately $4\frac{1}{2}$ per cent. In other words, Mr. Cushman has deliberately selected two samples, the observations of which disagree among themselves by nearly ten times as great an amount as the average disagreement of measurements for the rest of the series, and from this selection he attempts to draw conclusions as to the concordance of all the

measurements among themselves. Nor is this all—both of the samples to which he makes reference are taken from Series I, which is admittedly preliminary. If, in a similar manner, we take the average of the observations for each of the samples in Series II, and note the average deviation of a single observation from their means, the resultant average deviation for the entire Series II is slightly above 3 per cent. This series represents measurements on 19 alloys from which none are omitted in the above computation. Again making similar computation for Series III, which is by far the longest series, and which reports about 125 corrosion measurements, the average deviation of a single observation from their means is about 4 per cent. Thus Mr. Cushman has selected two measurements with an average deviation from the mean respectively ten and twenty times as great as the average; in fact, so great that, according to the laws for discarding observations, they should probably be considered as containing some gross error. We properly included them in our report for completeness, but it is obvious that no one intending to be fair should conclude as to the concordance of results among themselves, from the particular measurements which he has selected.

Opinions may vary as to whether or not the alloys described in our paper represent what would be produced from American Ingot Iron by the addition of small percentages of nickel, cobalt and copper following the regular manufacturing procedure. We have drawn no conclusions in this regard, preferring to wait until we are in a position to publish our work on the sheets supplied by the American Rolling Mill Company, which are more representative of such a condition. On the other hand, there can be no doubt but that the corrosion measurements on the discs, described in this paper, on the average show a remarkable concordance among themselves for any given sample. For example, the very alloy, No. 34204, for which Mr. Cushman quotes from Series I the values 1080 and 292 as the corrosion factors, in four independent measurements in Series III shows the values of the corrosion factors as follows: 638, 643, 638, 638. The average of these four measurements is 639, with an average deviation of a single observation from the mean of less than 0.2 per cent. It would be just as fallacious for us to characterize the concordance of all our observations by this particularly concordant set of measurements on Alloy No. 34204, as it was for Mr. Cushman to characterize them all by far the least concordant pair of measurements in the entire set of over 200 determinations.

In conclusion, let me say that we have no elaborate ideas as to the conclusiveness of our results, or of any other single set of measurements on so evasive a subject as atmospheric corrosion. We noted particularly that the primary purpose of our investigation was "measurement and the setting forth of data." These, we consider of the first importance, much more so than any conclusions we may have drawn from these data, and we admit that others may properly conclude at variance with ourselves. We do not, however, admit the particular points of exception which Mr. Cushman has raised, and we very much regret that he thought it necessary to hasten into a discussion savoring so much of the personal aspect and apparently based upon very little consideration of the technical data.

JACKSONVILLE, FLORIDA
February 16, 1917

HERBERT T. KALMUS

TWO LETTERS ON RELATION OF FAT IN MILK TO THE SOLIDS-NOT-FAT

Editor of the Journal of Industrial and Engineering Chemistry:

May I suggest that Messrs. Brown and Ekroth, in their article on milk published in *THIS JOURNAL*, 9 (1917), 297, have misinterpreted some of the standards referred to. Several standards specify minimum values for the fat and total solids

but many of these neither specify nor imply that the solids-not-fat must exceed that difference between these values. The case of 12 per cent of total solids and 2.5 per cent of fat referred to on page 297 is evidently that of Rhode Island and there is probably no difficulty experienced in complying with these values. The solids-not-fat are not specified and there is no warrant for assuming that the minimum value is 9.5 (12.0—2.5). The other case referred to, evidently that of Minnesota, presents reasonable ground for criticism and the 9.75 per cent of solids-not-fat is included in the standard. Probably this was inserted under the erroneous impression that a 13.0 per cent total solids and 3.25 per cent of fat standard also implied that the solids-not-fat should exceed 9.75 per cent. This, of course, is an absurd value and is impossible to meet. A similar error appears to have crept into quite a number of the state standards. My opinion is that standards are to be regarded as the minimum percentages of certain constituents that are to be contained in the article sold as milk and it is not essential for this purpose that they should bear any relation to their relative proportions in milk. The standards are definite specifications of what the consumer must receive and in this respect are very different from the English milk standards which are merely presumptive and admit rebutting evidence by the vendor.

As previously stated, the limiting values for the fat and total solids, or fat and solids-not-fat are to be considered separately; it often happens, however, that one standard is much more stringent than the other and that one is consequently redundant. In Ottawa the standard is 12 per cent of total solids of which at least 3.0 per cent shall be butter-fat. On looking over my records for the past year I find that in one group, farmers' raw milks, there are 2,154 samples and of these 10.80 per cent violated one or both standards, 10.75 per cent were deficient in total solids and 2.0 per cent deficient in fat. Only one sample (2.9 per cent fat) was deficient in fat and yet satisfied the standard for solids. The average fat content of the samples below the standard was 3.15 per cent. It is very evident that, in Ottawa, the standard could be simplified to one specifying only the total solids without altering its effect.

If the same samples were examined under the Dominion standard of 8.5 per cent solids-not-fat and 3.25 per cent fat, the samples deficient in fat would be increased to 2.8 per cent and those rejected on account of deficiency of solids-not-fat would have been 14 per cent. In other words the Dominion standard of 8.5 per cent of solids-not-fat is more stringent than the Provincial one of 12 per cent total solids. Less than 0.5 per cent of the samples passed the solids-not-fat test and were rejected by the fat clause.

The standard of 8.5 per cent solids-not-fat in New York is probably equal to one specifying 11.7 per cent of total solids and 3.15 per cent of fat and is therefore tantamount to raising the State standard.

CITY LABORATORY
OTTAWA, CANADA
March 10, 1917

JOSEPH RACE,
City Bacteriologist and Chemist

Editor of the Journal of Industrial and Engineering Chemistry:

We beg to suggest the following as comment on Mr. Race's criticism of our handling of the standards in our paper in the March issue of THIS JOURNAL. We believe the trouble with Mr. Race's whole argument is to be found in his statement: "My opinion is that standard one is to be regarded as the minimum percentages of certain constituents that are to be contained in the article sold as milk." It is quite true that the principle here enunciated is the principle on which many food standards are based. It is, however, obvious that all food standards of natural products should be based on the natural composition of the product. Inasmuch as milk was one of the first materials

legislated upon and as the legislation was largely done by persons unfamiliar with the principles which should govern the establishment of standards, we think it logical to suppose that these standards represented the ideas of legislators as to the natural composition of milk, based either on experience or on what was supposed to be reliable information. This is borne out by the fact that many of the states require that milk shall be sold as produced.

It follows that standards so made should conform in their requirements to the natural article. The other alternative, namely, the allowing of the manipulation of milk (such as the extraction of the fat) would appear to be foreshadowed by the present trend of ideas regarding milk standards. Such milk would necessarily have to be sold either with a statement on the label of the percentage of fat and total solids (or solids-not-fat) or would have to be sold as of a specified standard of composition, such as "sub-standard," "above standard," etc. In this case Mr. Race's contention that the fat and solids-not-fat need bear no definite relationship to one another is correct, but this, of course, would mean that the legal provision requiring milk to be sold as produced would have to be abrogated, and any milk would be adulterated only if it departed from this declared composition.

Having regard, however, to the present standards, most of them fail to prevent adulteration because their makers (like Mr. Race) appear to think, regarding the figures set for fat and solids-not-fat (or total solids), that "it is not essential for this purpose that they should bear any relation to their relative proportions in milk." The point can be illustrated from Mr. Race's letter. He says "Only one sample (2.9 per cent fat) was deficient in fat and yet satisfied the standard for solids," which, as he tells us, is 12 per cent in Ottawa. A sample of milk analyzed by us in New York City had the composition: fat 4.8, solids-not-fat 9.17, total solids 13.97. The dairyman supplying Mr. Race's sample evidently started with a milk of somewhat this composition, for we could reduce this milk to a fat percentage of 2.9 by the abstraction of about 40 per cent of its fat as cream, and still have milk within the legal limit of total solids ($2.9 + 9.17 = 12.07$), and this is probably what happened to the sample in question. It is, moreover, a legal sample under the Rhode Island law.

It is because the present unbalanced standards not only allow of but are, especially where certain strains of cattle furnish the milk supply, an invitation to such manipulation, that we object to them.

BUREAU OF FOODS AND DRUGS LUCIUS P. BROWN
NEW YORK CITY, March 16, 1917 CLARENCE V. KERKHOFF

THE FIXATION OF NITROGEN—CORRECTION

In my article under the above title, THIS JOURNAL, 9, 1917, 233, the following corrections should be made:

- P. 236, Equation 8, NaCN should read Na_2CO_3
P. 248, 6th paragraph should read: "The above shows exactly one can get, etc."
P. 246, foot note 1 should read: "1. CO_2 , H_2O , etc."
P. 248, and equation 2, Na_2CO_3 should read Na_2O
P. 250, 2nd column, 4th line from bottom of page: CO_2NH_2 HNO_2 should read CO_2NH_2 HNO_3
P. 251 equation near top of first column should read: $\text{CN} + \text{H}_2\text{O} = \text{CO}_2\text{NH}_2$

JOHN F. HINCH

THE GERMAN ALARM CLOCK—CORRECTION

In the article under the above title, printed in THIS JOURNAL, 1, 1917, 59, the following correction should be made:

Page 60, Column 1, Line 10: The figure 110,000,000 should read \$10,000.

H. F. HINCH

PERSONAL NOTES

President Stieglitz has appointed W. D. Bigelow chairman of the Membership Committee to succeed Frank K. Cameron, resigned, and F. G. Cottrell a member of the Committee to fill the vacancy caused by Dr. Bigelow's appointment to the chairmanship. The other member of the Committee is Charles L. Parsons.

Dr. H. E. Barnard has been elected, by the Council letter-ballot, a Director of the American Chemical Society to fill the unexpired term of Dr. E. G. Love. The Council also approved the election by the Directors of Dr. E. G. Love as Treasurer of the Society.

Prof. Wilder D. Bancroft addressed the Indiana Section of the A. C. S. on "Contact Catalysis," on March 9th.

Edward Dyer Peters, Professor of Metallurgy at Harvard University and the Massachusetts Institute of Technology, died at his home in Dorchester, Mass., on February 17th, in his sixty-eighth year. Prof. Peters became a lecturer at Harvard in 1903 and had been a professor of metallurgy there since 1904.

The lecture by Dr. John Uri Lloyd, which was to be given on April 13th at the College of the City of New York, has been indefinitely postponed.

Mr. Alex. L. Feild has decided to remain with the Bureau of Mines at Pittsburgh. He was noted in our March issue as having accepted a position with the Gulf Pipe Line Company, Houston, Texas.

Prof. Henry M. Howe has been awarded the John Fritz Medal for 1917 for his investigations in metallurgy.

Mr. Stanley B. Pennock has been killed by an explosion in the works of the Aromatic Chemical Company, of which he was a partner. He was working at the time of his death on a new process for chlorination.

Prof. C. C. Todd, of the State College of Washington, announces that early in the week of February 25th there was stolen from their laboratory a platinum dish weighing about 48.5 g. and marked with four ciphers, 0000.

Dr. Jeffery Stewart, of the Philadelphia Section of the A. C. S., has resigned as secretary and superintendent of the India Refining Company, of Philadelphia, and is now connected with the oil firm of E. F. Drew & Company, of that city.

Dr. Lloyd Balderston lectured on "Tanning" at the regular meeting of the Philadelphia Section of the A. C. S. on March 15th. The Second Annual Smoker of the Philadelphia Section will take place on April 12th.

Mr. Walter Laib has been appointed superintendent of The Ohio Salt Company at Rittman, Ohio. This plant has a daily salt capacity of 5000 barrels, in addition to its production of chlorate of potash, manufactured under Mr. Laib's patent.

Mr. Oscar W. Palmenberg announces the removal of his business from the Chemists' Building to the Hudson Terminal Building, 50 Church Street, New York City, where he has taken over the chemical and physical laboratories of Dr. Chas. F. McKenna, who intends to confine his attention to his consulting practice.

Mr. A. E. Marshall has severed his connection with The Thermal Syndicate and has taken up the works management of the Davison Chemical Company's plant at Curtis Bay, Md.

The Burdett Oxygen Company completed the erection of its Salt Lake City plant on March 1st, and is in a position to furnish pure oxygen to users in that territory. The capacity of their Los Angeles plant has recently been increased 50 per cent.

Dr. Gustav Drobegg has been superintendent of Plant D, of the Butterworth-Judson Corporation, at Newark, N. J., since the beginning of this year. He was formerly superintendent for Charles Pfizer & Company until 1912; then manager of manufacturing department for the Synflour Scientific Laboratory, Monticello; and for the past two years with the Beckers Aniline Chemical Works, in charge of research and part of plant.

The McGraw Publishing Company and the Hill Publishing Company have been consolidated as the McGraw-Hill Publishing Company Inc., with James H. McGraw as president. *Engineering News* (formerly Hill property) and *Engineering Record* (formerly McGraw property) will be consolidated under the name *Engineering News-Record*, with Charles Whiting Baker, now editor of *Engineering News*, as editor-in-chief.

The United States Civil Service Commission announces the following open competitive examinations: *Assistant chemist* (male), salary \$1,000 a year, on April 18, 1917; *assistant chemist in forest products* (male), salary \$900-\$1,500 a year, on April 18-19, 1917.

Mr. M. O. Lamar, of the General Electric Company, has taken charge of the analytical laboratory of the Norton Company, at Niagara Falls.

The Twenty-fifth Anniversary of the New York Section of the American Chemical Society was celebrated with a dinner and smoker at the Chemists' Club, on March 9, 1917. The opening remarks of Chairman Matthews were followed by addresses by Provost Edgar F. Smith, of the University of Pennsylvania, on "Robert Hare;" Dr. Wm. H. Nichols on "The Early History of the Society;" and Dr. E. G. Love on "The First Years of the New York Section." Dr. Charles F. Chandler, who was scheduled to speak, was unable to attend. In honor of the occasion, Dr. Charles A. Doremus presented to the Section a large steel engraving of Prof. J. W. Draper, first president of the American Chemical Society. The officers elected for the coming year are: *Chairman*, Dr. Chas. H. Herty; *secretary-treasurer*, Mr. Chas. F. Roth.

The Pacific Coast Borax Company announce that their potash plant at Searles Marsh started up on the 1st of April. They expect to turn out quite an amount of potash during the month of April and state that from that time forth the present unit should produce 1000 tons per month, running 80 per cent or better.

Harrison W. Craver, chief librarian of the Carnegie Library of Pittsburgh since 1908, has tendered his resignation to the Library Committee of the Board of Trustees of Carnegie Institute, to take effect April 1st. Mr. Craver has accepted a position as director of the library of the United Engineering Societies of New York, and left Pittsburgh the latter part of March to assume his new charge. His new position will put him in direction of what is believed to be the largest engineering library in the world, with approximately 150,000 volumes on technological subjects on its shelves.

Mr. Howard F. Weiss has resigned the directorship of the U. S. Forest Products Laboratory at Madison, Wis., and from April 1st will be connected with the C. F. Burgess Laboratories, Madison, Wis.

At a special meeting of the Cincinnati Section of the A. C. S. on March 7, Dr. Wilder D. Bancroft, of Cornell University, spoke on "Contact Catalysis." A regular meeting of the Cincinnati Section was held on March 28, with the following program: "The Composition of Menhaden Oil Fatty Acids," by Dr. Ernst Twitchell, and "The Progress of Chemical Industry," by Mr. H. B. Schmidt.

Mr. A. Brooking Davis, who is now with the Ault & Wiborg Company, Cincinnati, is chemical director of that concern.

Eimer & Amend give notice that the man under the name of F. H. (or H. F.) Frank, or Fisher, soliciting orders and obtaining money by using the name of their firm, is an impostor and acting entirely without their authority. He has been operating in Chicago, Cleveland and Grand Rapids, and perhaps elsewhere.

The University of North Dakota has been granted an appropriation from the State Legislature of \$90,000 for the first unit of a new chemistry building, construction of which will begin immediately. The department of chemistry has more than doubled in the last five years and was sorely pressed for room.

We are informed by Mr. Anton Richard Rose, of New York City, that the "Norsk hydroelektrisk Kvaelselst aktieselskab" has set aside 100,000 kr. to be transferred to the Nansen Fund trustees, Kristiania, Norway, for the promotion of chemical and physical research. Inasmuch as the founder of this company, Sam. Eyde, celebrates his 50th birthday on October 29th, the company desires that this fund be known as "The Sam. Eyde Fund for the promotion of chemical research." Only the interest from the fund is to be expended, and in such manner as the trustees may deem desirable for scientific investigations within the designated field. [See *Tid. Kemi, Farm. Terapi*, 13 (1916), 301.]

The New York Section of the Society of Chemical Industry held its March 23rd meeting in conjunction with the Home Economics Association. Prof. Lafayette Mendel, of Yale University, spoke on "Food Fads" and Dr. Graham Lusk, of Cornell University, on "Food Values."

The Williams Patent Crusher & Pulverizer Company, St. Louis, Mo., have taken larger quarters for their Pacific Coast sales office, at 67 Second St., San Francisco. Mr. O. J. Williams is in charge of the San Francisco office.

The Second Annual Drainage Conference of the University of Illinois was held March 13-15, 1917. The organization and financing of drainage districts, the surveying of drainage areas, the design of systems, and improved methods of construction were among the subjects considered by engineers and public officials of prominence. The meeting was in charge of the department of Civil Engineering, College of Engineering, Urbana, Illinois.

A Public Inspection Day for the new chemical building of the University of Cincinnati has been set for April 7. The program includes an address by Dr. Chas. H. Herty, and a subscription dinner at the Hotel Gibson Ball Room.

Dr. Charles A. Mann, of the University of Wisconsin, has been appointed associate professor of chemical engineering at Iowa State College, to succeed Prof. George A. Gabriel, who goes into practical work.

GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

BUREAU OF STANDARDS

A Study of Electromagnet Moving Coil Galvanometers for Use in Alternating Current Measurements. ERNEST WEIBEL. Scientific Paper 297. This paper gives the results of a study of the electromagnet moving coil galvanometer that has led to the construction of instruments with sensitivities much greater than those previously obtained and equal to those of the best direct current moving coil galvanometers. The theory of the instrument is developed.

The Recovery of Paraffin and Paper Stock from Waste Paraffin Paper. W. H. SMITH. Technologic Paper No. 87. 4 pp. "This paper describes a process for the recovery of the paraffin and paper stock from waste paraffin paper. The waste is pulped with exhaust steam in a vertical boiler. The wax rises to the surface, and is drawn off with the hot water through a screen, the stock settling to the bottom of the boiler. The stock is transferred to a heating engine and further treated for the removal of the residual paraffin. Paper prepared from the recovered stock was free from wax and satisfactory in every respect. Practically all of the paper stock is recovered, but about 10 per cent of the paraffin in the waste is lost during the process."

This paper is no longer available for free distribution; it can be procured only from the Superintendent of Documents. Paper, 4 cents.

Fees for Electric, Magnetic, and Photometric Testing. Circular No. 6, 7th Edition, 30 pp. "Information regarding tests, range of testing, instructions to applicants, and schedules of fees, for electric resistances and instruments, apparatus for radio communication, magnetic testing, testing magnetic parts of materials, radioactivity, and photometry."

National Electrical Safety Code. Circular No. 54, 2nd Edition, 323 pp. Paper, 20 cents, or Cloth, 30 cents. This publication is for examination, trial, and constructive criticism; it gives definitions of terms and rules for installation, operation and maintenance of central station and substation equipment, overhead and underground lines, grounding of apparatus and supports, and for the installation of wiring for electrical utilization apparatus.

Some Technical Methods of Testing Miscellaneous Supplies. P. H. WALKER. Unnumbered publication, reprinted from Bureau of Chemistry Bulletin 109, with notes and corrections. 68 pp. Paper, 15 cents. This report includes methods for paint and paint materials, ink, lubricating oils, soaps, etc.

Resistance of an Oil to Emulsification. WESLEY L. HILL. SENIOR. Technologic Paper No. 86. 37 pp. In this paper is described a new test for the emulsification of oils. Certain results obtained by such measurements are also discussed. The test may be briefly described as follows: An oil or the oil to be tested and twice that volume of distilled water are heated to 55° C. in a 100-cc. cylinder, 16 mm. inside diameter, and stirred for 3 minutes at a speed of 1100 revolutions per minute. The cylinder and contents are allowed to stand at the room temperature, and readings are taken at seven or ten frequent intervals according to the type of oil. The volume of oil that has risen from the water. From these readings a measure of the oil's ability, called "deemulsiability," is easily taken from a table. The paddle is simply a plate of metal 8 in. by 1 in. by 1/16 in. thick. The test is not sensitive to slight changes of pH. Furthermore, they need not be exact, and no calibration is required.

Studies on Paper Pulp. W. H. SMITH. Technologic Paper No. 88. 13 pp. Paper, 5 cents. "Samples of paper pulps, each representing a different method of preparation, with one exception of American manufacture, have been examined to determine their chemical properties. The loss in weight produced by reagents causing hydrolysis and oxidation and the gain in weight when nitrated have been determined with the same pulps. The effect of sunlight, temperature, and ozonized air on the chemical constants of ground wood has been ascertained."

A Specific Gravity Balance for Gases. JUNIUS DAVID EDWARDS. Technologic Paper 89. 17 pp. Paper, 5 cents. "The apparatus described provides a quick and accurate means of determining gas density. A form of balance-beam support has been devised which gives high sensibility. The needles which replace the knife-edge are easily adjustable and, in contrast with the metal or quartz knife-edge usually used, can be obtained almost anywhere, are inexpensive, and can be replaced as often as necessary. The success obtained in the use of this apparatus is mainly due to the high sensibility afforded by this means of support. It is necessary to remove the beam from the case only when it is desired to transport it. No leveling bottle is necessary in adjusting the gas pressure within the balance, this being accomplished by means of a needle valve which affords precise control. The portable outfit combines lightness of weight, convenience in use, and durability without any great sacrifice of accuracy. No preliminary calibration of the apparatus is necessary."

United States Government Specification for Portland Cement. ANONYMOUS. Circular No. 33; 3rd Edition. 43 pp. Paper, 10 cents. This specification is the result of several years' work of the joint conference representing the United States Government, the American Society of Civil Engineers, and the American Society for Testing Materials. It was adopted by the United States Government and by the American Society for Testing Materials, to become effective January 1, 1917.

BUREAU OF THE CENSUS

Census of Manufactures: General Totals for United States by Geographic Divisions, States, and Industries, 1914, 1909, 1904 and 1899. 26 pp. "General statistics for manufactures censuses for 1914, 1909, 1904 and 1899 are shown in two tables. Table 1 presents a comparative summary for the United States by geographic divisions and States, by number of establishments, average number of wage earners, primary horsepower, capital, wages, materials, and value of product. Table 2 gives comparative summary, under same headings as in Table 1, for 333 of principal industries for which statistics were gathered in 1914."

Cotton Production and Distribution, Season of 1915-16. Bulletin 134, 99 pp. Paper, 20 cents. This report includes statistics regarding the manufacture of cottonseed products which are of chemical interest.

FEDERAL TRADE COMMISSION

Fertilizer Industry. Senate Document 551, 64th Congress, 1st Session. 269 pp. Paper, 50 cents. This is a report of the Federal Trade Commission in response to a Congressional resolution calling for a report on an investigation of the fertilizer industry which was begun by the Bureau of Corporations.

NATIONAL MUSEUM

Newly Found Meteoric Stone from Lake Okechobee, Florida. GEORGE P. MERRILL. From *Proceedings*, Vol. 51 (December 21, 1916), 525-526. Reprint No. 2163.

Notes on Whitfield County, Georgia, Meteoric Irons, with New Analyses. GEORGE P. MERRILL. From *Proceedings*, Volume 51 (December 16, 1916), 447-449. Reprint No. 2157.

Recently Found Iron Meteorite from Cookeville, Putnam County, Tennessee. GEORGE P. MERRILL. From *Proceedings*, Volume 51 (November 24, 1916), 325-326. Reprint No. 2153.

DEPARTMENT OF AGRICULTURE

The following seven articles from Volume 8 of the *Journal of Agricultural Research* are of chemical interest:

(1) **Availability of the Potash in Certain Orthoclase-Bearing Soils as Affected by Lime or Gypsum.** LYMAN J. BRIGGS AND J. F. BREAZEALE. (January 2, pp. 21-28.)

(2) **Ewes' Milk: Its Fat Content and Relation to the Growth of Lambs.** E. G. RITZMAN. (January 8, pp. 29-35.)

(3) **Calcium Compounds in Soils.** EDMUND C. SHOREY, WILLIAM H. FRY AND WILLIAM HAZEN. (January 15, pp. 57-77.)

(4) **Effect of Fertilizers on the Composition and Quality of Oranges.** H. D. YOUNG. (January 22, pp. 127-138.)

(5) **Measurement of the Inactive, or Unfree, Moisture in the Soil by Means of the Dilatometer Method.** GEORGE ROUVINCOUS. (February 5, pp. 195-217.)

(6) **Arsenical Injury Through the Bark of Fruit Trees.** DEANE B. SWINGLE AND H. E. MORRIS. (February 19, pp. 283-317.)

(7) **Effect of Irrigation Water and Manure on the Nitrates and Total Soluble Salts of the Soil.** F. S. HARRIS AND N. I. BUTT. (February 26, pp. 333-358.)

Possibility of the Commercial Production of Lemon-Grass Oil in the United States. S. C. HOOP. Department Bulletin 442, from the Bureau of Plant Industry. 12 pp. Paper, 5 cents. Published January 25. This is a report of experiments conducted to determine the commercial possibilities of the cultivation of lemon-grass for the production of the oil which is used in the manufacture of perfumes and soaps.

Composition of Hawaiian Soil Particles. WILLIAM T. McGEORGE. Bulletin 42, Hawaii Agricultural Experiment Station. 12 pp. Paper, 5 cents. Published January 17.

Improved Apparatus for Use in Making Acidity Determinations of Corn. H. J. BESLEY AND C. H. BASTON. Circular No. 68. 4 pp. Paper, 5 cents.

PUBLIC HEALTH SERVICE

Commission on Milk Standards. Third Annual Report of the Commission on Milk Standards appointed by the New York Milk Committee. Public Health Reports, 32, 271-96 (February 16).

GEOLOGICAL SURVEY

Tungsten Deposits of Northwestern Inyo County, California. ADOLPH KNOPF. Bulletin 640-L, from Contributions to Economic Geology, 1916, Part II, pp. 311-333. Published February 8. "At present interest in the mining of the eastern black shales as a source of oil must confine itself to localities where one of three conditions is met. The shale can be utilized, first, where it outcrops in a position to permit mining on a large scale by steam shovel at a minimum cost; second, where coal that is overlain by bituminous shale is being stripped; and third, where a coal bed that is being mined has a black shale roof that comes down and must be removed from the mine in large amounts. Of these the second condition seems to offer the best opportunity for a trial plant, as the overlying black shale must be removed in mining the coal. At such pits it would require only that another shovel be installed to lift the shale, or the small shovel now used to lift the coal could be used to lift the black shale first. This black shale over the coal appears to have the advantage of a higher oil yield. Where the roof shale is as rich as at Cannelton, Pennsylvania, it may pay to mine the shale with the coal."

The Cleveland Gas Field, Cuyahoga County, Ohio. With a Study of Rock Pressure. G. SHERBURNE ROGERS. Bulletin 661-A, from Contributions to Economic Geology, 1917, Part II, pp. 1-68. Published March 2.

Useful Minerals of the United States. Compiled by FRANK C. SCHRADER, RALPH W. STONE AND SAMUEL SANFORD. Bulletin 624. This bulletin may be regarded as a thoroughly revised

edition of Bulletin 585, greatly enlarged and brought up to date. The present bulletin, like the earlier work, gives concisely the location, by states and counties, of the principal deposits of useful minerals, and includes a glossary showing the composition and character of each mineral and the location of its principal deposits. It gives also the principal uses of each mineral, a feature not appearing in the earlier bulletin. As a mineral directory it will be useful to scientific bureaus and educational institutions that deal with the numerous inquiries of the general public concerning what may be called commercial mineralogy, as well as to the prospector, miner, manufacturer, business man, and student of economic conditions.

Gold and Silver in 1915. (General Report.) H. D. McCASKEY AND J. P. DUNLOP. From Mineral Resources of the United States, 1915, Part I, pp. 767-803. Published March 2.

The Inorganic Constituents of Marine Invertebrates. FRANK WIGGLESWORTH CLARKE AND WALTER CALHOUN WHEELER. Professional Paper 102. 52 pp. Paper, 10 cents.

Baked Shale and Slag Formed by the Burning of Coal Beds. G. SHERBURNE ROGERS. Professional Paper 108-A, from Shorter Contributions to General Geology, 1917, pp. 1-10. Published March 3.

BUREAU OF MINES

Abstracts of Current Decisions on Mines and Mining. Reported from May to August, 1916. J. W. THOMPSON. Bulletin 143. 68 pp. Paper, 10 cents.

Refining and Utilization of Georgia Kaolins. IRA E. SPROAT. Bulletin 128. 49 pp. Paper, 15 cents. "Up to the present time mechanical principles only have been applied in the refining of kaolins, but in order to keep pace with the increasing requirements for better quality and uniformity of product, the application of the principles of colloidal chemistry is necessary.

"The investigation described in this report was carried on to determine the practicability of applying technical control of clay disperse systems to the refining of kaolins and the utilization of the prepared clay in the manufacture of vitreous china and wall tile.

"It is hoped that this report will prove a stimulus to the clay-washing industry; will point out a method of refining certain American clays, and will lead to the substitution of domestic kaolins for imported china clays by manufacturers of high-grade ceramic wares."

HYGIENIC LABORATORY

Experimental Studies with Muscicides and Other Fly-Destroying Agencies. EARLE B. PHELPS AND ALBERT F. STEVENSON. Bulletin No. 108. 37 pp. Paper, 10 cents. "A somewhat comprehensive survey has been made of other chemical substances having possible muscidial properties with a view to substituting them for the arsenic preparations now commonly employed.

"Of the substances frequently recommended, potassium dichromate and quassia sirup have been found to be of little value. Formaldehyde, on the other hand, when properly employed has been found to be much more efficient than the standard arsenite solution. The studies have indicated the most efficient strength of the formaldehyde solution to be from 0.5 to 1 per cent, which is equivalent to 1.25 to 2.5 per cent of the 40 per cent solution sold as formalin.

"A muscicide of almost equal efficiency and of distinctly superior qualities in many ways has been found in the substance sodium sacchylate, a 1 per cent aqueous solution of which is recommended.

"At midsummer temperatures the efficiency of either of these preparations is slightly greater than that of solutions prepared for commercial poison papers. Directions for preparing these solutions in the household and recommendations for their commercial preparation and sale are made."

COMMERCE REPORTS—FEBRUARY, 1917

The yield of indigo in British India for 1916-17 will be about 75 per cent greater than in 1915-16. (P. 449)

The production of Chinese wood-oil in China is described in detail. The methods of extraction are crude but fairly effective. In China the oil is largely used directly for painting boats, for the manufacture of water-proof varnish on cloth, in lacquer and other varnishes, soap, and leather dressing. In other countries, chiefly the United States, it is used in the manufacture of varnish from cheap gums. The possibilities of its cultivation in the Southern States of this country are promising. (Pp 457-60)

The sugar beet crop of Russia shows a marked decrease. (P. 469)

Efforts are being made to develop electric smelting of iron ore at Mysore, India. (P. 482)

The discovery of large deposits of molybdenum ore in Peru is reported. (P. 495)

Practically no wood pulp is now being made in Brazil, though steps are under way to develop the industry. (P. 508)

Direct shipment of cochineal from the Canary Islands to the United States is increasing. (P. 519)

The production and export of nitrate from Chili is now greater than at any previous time, even before the war. (P. 555)

Efforts are being made in Spain to prohibit the export of "green sulfur oil" (crude olive oil) to offset the shortage in Spain of other soap fats and oils. (P. 596)

Efforts are being made by the Bureau of Fisheries to develop the manufacture of leather from shark skins. (P. 635)

The amount of rubber shipped from Brazil and Peru to the United States is now over two and one-half times that shipped to Europe. (P. 642)

Efforts are being made to develop the cultivation of sugar beet seed in this country. (P. 669)

The mineral output of the Kingston district in Canada, includes mica, iron ore, feldspar, talc, pyrites, fluorspar, molybdenum and zinc ores, and graphite; most of which are controlled by American capital. (P. 692)

Efforts are being made in England to promote the spinning of yarn from kapok fiber, now used extensively in upholstery and life preservers. (P. 710)

The total production of potash in the United States in 1916 represented about 10,000 tons of K_2O . (P. 728)

Commercial methods used for the measurement of leather are being investigated by the Bureau of Standards. (P. 738)

Japan is exporting annually about 75,000 tons of sulfur, one-half to the United States. (P. 788)

STATISTICS OF EXPORTS TO THE UNITED STATES

KORE, JAPAN, 502	Liquors	RUSSIA, 610
Antimony ore	Ammonium sulfate	Alumina
Brown powder	Barytes	Ammonium sulfate
Campbor gum	Gum copal	Rubber
Copper	Castor beans	Crude oil
Alumina	Petroleum	Paper
Menthhol	Palm oil	Wool
Campbor oil	Leather	
Castor oil	Clay	
Cocunut oil	Steel	
Cottonseed oil	Iron	
Fish oil	Copper	
Peanut oil	Nitrate	
Rapeseed oil		
Soya bean oil		
Porcelain		
SILVER, CANADA, 461		
Admiral		
Chromate of iron		
Copper ore		
Hydro		
Maple sugar		
Paper		
Pulpwood		
Wood pulp		
Uranium		
Vanadium		
Zinc		
Artificial silk		

BOOK REVIEWS

A German-English Dictionary for Chemists. By AUSTIN M. PATTERSON, PH.D., formerly editor of *Chemical Abstracts*. xvi + 316 pp. John Wiley and Sons, Inc., New York, 1917. Price, \$2.00 net.

Dr. Patterson has performed a public service in the compilation of his German-English Dictionary for Chemists. His extended experience as Editor of *Chemical Abstracts* has given him exceptional qualifications for such an undertaking and the work shows the same painstaking care which characterized his successful work as Editor.

All chemists will understand the particular value of such a dictionary if they will recall their early efforts to read the German chemical journals, following a general two years' collegiate course in German and with the aid of the usually available German-English dictionaries. What a host of words and abbreviations presented themselves for the significance of which dictionaries gave no assistance. These old friends for whom we so long and fruitlessly sought are present in this new volume ready at hand and easy of access. So too for older chemists, already familiar with the German language, the book will prove of great value wherever accurate translation of any passage is required.

The printing is good, the covers are flexible, and the size is suited to the coat pocket. It meets a real need and it is safe to predict its general use.

CHAS. H. HERTY

How to Build up Furnace Efficiency. By JOSEPH W. HAYS, Combustion Engineer. Tenth Edition. 154 pp., 26 illustrations. Joseph W. Hays, Rogers Park, Chicago, Illinois. Price, \$1.00.

In the preface of this book the author explains that he has been led to write this rather technical subject of combustion in a really popular way, such as the public would want. The present tenth edition contains many new features. There are new charts, diagrams and illustrations to make clear some of the things that are hard to explain in the printed page. The author endeavors to show the manager, superintendent, engineer and fireman of the power plant how they may proceed actually to work a real reduction in the coal bills.

The object of the book is to make clear to engineers and firemen the proper way of operating a boiler furnace most economically, and the means suggested are not new, but the mode of expression is interesting and simple and as the author confesses "rather unvarnished," and he knows that the manager and engineer will accept his criticisms with the same good nature in which they are offered.

The subject discussed deals principally with the relation of the percentage of carbon dioxide in the flue gas, the draft in the furnace, stack temperature, leaks due to faulty boiler setting and how these affect the conditions for proper combustion.

The subject of fuel waste is enumerated and each loss is explained; it is further shown what the possible economies may be, how the wastes occur and how to overcome them.

In the appendix a number of charts are presented showing in a graphic way the relation between the constituents of the air and the products of combustion when burning different fuels such as oil, gas, wood, refuse and other material.

The book is written in "Five Reels." (1) Why Your Fuel Is Wasted; (2) How Your Fuel Is Wasted; (3) How to "Spot" Your Fuel Waste; (4) How to Stop Your Fuel Waste; (5) How to Keep the Waste Stopped. The book is of convenient size to have at hand and use as a guide.

OSCAR W. PALMENBERG

The Chemistry and Technology of Paints. By MAXIMILIAN TOCH. Second Revised Edition. D. Van Nostrand Company, New York, 1916. xi + 366 pp., 83 illustrations. Price, \$4.00.

The first edition of this book was published in 1907 and entitled "The Chemistry and Technology of Mixed Paints." It contained 166 pages as against 366 of the second edition, so that the enlargement is very material. Since the publication of the first edition there has been a large amount of attention devoted to the study of paint, and there are in consequence 28 chapters in this second edition as against 16 in the first, and such a subject as "Chinese Wood Oil" has 111 pages devoted to it whereas formerly it had 6, while considerable attention is given to the newer work on fish oil and soya bean oil. That portion of the work devoted to the analysis of paint materials has undergone most marked changes, for in the analytical methods applicable to paint materials, and especially to oils, the work done in recent years has been very extensive and the results are incorporated in this second edition.

One of the noticeable features of the book is the treatment in Chapter 10 of the inert fillers and extenders. Until comparatively recent years, these materials were regarded as adulterants of paint and are by many so regarded now. The author treats these as though, within their stated limitations, they were entitled to the same kind of consideration as the older pigments such as lead and zinc, and discusses their merits and demerits quite as fully and in a manner equally scientific and exact. It may be said of the work generally that it is up-to-date, that it covers the fields suggested by its title thoroughly, and that it is full of suggestions for further research and improvement.

P. C. MCILHINEY

Engineering Chemistry. By THOMAS B. STILLMAN. Fifth Edition. 743 pp., 8vo., with 150 illustrations. The Chemical Publishing Company, Easton, Pa., 1916. Price, \$5.00.

The appearance of five editions of this book since the first issue shows that it has been extensively used. On account of the death of the author in August 1915, when this edition was approaching completion, its final publication has been carried out by Messrs. Albert L. and Thomas B. Stillman. The book has been considerably enlarged and modified, but the main features of the previous editions have been retained.

The sub-title of the work describes it as "a manual of quantitative chemical analysis for the use of students, chemists and engineers," but it is to be observed that descriptions of many physical tests, copies of specifications, and other topics not dealing strictly with chemical analysis are included. On the other hand the book deals with only a restricted field of analytical chemistry, confining itself practically to the testing of such materials as are used in civil or municipal engineering.

It does not deal with mineral analysis or organic analysis in general, nor does it deal with the analysis of the important products of chemical industry, such as acids, alkalis, salts, bleaching materials, dyes, medicinal products, etc. However, the book presents much that is useful in its particular field.

Among the subjects most extensively treated are the proximate analysis of fuels, their colorimetry and their physical examination, the analysis of iron, steel and a number of non-ferrous alloys, the analysis and physical tests of cement, concrete, clay, sand and building stones, the examination of asphalt and other bituminous road materials, of coal tar, lubricating

oils, illuminating oils and fuel oils, soap, paint and varnish analyses, the chemical and physical examination of paper, the analysis and treatment of potable waters and boiler waters, the analysis of flue gases, illuminating gases, etc., the manufacture of producer gas, water gas and acetylene, photometry and pyrometry. Many official methods are quoted and many interesting details of manufacture are given. The book is to be highly recommended to those interested in these lines of examination.

The book contains several condensed tabular schemes of analysis, which, while useful to experienced analysts as aids to memory, give hardly sufficient details for the use of beginners. One of them, dealing with the analysis of potassium cyanide, has a misprint of "K T" for "K I" and it is certain that the inexperienced analyst would fail to determine cyanogen if he should use potassium tartrate in place of the iodide.

H. L. WELLS

Vinegar: Its Manufacture and Examination. By C. A. MITCHELL. 201 pp. and 54 illustrations. Published by C. Griffin & Co., London, and by J. B. Lippincott Co., Philadelphia. Price, \$2.75.

The first third of this volume is devoted to the history of vinegar making, the second to the manufacture of vinegar, and the last to the methods of examination and characteristics of the various kinds of vinegar. So far as the book is concerned with modern practice, it deals almost exclusively with the English practice which is based on an acetic fermentation taking place at 105 to 110° F., while the rest of Europe, and America, ordinarily use bacteria which have their maximum activity at about 90° F.

The reviewer wishes to take issue with the opinion (p. 117) that the more rapid the vinegar formation the greater will be the clogging of the quick vinegar generator by "mother of vinegar."

The relation of the amount of oxygen available in the quick vinegar generator to the growth of the vinegar eel does not seem to be appreciated (p. 120) and the common method of getting rid of this pest by completely shutting off the air supply for a few days is apparently unknown in the English vinegar factories.

The rapid destruction of the acetic bacteria by the larvae of the vinegar fly seems to have been overlooked by the author, for it is stated (p. 128) that this fly "does not in any way affect the manufacture" of vinegar.

Taken as a whole the volume is one written by an Englishman for the English public and deals mostly with strictly English procedure. The book is of little value to American readers and is not to be compared with the standard works on vinegar which are available in German and in English.

RALPH H. MCKER

Modern Chemistry and Its Wonders. By GEOFFREY MARTIN, Ph.D., D.Sc., London. xvi + 351 pp. D. Van Nostrand Co., New York. Price, \$2.00.

In the preface of Dr. Martin's latest book he states: "My recently published book, 'Triumphs and Wonders of Modern Chemistry,' met with such an enthusiastic welcome by the chemical reading public . . . that when my publishers approached me with the request to write a companion volume to that work, treating of matters omitted for want of space in the first book, I gladly acceded to their proposal. The present book is the result. The treatment is popular, technicalities being avoided as much as possible. However, in it I suppose the reader to be familiar with the ordinary conception of chemistry, such as have already been explained in a popular manner in the first book. The book is not intended for student, wishing to study for one or other of the innumerable examinations

of our somewhat chaotic examination system. Rather it is intended to interest the cultured, general reader in some of the really wonderful achievements of scientific chemistry."

The author has accomplished the above in this, his latest work. To the reviewer, a teacher of General Inorganic Chemistry, the reading of the book was such a pleasure and an inspiration that it was read from cover to cover. Such a variety of interesting facts of every-day chemistry was presented in a manner and language that made one realize that the language of the chemist should not be foreign to the cultured layman. To a teacher the book is invaluable with its suggestions for presenting in clear concise manner the fundamental facts and principles of every-day chemistry. This is especially true for beginners' classes and popular lectures.

The average, dyed-in-the-wool chemist, or chemistry teacher is apt to undervalue books of this type (and we have too few of them); these are the very books we need, both for the teachers, our students and more especially for the cultured public.

Text-books are for the most part incomprehensible to an intelligent reader without the teacher, the classroom, and the laboratory. Should a layman of average education have the misfortune to pick up the average chemistry text-book, even a book intended for beginners, he proceeds only a few pages and closes it in disgust, concluding that chemistry is fit only for highbrows. The text-books have their place and we have a deluge of them, but we have too few of the popular type books.

The reviewer felt that the main worth of the book rested with its value to students of chemistry, and more especially the layman of average education. A class of sixteen freshmen, who had just finished their first half-year of college chemistry, and had elected a sequence in honors chemistry, were assigned summer reading consisting of a history of chemistry, Robert Kennedy Duncan's books, "The New Knowledge," and the "Chemistry of Commerce," and Geoffrey Martin's books. At the opening of the fall term, the class was unanimous in that "Modern Chemistry and Its Wonders" was the most instructive and inspiring of the list. With the layman in view, the book was placed in the hands of a friend who had never studied chemistry. The results were that the book was not only read, but was read on until the small hours of the morning. In a few days when he was asked how he liked the book, the reply came—"That is the first chemistry book I could understand and really enjoy."

The topics are varied, and each chapter is in itself a short story not dependent on preceding chapters. The Romance of Coal Tar, the Romance of Salt, Artificial Precious Stones, The Romance of Alcohol, of Explosives, of Hydrocarbons, are some of the live topics of every-day chemistry treated in a lucid manner. The author has even been bold enough to devote a chapter to Radium, and one to the Mystery of the Periodical System.

What the science of chemistry needs to-day is expansion in research. Research is expensive, and who carries the financial burden of research? The poorly endowed college or university? The chemist? The chemistry teacher? The University does her share, the chemist and teacher are usually too poor. It is the well-to-do reading public, and you cannot make the public interested in research in chemistry unless you have some means of letting them know what chemistry is, what it has accomplished for mankind, and an insight into the possibilities of further as well as endowed scientific endeavor and which are based on pure enterprise. Let us have more books of this type and have their circulation be enormous, with the end that they may begin to a considerable extent to finance the research that must be financially in our public (the general) and the classroom of the reading public.

The book is a most appropriate, the style and illustrations are well chosen, and of good workmanship, and the volume is free from errors in chemical nomenclature and chemical facts.

ARTHUR C. JONES

LITERATURE OF THE NITROGEN INDUSTRIES, 1912-1916

By HELEN R. HOSMER, Research Laboratory, General Electric Company

INTRODUCTION

In the following general review of the literature of the Nitrogen Industries it is attempted to give in convenient form the essential statements of papers published during the last five years. The earlier literature is very general and often vague in nature, and is sufficiently well covered by a number of books. Moreover, it is the recent material with its more specific treatment of technical and cost details which is now of particular interest in connection with the attempts being made to establish an adequate domestic supply of nitrogen compounds for the United States.

The purpose has been to present an outline giving the salient features of the subject, as stated by various authorities, together with a bibliography of such a kind that the original articles need not be consulted in order to find which contain the particular information desired. The aim has not been exhaustiveness but rather the listing of references generally available in this country. It is believed, however, that the field is fairly well covered by these and that extension of the list would but lead to duplication, or to the inclusion of trivial articles.

The arrangement is inversely chronological except where entire consistency might have separated related items. The appendix contains material not properly a part of the subject but of possible use to those interested in the present-day problem. In this latter no effort is made to cover the fields at all completely.

It should be kept in mind that in all cases the statements made are those of the authors quoted. This accounts for some repetition and for contradictory data on some points. In cases where the material of different writers was obviously taken from the same authority this fact is noted and only one is quoted in detail.

In regard to the fact that the testimony given favors certain processes very markedly it must be remembered that certain industrial interests now prominent in this country have contributed disproportionately to the literature. It may well be that some of the processes not praised at all highly here, may yet prove to be cheaper and more efficient.

Very recently information of a fragmentary nature seems, for instance, to indicate that the Germans have been placing their reliance upon the Haber process, which may well have been much improved and developed during the last two years. In all cases, the data given here should be taken for what they are worth and not as authoritative.

I—DESCRIPTION AND CHEMISTRY OF PROCESSES

GENERAL*

Washburn¹³ (1916) discusses in some detail the factors having bearing upon the problem before the United States of establishing a domestic supply of nitrates adequate to war demands. He analyzes the various proposals made. Gilbert¹⁴ gives similar data in a condensed form.

Norton¹⁷ (1916) discusses the various water powers in the United States which are available and adaptable to the nitrogen fixation industry. He favors the establishment of three plants to supply the needs of the sections of the country having the largest demands. He also mentions the possibility of getting 7,400,000 horse power during 14 hours of the day from complete harnessing of Niagara Falls. The details of this plan are given by Dunn¹⁰ (1915); see also References 15 and 127.

Merrill¹⁸ (1916) gives similar data for Western water powers. Skerrett²⁴ (1916) gives a very general and brief treatment of the nitrogen situation, mentioning the importance of its consideration in connection with preparedness, and outlining very

briefly the arc and cyanamide processes. He quotes from Norton, and most of his other data are to be found in Washburn's articles and statements.

Cushman²⁸ (1916), in an article entitled "Rôle of Chemistry in War," has discussed, among other things, the status of our nitrogen supply and the methods available for remedying this situation. His data on this point are taken from Summers³² (1915), and Baekeland³⁸ (1914).

Cresap³⁸ (1915) gives in very general terms the compositions and characteristics of some 15 of the more common military explosives. It is to be noted that nitric acid is required for the preparation of all.

Baekeland⁴⁸ (1914) gives a brief history of the nitrogen industries and their present status, explaining the cause of failure of the Bradley and Lovejoy process. He mentions that a French Company has taken up the application of the Serpek process.

Merrill⁴⁸ (1915) gives full statistics of the water power resources and electric power development and control in the United States. The conclusions of his report are, however, severely criticized in Reference 31 (1916).

Martin and Barbour¹ (1916) in their book on "Industrial Nitrogen Compounds and Explosives" present a general review of the whole subject with references. They describe the most important processes and give diagrams and photographs of the apparatus. They also discuss the more general aspects of the subject and include statistics and many patents.

Roerber⁴⁹ (1910) gives a good general review of the nature of the various processes for nitrogen fixation, and their present status.

Summers⁵² (1915) discusses in detail the physical chemistry and thermodynamics of the endothermic reaction between nitrogen and oxygen, giving the results obtained by Nernst from investigation of the equilibrium at temperatures between 1500 and 3500° C., by Nernst and Jellinek on rate of dissociation of NO at various temperatures and by Haber and Koenig working at reduced pressures. He computes that owing to the extreme dilution of the product there is a loss of some 95 per cent of the energy employed. He also mentions briefly the physico-chemical factors involved in the Cyanamide and Serpek processes.

The only arc processes in actual operation according to Landis⁴⁶ (1915) are the Birkeland-Eyde, the Schönherr, and the Pauling, all of which give as a product a gaseous mixture containing from 1 per cent to 2 per cent by volume of nitric oxide, from which the present well standardized condensation plants recover nearly 95 per cent in the form of 30 to 35 per cent nitric acid. This can be concentrated to 50 per cent by utilizing the waste heat of the process, but must then be further concentrated by special processes, or else converted into calcium or ammonium nitrate, before it is available for commercial purposes. The ammonia for such conversion is obtained in most cases from cyanamide.

These are processes require enormous quantities of cheap electrical energy⁴⁶ (1915).

For a detailed discussion of the reactions involved and the thermodynamics of the case, Knox⁹⁷ (1914) should be consulted. He gives a full and critical review of the literature down to 1913, devoting over 86 pages to the chemistry of the processes, with references to the original articles.

Knox also describes the commercial processes and furnaces, taking up the Birkeland-Eyde, Pauling, Schönherr, Haber, Serpek, Cyanamide, and some other less important ones. The book is an extremely good résumé of the subject but lacks entirely yields, cost data, and technical details.

Haber⁶⁴ (1914) mentions the thermodynamical conditions limiting the yields of the arc and synthetic ammonia processes

* Numbers refer to References in Bibliography, pages 437 and 438.

for fixing nitrogen. He believes that each process has its own field in which it may be successfully operated.

In his book, Perlick⁴⁶ investigates the general economic bearing of the nitrogen fixation industry and its relation to other industries and to agriculture, especially from the point of view of Germany's producing the nitrogen compounds necessary for her own consumption. The contributions to be expected from each of the processes available are discussed. From a consideration of costs he concludes that the demands of the chemical industries can be satisfied either by the arc process or by the Ostwald process of ammonia oxidation. The problem of supplying the needs of agriculture without increasing the cost is still unsolved. The Haber and Serpek processes seem to offer the most promise for this purpose. Statistics of consumption and production of various nitrogen sources are given.

The chemistry and reactions involved in the oxidation of nitrogen and the absorption of the acid formed are discussed by Scott¹²⁷ (1912) who gives the equations. He also discusses the theories for the process of oxidation, mentioning particularly the probability that ozone is an intermediate product and very essential to the course of the reaction.

Norton's¹²⁸ (1912) book like Knox's is a résumé of the nitrogen situation, including material collected from the literature, patents and personal observation. It is extremely full and comprehensive, and supplements Knox's book just where the latter is lacking, *i. e.*, on the technical and commercial side. The development of the industry and the various plants are given special attention. Methods of producing the materials required by the various processes are considered in their bearing upon an American industry. The properties and applications of the products are taken up. The organization of the European industry is described.

The chemistry of the processes and the possibilities for improvement are mentioned. He discusses the probable future of the industry particularly with regard to the effect of the cost of power and price of Chilean nitrate.

Norton also takes up the thermodynamics of the various processes. He describes also the less well-known patented processes and furnaces such as those of Guye, Von Kowalski and Mosicki, Thorsen and Tharaldsen, and Albion. In fact he pays especial attention to patents. He includes non-electrical processes such as that of Häusser.

The uses of the various products, the syntheses of related products such as cyanides, statistics of the world's supply and consumption of nitrogen compounds, recovery of waste nitrogen products are all reviewed.

Norton's book is, in fact, the most complete treatise on the subject that has been published. Relatively few references to the literature are given, though many patents are reviewed.

OXIDATION PROCESSES

ARC PROCESSES

Summers⁴⁷ (1915) describes with diagrams the comparative operation of the three commercial types of furnace for direct combination of the oxygen and nitrogen of the air: the Häusser, and the Birkeland-Eyde, Schönherr, and Pauling. The three last, which are arc processes, take alternating current at voltages of from 4000 to 6000 between the electrodes.

The Birkeland-Eyde furnace, which has had the most extensive application, employs a series of commercial arcs rapidly expanded by means of a powerful direct-current magnet around the incoming air. The products are withdrawn at a temperature of about 1200° C. and contain about 2 per cent of NO. The recent furnaces have a 1000 kw. capacity and give a yield of 450 to 600 kg. of nitric acid per kw. yr. or 65 to 90 g. per kw. hr.

Scott¹²⁷ (1912) states that some furnaces take over 1000 horse power. At Notodden there are 12 furnaces using from 600 to 1000 kw. each and at Saheim 8 of 1500 kw. each.

The Schönherr furnace uses a quietly burning arc some 23 feet long, around which the air circulates with a vortex motion. The gases pass over a water-cooler, and are withdrawn at about 850° C. after having given up a further part of their heat to the incoming air. The NO concentration is about 2.25 per cent. The largest furnaces have 800 kw. capacity, and yield 550 to 575 kg. of nitric acid per kw. yr. or 65 g. per kw. hr.

Scott¹²¹ (1915) states that the Christiansand works have twelve 450 kw. furnaces of this type, and the Saheim ninety-six 1000 kw. furnaces.

The Pauling furnace makes use of a series of rapidly succeeding arcs, driven upward by the blast of incoming air, and broken by the diverging horns of the electrodes. The effect is an arc flame 30 in. high in intimate contact with rapidly moving air. The yield of NO is from 1.25 to 1.5 per cent in the 400 kw. furnace, with yields of from 525 to 540 kg. per kw. yr. or 60 g. per kw. hr.

Scott¹²¹ (1915) says that this furnace is employed in factories at Gelsenkirchen, Innsbruck, Milan, Roche-de-Rame, and in South Carolina. The last plant is stated to be merely experimental.

Scott¹²¹ (1915) describes the Birkeland-Eyde, Schönherr-Hessberger, and Pauling furnaces and operation in considerably greater detail than Summers, and gives a comparison of their disadvantages.

Scott¹²⁷ (1912) gives the temperatures of the flames and escaping gases respectively as 3500 and 800-1000° C. for the Birkeland-Eyde furnace, 3000 and 1200° for the Schönherr, and — and 1000° for the Pauling. The current supplies required for each furnace are as follows:

Birkeland-Eyde	Direct current for magnetic field of 3500 lines of force per sq. cm. — Alternating current 5000 volts, 50 periods, 600-3000 kw.
Schönherr	— Alternating current 4200 volts, 50 periods, 600 H.P.-1000 kw.
Pauling	— Single-phase alternating current 4000-6000 volts, 50 periods, 400 kw.-1000 H.P.

Eyde¹²⁷ (1912) gives similar values for his furnace which he states is the only type used at Notodden. Both Birkeland-Eyde and Schönherr systems are used at Rjukan. He also gives cuts, diagrams, and photographs of plants and discusses power developments. Scott's (1912) article and this are very similar in context.

Scott¹²⁷ (1912) gives the most detail concerning the construction of the furnaces, conditions of operation, layout of plants, yields, etc., for the arc and cyanamide process with photographs from the plants. He also describes the absorption methods. He states that the power-factor-for nitrogen fixation processes is about 0.6.

He also discusses the relative advantages of the three arc processes, and describes the electrical equipment with its guarantees, used by the Birkeland-Eyde plant at Rjukanfos. This last is described in considerable detail.

Scott also¹²¹ (1915) describes the Kilburn-Scott arc furnace and process for oxidizing nitrogen. The apparatus employs a three phase current giving, under the effect of air, an inverted cone of flame. An anvil with oxygen is held in the middle, whereby it is expected to increase the yield of NO as product. Direct absorption in water is claimed to give a pure acid nitric acid.

The process does not appear to have been carried out commercially as yet. Operating factors and their effect upon yield are mentioned but no data given.

The design of a commercial apparatus, similar to the experimental one, is given, for which the advantages of simplicity, conservation of heat, low first and maintenance costs, etc., are claimed.

Patents of methods for the fixation of atmospheric nitrogen by arc processes issued in recent years are reviewed in Engineering 34 (1916).

Lamy¹⁴¹ (1911) gives a general review of the cyanamide and arc processes for nitrogen fixation. His description of the Birkeland-Eyde, Schönherr, and Pauling processes, illustrated with diagrams, is very good.

Auzies¹⁴¹ (1912) discusses the theory of nitrogen oxidation and gives tables showing the relation between temperature and yield. The catalysis of the reaction by oxides of cobalt, magnesium, chromium, nickel, platinum, palladium, barium, lead, cerium, and thorium has been effected. Cerium works best. Work has also been done on the catalysis of the reaction between nitrogen and hydrogen.

Tausent¹³¹ (1912) shows the advantage of vertical arcs over horizontal, both in stability and yield of nitric acid.

Ehrlich and Russ¹³⁹ (1911) conclude from experiments on mixtures of nitrogen and oxygen that ozone is an important factor in the oxidation of nitrogen. They give the variation of per cent of nitric oxide formed, with the oxygen in the original mixture.

Vanderpol¹⁴³ (1911) gives a detailed description with diagrams for the Pauling process and absorption towers at La-Roche-de-Rame, Hautes-Alpes, France.

Haber, Koenig, Platau and Holwech¹⁴⁷ (1910) have studied the effect of high voltage, high frequency alternating-current, cooled direct-current arcs, and pressure upon the oxidation of nitrogen and give their experimental data in considerable detail.

Holwech¹⁴⁸ (1910) has studied the formation of nitric oxide in the short direct-current arc at various temperatures with a cooled anode. He obtained the best results with the shortest arc and the highest field strengths compatible with the proper temperature, getting yields as high as 80 g. of nitric acid per kw. hr. at a maximum concentration of 9 per cent of NO.

Wolokitin¹⁵¹ (1910) has studied the formation of nitrogen oxides in the flame of hydrogen and discusses the thermodynamics of the reaction.

Zenneck¹⁵² (1910) gives a general discussion of the various methods for oxidizing nitrogen in the arc.

Koenig⁴⁴ (1915) discusses rather fully the subject of active nitrogen and its relation to nitrogen fixation. He reviews the literature and gives the results of work of his own upon the activation of nitrogen, oxygen, and hydrogen.

Hene⁶⁶ (1914) got a higher yield from sparking oxygen before mixing it with nitrogen than from sparking the nitrogen. He concludes that ozone is formed.

The reaction of active hydrogen and oxygen has been studied by Koenig and Elöd⁸⁸ (1914) and the conclusion reached that the electric discharge must also produce an active form of oxygen.

Lowry⁷⁰ (1914) finds spectroscopically that when active nitrogen and ozonized air are mixed, nitric oxide is produced, and suggests that the fact may throw light upon the molecular condition necessary for the oxidation of nitrogen.

Koenig⁹¹ (1913) criticizes the conclusion of Fischer and Hene¹¹⁸ (1912) that the electrical discharge activates the oxygen and not the nitrogen.

Fischer and Hene¹¹⁸ (1913) conclude from a study of the effect of subjecting nitrogen and air separately to the action of electric discharges, that the oxidation of nitrogen in the arc flame is dependent upon the dissociation or activation of the oxygen and not of the nitrogen. In Reference 87 (1913) they reply to Koenig⁹¹ (1913) and give their experimental data in detail.

Lowry¹²¹ (1912) got increased yields of nitrogen peroxide from mixing air which had been subjected to the action of a series of spark gaps, with ozone.

Russ¹²⁸ (1912) discusses the evidence of various investigators that the reaction is not purely thermic but may involve electronic factors and points out that the formation of active nitrogen might be harmful.

Strutt¹³⁹ (1912) states that active nitrogen is not oxidized by

oxygen but that the latter probably acts as a catalyzer to destroy the active modification.

Strutt¹⁴³ (1911) has studied the flame arising from the nitrogen-burning arc and concluded that it, like the afterglow phenomena in vacuum tubes containing air, is due to the oxidation of oxides of nitrogen by ozone.

Dary¹⁹ (1915) states that Nodon has been able to obtain nitric acid very economically by electrolyzing peat under 10 volts. Peat contains 2 per cent by weight of nitrogen, which is converted into nitric acid by the combined action of nitrogen bacteria, the oxygen of the air, water, and heat from the electric current. The yield of nitric acid per ampere hour is 1 g., or 432 kg. in 24 hours per ha consumes 180 kw. hr. The yield per year on 150 ha is 100,000 tons of nitrate.

HÄUSSER PROCESS

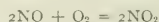
The Häusser process⁹² (1915), of which a single commercial installation has been made in Germany, employs coke oven gases mixed with air under pressure in an explosion bomb, fired by a high tension spark. The products are cooled at once by a high pressure spray of water. The temperature attained is 2100° Å. and the concentration of NO, 0.5 per cent. The maximum yield is 99 g. of nitric acid per cu. m. of gas equal to 6.2 lbs. per 1000 ft.

Dobbelstein¹¹⁶ (1912) has experimented with the Häusser process using coke oven gas in a bomb of 100 liters capacity. Diagrams of the plant are given as well as curves showing the relation of yield to pressure, temperature of gas, and per cent of oxygen. The advantages and costs are compared with other processes.

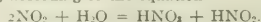
Häusser¹¹⁹ (1912) gives a detailed account of investigations upon nitrogen fixation by the explosion of gas mixtures and the influence of the various factors of pressure, etc. Increase in size of bomb gave larger yields.

ABSORPTION

The NO mixtures⁹² (1915) produced by all these processes are cooled, passed into a gas holder, where time is allowed for the reaction



and are then sent to counter absorption towers, where they react with water, according to the equation

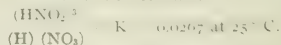


The nitrous acid is oxidized by the excess oxygen. An acid of 30 to 50 per cent concentration is thus obtained. The residual gases are circulated through towers containing weak alkaline solutions yielding nitrite-nitrate salts. About 2 or 3 per cent of the original NO gas is discharged with the waste gases.

Scott⁸¹ (1915) discusses his absorption system and compares its operation and the concentration and nature of the products with those of the ordinary systems.

Briner and Durand¹¹⁵ (1912) have studied the equilibria of nitrous and nitric acids formed when oxides of nitrogen are absorbed in water and conclude that increase in the pressure of NO and lowering the temperature favor the formation of nitrous acid.

Lewis and Edgar⁴² (1911) have also studied the equilibrium between nitrous and nitric acids in aqueous solution and get as the value for the dissociation constant for



REDUCTION PROCESSES

HABER PROCESS SYNTHETIC AMMONIA

The Haber process depends upon the direct combination of nitrogen and hydrogen at temperatures of about 500° C. under the influence of uranium as a catalyzer, and is carried out under pressures of 200 atmospheres. The 8 per cent of ammonia formed is condensed out by cooling the mixture. The power expenditure is about 1.5 kw. hr. per kg. of nitrogen, the lowest

of any of the fixation processes. The preparation of the nitrogen and hydrogen, and the compression required, increase the costs very considerably⁵² (1915).

Haber⁴² (1915) and his co-workers have made extended investigations of the heat of formation of ammonia at temperatures from 659° C. to 466, and at ordinary temperatures, and have determined its specific heat.

They⁴³ (1915) have also determined the equilibria at various temperatures, at ordinary pressures, and at 30 atmospheres.

Landis⁴⁶ (1915) doubts whether even the Badische Company, with its supply of waste sulfuric acid and hydrogen, is able to supply ammonium sulfate at a profit in normal times. The process, while not requiring very much electric power, does demand a great deal of skilled labor, and so probably has no future in the United States, in competition with the cyanamide process, which provides the same end product, ammonia.

Crossley⁴¹ (1914) gives a brief outline of Haber's synthetic ammonia process.

Haber⁴³ (1914) discusses in detail the history of the development and thermodynamics of the process for the production of synthetic ammonia.

Reference 89 (1913) gives the report of Haber and Le Rossignol, presented to the Badische Anilin- und Soda-Fabrik in 1909, which led that company to take up the large scale development of the process for synthetic ammonia. The thermodynamics of the reversible reaction between hydrogen and nitrogen are discussed and the reasons for working the process between 500 and 700° C. and under 200 atmospheres pressure are explained.

Bernthsen¹¹² (1912) gives a detailed but general review of the history of the development of the process for making synthetic ammonia. He mentions the various catalyzers tried, their adaptability and the effect of poisons and "promoters."

Biliter¹¹³ (1912) finds that the rapid exhaustion of cerium hydride and nitride, which are quite active catalysts at 200-300° C., is due to gradual oxidation.

Serpek⁷³ (1914) discusses the general problem of inorganic ammonia synthesis taking up the chemistry of each of the several processes known. He quotes his material mainly from patents.

CYANAMIDE PROCESS

The fixation of nitrogen by the cyanamide process depends upon reactions that are generally expressed by the equation



which is not only reversible, but so complicated that its equilibrium constants have not yet been established. Landis⁴⁶ (1915) points out a few of the difficulties and special problems to be met and solved in preparing satisfactory grades of carbide and nitrogen, and then combining them on a commercial scale.

Summers⁴³ (1915) discusses the thermodynamics of the reactions involved in making calcium cyanamide from the elements, giving figures to show that the yield per unit of electrical energy is 4 to 5 times that of the direct oxidation methods, but this advantage is partly offset in practice by other costs, such as that of the preparation of nitrogen.

A history of the development of the cyanamide industry in America, with descriptions of operations, and illustrations of the apparatus and buildings of the American Cyanamide Company is given in the *Engineering News*⁴⁶ (1915). The output of the various factories of the world is given. (See CYANAMIDE PROCESS, p. 431.)

Landis⁴⁶ (1915) also describes the various subsidiary installations, such as the calcium carbide, lime, and coal gas plants, necessary to the operation of a cyanamide plant. Photographs are given, and capacities stated.

Reference 89 (1913) describes in great detail the electrical equipment and water power development employed in making calcium carbide and cyanamide in Norway and Sweden, under the control of the Nitrogen Products and Carbide Co., Ltd., which also owns plants in Belgium for making ammonium nitrate by

the Ostwald process. The history of the development of the business is also outlined.

Reference 82 (1914) is a short general article describing with photographs the coal-gas and lime plants of the American Cyanamide Company's works at Niagara Falls.

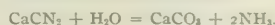
Pranke⁹⁸ (1913) gives a brief history of the development of the process and its chemistry, and mentions the uses of the material.

Pranke's book⁹⁹ (1913) discusses very fully the history and chemistry of cyanamide, its preparation, conversion products and uses, and their reactions, and its action in the soil. Reports of tests and analyses are also given. Over two-thirds of the book is devoted to its agricultural value and properties. Extremely little manufacturing or cost data is given.

Foerster and Jacoby¹⁴⁶ (1907) have studied the reaction between calcium carbide and nitrogen with especial attention to the lowering of the temperature required, produced by the admixture of calcium chloride or fluoride.

AMMONIA FROM CYANAMIDE

Calcium cyanamide²⁵ (1906) is readily and almost quantitatively (98-99 per cent) converted into ammonia by treatment with steam, in accordance with the reaction



This reaction is exothermic, evolving from 200 to 300 lb. cal. of heat per pound of ammonia, and to realize the advantage of this fact the commercial process (U. S. Patent 1,149,633, Aug. 10, 1915) is carried out in autoclaves. Lime nitrogen is fed slowly and with constant agitation into water, or mother liquor from a previous run, with ventilation to carry off the acetylene evolved from unconverted carbide, soda and lime added, the autoclave closed, and steam admitted up to a pressure of 3 or 4 atmospheres, at which temperature the reaction starts at a fair rate, generating ammonia and steam so rapidly as to necessitate relief of pressure by special valves. Even then the pressure generally reaches 12-15 atm. in 20 minutes, then falling off again. The steaming operation is repeated once or twice more to expel the ammonia from the solution, which is then filtered from the mud, the latter going to the dump.

The course of the reaction is illustrated by curves, showing the variation of pressure, rate of discharge, and percentage of ammonia in the ammonia-steam mixture, with time for quantities of from 7000-8000 lbs. of lime-nitrogen. Less than 0.2 per cent of ammonia remains in the sludge.

The mixture of ammonia and steam may either be absorbed directly, producing a high-grade ammonium sulfate, or passed through a simple rectifying column, giving an ammonia gas which is stated to be so pure that it can even be oxidized directly with no trouble from poisoning of the catalyzers.

Reference¹⁰⁰ (1913) gives a brief description of the method for obtaining ammonia by treating cyanamide with steam and states that ammonia of 99.8 per cent purity is thus obtained. Figures are given showing the completeness of decomposition.

Landis⁴⁶ (1915) considers it certain that the process for the preparation of ammonia by treating cyanamide with steam is already in successful operation in Norway, France, Switzerland, Italy, and Japan, and was installed in Belgium before the war. The bulk of the product is used, in the form of ammonium sulfate, by the chemical and fertilizer industries. Norway produces large quantities for absorption of nitric acid, and the Birkeland-Edyde plants in Germany are making enormous quantities for oxidation to nitric acid.

The American Cyanamide Company has had a small plant in successful operation in the United States for six months and is producing several tons per day of pure ammonia gas.

OTHER METHODS

The Serpek process is typical of the methods depending upon the formation of a nitrous acid which ammonia may be obtained

by treatment with steam. The reaction which it involves is represented by the equation



and is carried out at a temperature of from 1800 to 1900° C. in a revolving barrel type of electric resistance furnace which affords the constant agitation necessary. Bauxite and coal from a producer type of furnace are fed into this and the product is discharged as aluminum nitride containing from 26 to 34 per cent of nitrogen.

Summers⁹² (1915) calculates that under the most favorable conditions 9 to 10 kw. hrs. of electrical energy will be required per kg. of nitrogen, besides the heat from the coal and producer gas. The cyanamide process requires about 16.2 kw. hr. per kg. of nitrogen, or if all energy be supplied by the electrical current, the two processes will have practically the same power consumption. The Serpek process is hampered by the necessity for disposing of the by-product alumina.

Reference⁷² (1914) discusses the nitride reactions and the chemistry of the Serpek process mentioning the catalytic effect of hydrogen and iron.

Reference⁸⁴ (1914) gives briefly the history of the reactions fixing nitrogen by the formation of metallic nitrides. Of these, the only one to find commercial application is that involving the production of by-product alumina which has been developed by Serpek.

The starting point is impure oxide, or bauxite, which is mixed with carbon and heated in the presence of nitrogen. Combination occurs at about 1550° C. without any carbide formation, and is hastened by the presence of certain catalyzing reagents such as iron, silica, titanium oxide, nickel, and manganese, of which the first is most effective. The reaction temperature is further lowered by the presence of hydrogen, and aluminum nitride may thus be prepared at from 1250 to 1300° C. provided a large excess of nitrogen be used. At higher temperatures this is unnecessary, and the rate of the reaction is much increased. At 1900° the alumina is completely converted into nitride in 5 minutes, and recently Serpek has reduced the time to a fraction of a second by suitable control of the reaction mixture and of the nitrogen supply.

The nitride is easily decomposed into aluminum hydrate and ammonia by heating under several atmospheres pressure for 3 or 4 hours. Pure alumina may be produced as a by-product. The yield is 2 tons of alumina and 500 kg. of fixed nitrogen per kw. yr.

The process is in operation only in an experimental installation at Saint Jean de Manrieme in Savoy, though other plants are under construction at Arendal, in Norway, and in the United States.

Fraenkel⁸⁸ (1913) has investigated the progress of the reaction for the formation of aluminum nitride from alumina, carbon, and nitrogen, which he finds begins under suitable conditions at 1400° C. He has determined the effect of various factors upon the velocity.

Richards¹⁰⁰ (1913) gives the history of the reactions involved in the Serpek process, and outlines the process as patented.

Ross¹⁰¹ (1913) has carried out some preliminary experiments upon the fixation of nitrogen by the alumina in feldspar, as a by-product in the preparation of potash. Larger percentages of nitrogen were fixed than corresponded to the aluminum present.

Russ¹⁰² (1913) has been able to demonstrate the exothermic formation of aluminum nitride from the elements.

Tucker¹⁰⁸ (1913) has studied the chemistry of this process and concludes that it is of commercial interest only where the by-product of pure alumina may find use in the aluminum industry. He compares the advantages and disadvantages of this and the cyanamide process for ammonia.

Reference 107 (1913) gives an abstract of the patent (U. S. 1,040,439) discussing the chemistry of the Serpek method for decomposing aluminum nitride by means of alkaline aluminates.

Tucker and Read¹²³ (1912) have studied the reaction between nitrogen, alumina, and carbon, and state the necessary conditions for a good yield.

Stähler and Elbert¹³³ (1913) have studied the reaction for the formation of boron nitride by heating boron oxide or boracalite with carbon in the presence of nitrogen at various pressures. From the mixture containing oxide a yield of more than 85 per cent of BN was obtained under increased pressure at temperatures between 1500 and 1700° C. Using instead of oxide, boracalite (CaB_4O_7), a nearly theoretical yield was obtained between 1400 and 1800° C. without effect from pressure.

OXIDATION OF AMMONIA (OSTWALD PROCESSES)

Zeisberg⁴ (1916) reviews the history of the process and development of the industry for the catalytic oxidation of ammonia to nitric acid with estimates of costs for American conditions. (See p. 433.) He reviews recent patents and other literature. He states that a successful plant in Westphalia built in 1909 had an annual production of 2400 tons of 53 per cent nitric acid. From Jan. 1911 to Aug. 1912, the efficiency was 89.6 per cent on a monthly production of 130 tons of ammonium nitrate. The efficiency of conversion was 83 per cent and of absorption 97 per cent. This plant operates on coal-tar ammonia. It is stated that this product has never appeared in the market. In 1912 and 1913, 8 per cent dividends were paid to stockholders. In 1910 the process was purchased by a London company capitalized at £2,000,000 and a new plant was erected in Belgium.

It is stated that the diagrams of the converter given by Schüpphaus²⁹ (1916) are the only ones ever published. It is not possible to ascertain actual dimensions used. A few other details of the probable methods of operation of the process are mentioned.

According to Schüpphaus²⁹ (1916) the nitric acid needed for the manufacture of sulfuric acid by the chamber process was supplied in Germany, after cutting off of other sources at the beginning of the war, by oxidation of ammonia from ammonia water. He describes the process and the apparatus which is manufactured and sold by the Berlin-Anhaltischen Maschinenbau-Aktiengesellschaft in Berlin.

The ammonia gas is liberated by treating a spray of its 3 per cent solution, mixed with milk of lime, with steam. The gas is passed through coolers to condense the water-vapor and then through caustic soda scrubbers to a gas holder.

The ammonia gas is thoroughly mixed with air and passed over very fine meshed platinum gauze heated by electric current (24 to 26 v., 120-125 amp.) to about 700°, where almost quantitative reaction forming nitrogen oxides and water occurs. The oxides then go to the lead chambers.

The apparatus is illustrated by cuts and a photograph, showing the arrangement of the parts of the system. Details of construction are given, but no exact dimensions nor capacities.

Reference 106 (1916) mentions that this process has been in successful commercial operation for some time in Belgium and probably has a great future.

The process for the oxidation of ammonia gas to nitric acid (generally known as the Ostwald process) is described in detail in Reference 109 (1913) with the history of its development. Cuts show the arrangement of a plant capable of converting 25 tons of ammonia per month into about 150 tons of 36° Bé. commercial nitric acid. The reaction



is brought about by passing the mixture of gases over spongy platinum, platinum, or platinum black as a catalyzer at a temperature of about 300° C. at a velocity of 1 to 5 meters per second. The time of contact between gas and catalyzer should not exceed $\frac{1}{100}$ of a second, or decomposition of the product into nitrogen and water will cut down the yield very seriously. Under

properly adjusted conditions the yield is very nearly the theoretical.

The condensation plant is also described in detail, and costs are estimated. See Reference 109 (1913).

The successful development¹¹⁰ (1913) of the process using platinum for a catalyst is mentioned with outline of its development at Odda and other places in Norway, Iceland and England.

Meneghini⁸⁴ (1913) has investigated the oxidation of ammonia by various oxides as catalysts. His efficiency was highest with increased rate of gas flow and with those oxides that were effective only at the higher temperatures, exceeding 95 per cent for burnt pyrites, chromic oxide, and oxides of rare earths. Values are given for various temperatures.

Kochman¹²⁰ (1912) mentions the oxidation of ammonia by metallic contact agents at relatively low temperatures as a practical problem and gives a description and drawing of a furnace.

Meneghini¹²² (1912) had previously studied the catalytic action of electrically heated platinum and found that no reaction occurred below 350° C. Rapid action occurs between 400 and 450° C. The principal product was nitrous acid.

Reinders and Cats¹²⁵ (1912) also studied the conditions for this catalysis using platinum, ferric oxide, platinumized copper, thorium. With the first two 80-90 per cent of the ammonia was oxidized to nitric acid and nitrogen trioxide. The velocity of the gas current is very important, there being an optimum for each catalyzer. The best temperature found for platinum was 500° C. and for ferric oxide 650-700° C.

II—PRODUCTION GENERAL

Kubierschky⁴⁹ (1914) gives the average yearly increase in production of fertilizer materials during the past few years. The figures for several items are as follows:

	Years	Av. Annual Increase Per Cent
Cyanamide.....	1907-12	212.0
Norway saltpeter.....	1903-11	170.0
Ammonium sulfate.....	1901-11	10.5
Chile saltpeter.....	1901-11	6.8

The world's production in 1913 is given by Reference 83 (1914) as follows:

	Metric Tons
Ammonium sulfate.....	1,365,000
Chile saltpeter.....	2,740,000
Lime nitrogen.....	80,000
Norwegian nitrate, Ca(NO ₃) ₂	30,000

CHILE SALT PETER

Summers⁸² (1915) gives the present annual output of Chile nitrate as 2,500,000 tons, of which the United States takes from 600,000 to 700,000 tons. The government tax has netted Chile about \$500,000,000 in the last 30 years.

Reference 96 (1913) gives the yearly production from 1902 to 1912.

Bernthsen¹¹⁸ (1912) gives figures for the exports, price, and value of Chile nitrate for each year from 1900 to 1912, and for the world production, etc., of ammonium sulfate for certain years, during the same period.

Scott¹²² (1912) gives the annual exportations of nitrate from Chile at intervals during the years 1830 to 1911, in which time it has increased from 935 tons long² to 2,420,400 tons.

AMMONIUM SULFATE

Turrentine⁶ (1916) advocates reliance by the United States upon the coke oven by-product for both the war time and agricultural consumption of nitrogen products, and gives statistics of the present and probable future production. He states that the 68 per cent wasted in 1914 equals 350,000 tons of ammonia from which 300,000 tons of 100 per cent nitric acid might be made. He also estimates that from the surplus coal gas now wasted 800,000 continuous horse power could be generated with which 1,400,000 tons of ammonium sulfate could be produced by nitrogen fixation processes in time of emergency. He mentions special

measures that should be taken which would further increase this production.

In a later Reference (5) he discusses the matter in much greater detail, giving statistics of the past development of the coke-oven by-product industry and estimates of its future. He gives the production of ammonium sulfate in the United States for each year from 1900-17 and both the probable and possible increase by 1920. He states that at the present (1916) rate of increase the total production from coke-ovens alone will be 800,000 tons of ammonium sulfate. In time of emergency he would withdraw all of the supply going into fertilizers. From the output at the rate normal on April 1, 1916, nitric acid could be made by the Ostwald process equivalent to 271,000 tons of sodium nitrate (the importation of sodium nitrate during 1915 was 577,000 tons) which would more than supply the needs for explosives, in times of peace. His conclusion is that such a supply of nitrogen compounds is adequate for the United States for both times of peace and of war.

Lynn also² gives curves showing the consumption and production of ammonium sulfate in the United States between 1900 and 1913, together with imports and word production.

Reference 11 (1916), a pamphlet issued by the by-products interests, gives data on the rate of production, and arguments intended to show that the ammonium sulfate produced is sufficient to insure a supply of nitric acid in time of war. The objections to depending upon such a supply are not mentioned, far less answered. The pamphlet objects to government manufacture of nitrates on the ground that it will lower the price of sulfate and discourage the by-product industry.

Porter² gives almost the same data and conclusions as Turrentine⁶ and continues with arguments against recent legislation for the government's establishing a plant for nitrogen fixation. He gives a list of the by-product coke plants in the United States in September, 1916. In connection with Porter's statement that at the outbreak of the war, Germany had almost reached the limit in the production of by-product ammonia, it is of interest to note that Reference 7 says that at that time only 1/3 of her coal was coked. The coking industry has been much extended since but yet it has been found necessary to make ammonia by the Haber process in quantities placed at 300,000 tons per year. In other words, the proposal made by Turrentine⁶ that the United States Government should meet an emergency by going into the coke business does not seem to have been economical there.

Washburn¹³ (1916) discusses the availability of by-product coke oven ammonia as a source of nitric acid in time of war, and points out that its extreme variability, depending upon the fluctuations of the iron industry, and the fact that the supplies must be gathered from scattered localities, are important drawbacks. The present maximum output, from 21 widely scattered points, is equivalent to only about 120,000 tons of concentrated nitric acid, which is perhaps two-thirds of a minimum safe reliance for war: 37 per cent of this total production is used for refrigeration and so could not be diverted, particularly in time of war. 10 per cent is already used in explosives and chemicals, and the remaining supply is used in agriculture, where it could be ill spared at a time when imported fertilizer materials were cut off.

Germany, with the greatest metallurgical industry in Europe, and making 60 per cent of her coke supply as by-product, has to turn to atmospheric nitrogen for war supplies.

Childs⁸ (1916) gives the probable increase in production of ammonium sulfate in the United States during 1916 as 20,000 to 30,000 tons. He gives the statistics of production, imports and consumption in the United States from 1900 to 1915, and states that the present production from coking is only 20 per cent of that possible if by-product gases were intensively used. He discusses the future of coke by-products, mentioning the probable competition after the war of German products from their highly developed fixation processes. He states that the

semi-direct method is the one used mostly in the United States. He also discusses the uses and demand for various by-products.

Landis⁴⁶ (1915) points out that the supply of ammonia from coke ovens has the disadvantages inherent in by-product sources. A ton of coal yields only 5 to 6 lbs. of ammonia. Any industrial depression, and particularly such as results from war [see *Mineral Industry*, 23 (1914), 412-13, 417-22], cuts down the supply at once. In Germany, regulations prohibiting the use of coal were passed, in order to force the production of coke and its by-products.

Clarke⁹ (1915) gives an up-to-date list of by-product coke ovens built or under construction in the United States. He states that tar and ammonia yields are much lower here than in Europe.

The annual production of ammonium sulfate is now about 1,250,000 tons, practically all coming from by-product coke ovens or from gas-house retorts. The production in the United States per year is equivalent to about 70,000 tons, and is increasing annually at the rate of some 15 per cent⁴⁹ (1915).

In discussing Peacock's⁴⁹ (1915) paper, Johnson states that the production of ammonia possible in the United States, if all coking were done in by-product ovens, is about 225,000 tons annually. Only 30 per cent of this amount is saved at present.

American coals⁵² (1915) contain from 0.9 to 1.4 per cent or 18 to 28 lbs. of nitrogen per ton, of which 20 per cent, or from 4½ to 7 lbs. of ammonia per ton of coal distilled is recovered. This yields 18 to 28 lbs. of ammonium sulfate per ton of coal.

Lyman²⁷ (1916) gives a table of the nitrogen content of coals from different parts of the United States.

The Mond producer gas system recovers 75 per cent or from 15 to 20 lbs. of nitrogen, or 60 to 80 lbs. of ammonium sulfate per ton of coal consumed. This plant, although installed abroad, is not very extensively used in America, as the expense of installation is relatively high.

Wagner²⁴ (1916) gives the yields per ton of various American coals in tar, ammonia, sulfur and naphthalene. The ammonia yield varies from 4.33 per cent for Alabama coal to 9.60 for Oak Creek, on the basis of ash and moisture-free coal. He discusses the subject of coke and coal and furnaces for coal distillation, etc., very fully but says little about by-products.

The world production for 1914 is estimated by the American Coal Products Company⁵⁷ (1915) to have been 1,300,000 to 1,350,000 metric tons against 1,409,000 in 1913. England produced 426,413 tons, or about 6200 tons less than in 1913. Figures could not be obtained for Germany. (See Consumption, Ammonium Sulfate, p. 432.)

In the United States, 183,000 tons, or 12,000 tons less than in 1913 were produced. This decrease was mostly during the last six months, and was due to the depression in the iron and steel trade caused by the war. The recovery possible from the coal now coked is 700,000 tons⁵⁷ (1915).

The principal source, and the one promising the greatest extension in the near future, is the by-product coke oven. The Coal Gas Works have the next largest total output, though the unit production is much smaller and widely scattered. Other sources are the by-product recovery gas producer, shale oil distillation, and the English blast furnaces using splint coal⁵⁷ (1915). Statistics of production for the years from 1900-14 for the different countries are given, with sources in each.⁵⁷

Tutwiller⁷⁴ (1914) gives a table showing the rate of production and value of coke, tar, ammonium sulfate, etc., from 1903-1908.

Reference 83 (1914) gives the world's production of ammonium sulfate in 1913 as 1,365,000 tons, compared with 1,214,000 tons (metric) in 1912. The production of the various countries in tons was as follows:

	1913	1912
Germany.....	549,000	492,000
England.....	420,000	379,000
United States.....	177,000	151,000
France.....	75,400	69,000
Belgium.....	48,600	50,000

In 1913⁸¹ (1914) the production of ammonia in terms of ammonium sulfate in the United Kingdom was about 420,000 tons (long). The exports were 325,000 tons.

Canada produced in 1913⁷⁸ (1914) 10,608 tons of ammonium sulfate from coke ovens.

The production in 1910 and 1911 in the United Kingdom¹⁴⁴ (1912) calculated as sulfate was 367,500 and 378,500 tons (long).

The production of Great Britain in 1911 and 1912, calculated as sulfate, was, according to Bradbury and Hirsch⁸ (1913), as follows, in long tons:

	1911	1912
Gas works.....	169,000	166,000
Iron works.....	20,000	20,000
Shale works.....	61,000	61,000
Coke, carbonizing works and producer gas plants.....	135,000	132,000
	385,000	379,000

The figures given in Reference 108 (1913) are:

	1912	1911	1910
Gas works.....	172,094	168,783	167,820
Iron works.....	17,026	20,121	20,139
Shale works.....	62,207	60,765	59,113
Coke oven works.....	104,932	108,343	92,665
Producer gas and carbonizing works.....	32,049	29,964	27,850
	388,308	384,976	367,587

Scott¹²⁷ (1912) gives similar data for 1906, 1909 and 1910.

A comparison of the export trade of England and Germany during 1912 and 1913 gives the following totals in metric tons:

	1912	1913
Germany.....	56,897	74,318
Great Britain.....	285,134	270,697

The amounts exported to each country are given in Reference 78 (1914).

Tufts¹⁴⁴ (1911) reviews briefly the various commercial sources of ammonia. He believes that the by-product coke oven cannot long be a leading factor in the situation as the world's demand for ammonia is increasing at a rate that in seven years will take almost all the production possible if all the world's coke were made in by-product ovens. A corresponding rate of increase in coke consumption cannot be expected.

OXIDATION PROCESSES

Washburn¹³ (1916) states that the world's yearly fixation of nitrogen by the arc process is some 32,000 net tons compared to 200,000 tons by the cyanamide process. The former process is practically confined to Norway, while the latter has been applied in Norway, Sweden, Germany, Austria, France, Japan, and Canada.

He (1916) also states¹⁸ that there are employed in the World's Nitrogen Fixation industry 1,000,000 continuous horse power, and gives the distribution as follows:

Canada.....	30,000
Germany.....	350,000
Norway.....	450,000
Dalmatia, Italy, Switzerland, Japan, France.....	150,000
	980,000

From the condition of operating no arc processes, Germany has developed in 18 months an industry producing nearly 10,000 tons of nitric acid per year²¹ (1916).

James B. Duke⁸² (1916) is accredited with the statement that the Southern Electrochemical Company will shortly be producing at Great Falls, S. C., by the Pauling process, nitric acid at the rate of 4 tons per day. The product will be placed on the market at a price lower than that of acid made from sodium nitrate.²³ The plant uses 3000 kw. and is the only nitrogen fixation plant in the United States.

Reference 133 mentions that operation of a plant using the Pauling process with an estimated capacity of 8 tons of calcium nitrate has been begun by the Southern Electrochemical Company at Nitrolee, S. C.

Earlier press notices¹³⁴ (1912) stated that this plant, which was designed to use the surplus power of the Southern Power Company, would turn out 5 tons of nitric acid or 8 tons of cal-

III—CONSUMPTION GENERAL

In the year before the war⁶ (1916) Germany consumed 217,000 metric tons of inorganic nitrogen as follows:

Chile saltpeter (imported).....	100,000
Calcium nitrate (imported).....	3,000
Ammonium sulfate (domestic production).....	95,000
Cyanogen cyanamide (imported).....	17,000

During the first year of the war only 12½ per cent of this quantity was obtained or produced. By the aid of a government grant of £7,500,000 large quantities of cyanamide and ammonium salts were made for military purposes⁸⁵ (1916).

England's consumption of ammonium sulfate in 1914 was 106,000 tons and exports 313,877 tons. German sales of the Deutsche Ammoniak-Verkaufs-Vereinigung for home consumption was 321,404 tons. Her exports for the year were 75,868 metric tons, and imports 34,628 metric tons⁸⁷ (1915).

In 1913⁸⁸ (1914) the United Kingdom consumed ammonia calculated as ammonium sulfate to the amount of 97,000 tons (long). The estimated home consumption in Great Britain was 90,000 tons⁸⁸ (1913). The consumption¹¹⁴ (1912) of ammonia in the United Kingdom in 1911, calculated as sulfate, was 85,500 tons.

The consumption in the United States was 272,000 tons, compared with 262,000 in 1913⁸⁷ (1915).

The world consumption in 1913 is given⁸⁹ (1914) as follows:

	Metric Tons
Germany.....	460,000
United States.....	235,000
Japan.....	115,000
England.....	97,000
France.....	90,000

The world consumption of sodium nitrate⁹⁰ (1913) for 1910–12 is given as follows in long tons:

	1910	1911	1912
Shipments from South America.....	2,300,000	2,412,000	2,478,000
Consumption in U. K.....	120,000	132,000	130,000
Consumption on Continent.....	1,531,000	1,564,000	1,778,000
Consumption in U. S.....	501,000	556,000	481,000
Consumption in other countries.....	89,000	103,000	115,000
Consumption in world.....	2,241,000	2,355,000	2,504,000

Reference 96 (1913) gives the yearly consumption from 1902 to 1912.

Berntsen¹¹² (1912) discusses the increasing demand for nitrogen compounds, giving the world production, increase, and price for sodium nitrate, and ammonium sulfate during the ten years from 1900.

Lamy¹¹¹ (1911) gives the growth in exports of nitrates from South America as follows:

1830.....	800 tons	1880.....	300,000 tons
1835.....	7,000 tons	1890.....	800,000 tons
1850.....	20,000 tons	1900.....	1,300,000 tons
1860.....	70,000 tons	1905.....	1,500,000 tons
1870.....	150,000 tons	1909.....	2,000,000 tons

The approximate consumptions (tons) in 1910 were:

France	Great Britain	Germany	Belgium	United States
250,000	100,000	500,000	200,000	400,000

USES

Washburn¹² (1916) states that even the Allies are employing 500,000 continuous horse-power in the fixation of nitrogen for explosive materials.

Washburn¹⁸⁻¹⁸ (1916) estimates that a war supply of nitric acid for the United States should amount to at least 180,000 tons per year, which is⁹⁴ (1916) two-thirds of the estimated consumption of the German army.

He also points out what Germany has accomplished by the liberal use of fertilizer, that is, in quantities seven times as large per average acre cultivated as is the practice in the United States. From an area less than 80 per cent that of the State of Texas, she now raises 95 per cent of the food for a population nearly 70 per cent as large as that of the United States. In ten years our exportation of wheat and flour has fallen from 31 to 13 per cent of the production, and general crop production has increased only 10 per cent, while the population increased 21 per cent. From less than one-half the area Germany harvested in 1907 over double the quantity of grain and potatoes. While

cost of food rose 80 per cent in the United States it increased only one-half as much there.

Reference 7 (1916) gives the German consumption of nitrogen for 1913 as follows:

	Tons	Tons of Nitrogen
Ammonium sulfate.....	460,000	92,000
Nitrate of lime (Norwegian).....	35,000	4,500
Nitrate of lime.....	30,000	6,000
Ammonia, Haber process.....	20,000	4,000
Nitrate of soda.....	750,000	116,000

The consumption of Chile nitrate increased from 155,000 tons in 1885 to 747,000 tons in 1913; of ammonium sulfate, from 125,000 tons in 1900 to 460,000 tons in 1913. The yield of wheat per hectare had doubled in Germany while increasing only 1/10 in France in which latter country only 1/10 as much potash and 1/2 as much nitrate of soda is used per hectare as in Germany.

Figures giving the yields per acre of five principal crops in different countries are given by Harris⁹ together with data showing Germany's large consumption of nitrogen fertilizers. The material seems to come from the same original source as Reference 7.

Landis⁹¹ (1916) gives the present annual nitric acid consumption of Germany as 250,000 to 300,000 tons for munitions, besides the equivalent of 850,000 tons of sodium nitrate, 40,000 tons of nitrate of lime, and about 20,000 tons of Norwegian cyanamide, for agricultural and manufacturing purposes. The last items are estimated from the normal importation, which is now wholly cut off, and replaced by domestic production. The investment involved is over \$100,000,000. It is quite possible, however, that the agricultural consumption is curtailed.

During 1912 Germany consumed 750,000 tons of Chile saltpeter, 425,000 tons of ammonium sulfate, 50,000 tons of lime nitrogen, and 50,000 tons of Norwegian saltpeter⁹² (1916).

The imports of nitrates into Germany and Austria amount to about 750,000 tons annually. The consumption during the war is estimated at 750,000 tons of nitric acid for each side. This is based on an average consumption of 5 tons (3 to 10) of nitric acid per ton of explosives made, and 150,000 tons of explosives used per year⁹³ (1916).

Christopher⁹⁶ (1913) mentions that in Germany practically the whole production of ammonium sulfate is used on the soil, while in England, out of a production of 369,000 tons a year, only 70,000 tons are so used.

Sodium nitrate and ammonium sulfate constitute 80 to 85 per cent of the value of the raw nitrogen compounds produced in the world amounting in 1913 to nearly \$200,000,000. Of this it is estimated that 80 per cent went for agricultural purposes. The farmers' purchases of nitrogen used east of the Mississippi during 1914 came to about \$75,000,000, of which more than 90 per cent was in the form of ammonia. The normal annual consumption of nitric acid in the same region is about \$7,000,000. The price per unit of nitrogen and the present rate of increase of consumption (10 per cent) is about the same for the two forms⁹³ (1915).

The fertilizer question is one of great importance to the United States⁹³ (1915). In the ten years from 1900 to 1910 population has increased 21 per cent, and the crop production only 10 per cent. Beef production fell 32 per cent, and the importation of foodstuffs more than doubled, with a marked decrease in the exports. Foodstuffs advanced in cost by 80 per cent between 1896 and 1912, and the increase in the cost of living was 59 per cent.

These figures indicate the necessity for increasing yields, as has been done in Europe, where the yield per acre is from 50 to 100 per cent greater than the United States, chiefly because of the use of fertilizers, which in Germany is, for instance, per acre, 15 times, in value in the United States, the average used on cultivated lands east of the Mississippi. Experiments in Indiana and Illinois have shown an increase in yield of wheat valued at from 2 to 3 times the cost of the fertilizer.

The present artificial fertilizers, however, contain from 85

to 90 per cent of material having no fertilizer value. To meet the conditions of long distance transportation and haulage over roads nearly impassable in the spring, it is essential that for the present mixtures should be substituted a concentrated substance of the proper composition and with the required physical and chemical properties.

Peacock⁴⁹ (1915) emphasizes the necessity of lowering the present prohibitive price of nitrogen products to check this increase in price of farm products.

Washburn⁵³ (1915) points out that arc methods of fixation cannot supply ammonia, and so must be limited to supplying the relatively small demand for nitric acid. The ammonia processes, on the other hand, supply a product for the conversion of which into nitric acid processes have already been sufficiently developed to leave little doubt of their ultimate success, even though as yet no thoroughly workable commercial plant is perfected, or in entirely satisfactory operation (in the U. S.).

Furthermore, the product of the arc processes, nitric acid, is not suited to the long-distance transportation from the remote localities where power is cheap enough to permit of its manufacture. Calcium nitrate is too hygroscopic for fertilizer purposes.

Washburn tends to the conclusion that the most promising solution of the fertilizer problem lies in the production of an ammonium phosphate compound deriving its ammonia from the cyanamide process.

Peacock⁴⁹ (1915) gives the annual nitrogen consumption of the fertilizer industry in the United States as equivalent to more than 100,000 tons of ammonia, increasing by about 8 per cent each year.

About 50 per cent of the Chile nitrate imported into the United States is used in the manufacture of explosives, and another 25 per cent in the arts requiring nitric acid⁵³ (1915).

IV—COSTS PRICE OF COMBINED NITROGEN

The price of combined nitrogen^{52,49} (1915) is fixed by the price of Chile saltpeter, of which the 95 per cent pure contains about 15.5 per cent of nitrogen. When the latter sells for 2 cents per lb. for the 15 per cent grade, the price of nitrogen is 13.2 cents per lb. and the price of ammonium sulfate containing 21 per cent of nitrogen should be 2.7 cents per lb. The cost of converting nitrate into nitric acid increases its value 50 per cent. Hence, there is this added margin for the direct production of acid by other processes.

The price of Chile saltpeter has averaged since 1909, \$35 to \$40 per ton f. o. b. Chile, or \$45 f. o. b. Liverpool. The present cost of production is from \$10 to \$20 per ton, leaving a profit on the mining of \$5 to \$10 after paying a tax to the Chilean government of \$12.25 per ton.

The Liverpool price of ammonium sulfate approximates that of sodium nitrate, varying from \$45 to \$60 per ton. The nitrogen content is about 21 per cent.

The cost of converting ammonia into ammonium sulfate is about \$15 per ton of the salt, and the cost to the by-product coke oven of producing the ammonia required for a ton is about \$10.

Peacock⁴⁹ (1915) considers that it will be necessary to get the production cost at the factory down to cents per lb. of ammonia, in order to have any process of nitrogen fixation compete successfully with by-product ammonium sulfate. This seems to necessitate a process giving other by-products of value. A low-priced ammonia once obtained, oxidation processes will follow easily. A concentrated end product such as potassium or ammonium nitrate, or ammonium phosphate, with a factory cost not exceeding 5 cents per lb. of combined nitrogen in the form of ammonia will probably be necessary in order to meet the competitive resources of by-product ammonia.

Summers⁵⁸ (1914) also believes that the solution of the problem must be sought through improvement of processes.

Carlson⁵⁹ (1914) gives the value of a kilogram of nitrogen in the various forms showing the increase from the value as element up to a complex drug like veronal.

FIXATION COSTS

Washburn⁵³ (1916) claims that the arc process is at a great disadvantage compared with the cyanamide. For the fixation of a unit of nitrogen the former requires from five to six times as much power as the latter. The production of 180,000 net tons of concentrated nitric acid per annum requires 540,000 continuous horse power by the former and 100,000 continuous horse power by the latter method. At the moderate American cost of installation of \$100 per continuous horse power, the total installation cost of the arc process for the above rate of production would be \$80,000,000—and for the cyanamide process, \$30,000,000. Even at an installation cost of \$60 per continuous horse power on the switchboard, concentrated nitric acid costs a third more by the arc process. Even with power at the abnormally low figure of \$10 operative cost per continuous horse power on the switchboard, the pound of nitrogen by the arc process costs for power alone as much as the total cost of the pound of nitrogen by the cyanamide process, including power, materials, labor, interest, amortization, and depreciation.

He also states that the cost of production of nitric acid by the cyanamide process as it is being established by an English Company throughout the allied countries is substantially 70 per cent of the cost of production from Chilean nitrate.

Gilbert¹⁴ gives a comparative cost analysis of the arc and cyanamide processes. He does not state his authorities but his conclusions coincide with those of Washburn and others.

The German nitrogen monopoly agrees to sell nitrogen after the war at a maximum price of less than half what farmers normally pay⁵⁴ (1916) in the United States.

Germany has expended on her nitrogen fixation industry since the beginning of the war, \$100,000,000⁵⁴ (1916).

Washburn⁵³ gives the cost of Chilean nitrate as \$2.40 to \$2.60 per unit of ammonia (20 lbs.) (= \$50 a ton), and of cyanamide as 80–90 cents per unit of ammonia.

Norton¹⁷ (1916) believes from observation of European practice that the minimum-sized plant for economical fixation of nitrogen is about 30,000 horse power.

He also states that in order to compete with the cyanamide process using power at \$20 per horse power, the arc processes must get power at \$3 or \$4 a horse power, but if the final product desired be nitric acid, the arc process can compete at \$7, \$8 or \$10 per horse power.

Summers⁵⁸ (1915) considers in detail the relative costs of the various processes for fixing nitrogen. From certain initial estimates of costs of labor, etc., he concludes that under the best conditions the manufacturer cannot meet expenses and pay more than \$15 per kilowatt year. Hence the acid cannot find application in fertilizers, and the process can be utilized only if it may be coupled with some other product.

He computes that the electrical power requirements of the various processes are as follows:

Direct oxidation process, require per kg. of nitrogen	400 kwh. hr.
Cyanamide process, require from preparation of nitrogen gas, require per kg. of nitrogen	100 kwh. hr.
Harper process, require energy from coal, require per kg. of nitrogen	100 kwh. hr.
Water electrolysis, ammonia process, require preparation of nitrogen and heat gas, require per kg. of nitrogen	100 kwh. hr.

Table 1, 1915, gives the yields and costs of the various arc processes as follows:

	Yield of acid per ton of ammonia	Yield of acid per ton of ammonia	Yield of acid per ton of ammonia
Ammonia	100	100	100
Proton	100	100	100
Proton	100	100	100
Proton	100	100	100

Hence at a market price of \$100 per kg. of nitrogen as calcium nitrate, the processes can only be made at a profit.

where power can be obtained in sufficient quantities at a price less than 0.5 centime per kilowatt hour.

The lime-nitrogen process requires about 2 kw. yr. per ton of nitrogen fixed, and the Haber or synthetic ammonia process, 3 kw. yr. per 1000 kg. of nitrogen.

Washburn⁸⁵ (1915), while giving no specific cost data, draws comparisons which he states are derived from actual working records, between the costs of the various processes.

Under the most favorable conditions the factory cost, exclusive of all power costs, of nitrogen in the form of commercial nitric acid, made by the arc process, is greater than the total cost of nitrogen as cyanamide, including power used at \$10 per continuous horse-power year. Hence the cyanamide process can fix nitrogen, with power at \$10 per horse-power year, cheaper than the cheapest of the arc processes with power free, or with all labor, raw materials and supplies free, and a charge of from \$8 to \$10 per horse-power year. The total cost of nitrogen in nitric acid from the arc process cannot by any chance be less than double that of nitrogen in cyanamide, thus giving the latter form a wide margin for its conversion into nitric acid, if desired. The indications are that weak nitric acid can be made by the cyanamide process for about 3/4 of the cost by the arc process, but as power is brought below \$10 per continuous horse-power year, the production cost of the latter process will diminish until it becomes about the same as for the former at \$4 per horse-power year.

The cost of producing ammonia gas by the Haber process under the most favorable conditions, is nearly double that by the cyanamide process.

The investment necessitated by the arc process per unit of nitrogen as weak nitric acid, assuming the investment for power to be between \$50 and \$75 per horse power upon the switchboard, is about three times that per unit of nitrogen as ammonia, or twice that per unit of nitrogen as nitric acid derived from cyanamide. The fixed investment for ammonia production for the cyanamide process may be as low as one and one-half times the market value of the annual product compared with three times for the Haber process. For nitric acid by the cyanamide process the investment may be only one and one-fourth times the annual product, while for the arc process, with a power investment of \$75 per continuous horse power, the fixed investment would be from three to four times.

In the United States the majority of manufacturing concerns vary in fixed investment from one to one and a half times the market value of the annual product, exceeding this proportion only in very special cases. The most reliable class of investments, such as public utility corporations do not exceed \$4 to \$6 investment per dollar of gross revenue.

Washburn⁸⁵ (1915) points out that though the Haber process demands relatively little power, yet the cost in the vicinity of New York of the electrical energy demanded is as much as the total power cost for cyanamide at other available sites. Its successful employment by the Badische Company is due to their pressing need for a way of disposing of large quantities of by-product sulfuric acid.

Peacock⁴⁹ (1915) believes that synthetic ammonia processes such as that of Haber may have local application, but will never become commercially important.

The plant investment required for the production of cyanamide ammonia is about half that for Haber, or synthetic ammonia. The cyanamide plant costs per unit of nitrogen fixed, about one-quarter as much as the arc process-plant, and even the cyanamide-ammonia-nitric-acid plant costs only from one-third to one-half as much to install as the arc. The electric power required per unit of nitrogen fixed is one-fifth and the labor about the same as that of the arc process. The further conversion of the ammonia into nitric acid requires only a small fraction of additional power and labor. Moreover, the cyanamide is

readily transported, and can be easily and economically converted into ammonia and nitric acid by small units at the point where used⁴⁶ (1915).

Haber⁴⁴ (1914) states that the Frank and Caro or cyanamide process fixes 50 g. of nitrogen per kw. hr. including all power.

The energy consumption in the fixation of one ton of nitrogen as calcium cyanamide is given by Pranke²⁹ (1913) as about three horse-power years including manufacture of carbide and all subsequent factory operations.

Kroczeck²² (1913) gives the horse-power consumption of the various processes as follows:

	H. P. hr. per kg. (2.2 lb.)
Kawalsky-Pauling.....	97
Birkeland-Eyde.....	84
Schönher.....	80
Calcium cyanamide.....	33
Aluminum nitride.....	16

Scott¹²⁷ (1912) gives the nitrogen content and comparative prices of various artificial fertilizers as follows:

	Per cent Nitrogen	Price per Ton (Long)
Ammonium sulfate from gas works..	19.75	£13
Chile nitrate.....	15.50	£ 9 15s
Norwegian calcium nitrate.....	12.75	£ 8 10s
Calcium cyanamide.....	18.00	£10

Roerber¹⁴⁹ (1910) gives the yields of the various processes as:

Schönher (Badische Co.).....	75 g. HNO ₃ per kw. hr.
Birkeland-Eyde.....	70 g. HNO ₃ per kw. hr.
Pauling.....	60-75 g. HNO ₃ per kw. hr.
Cyanamide.....	76 g. HNO ₃ per kw. hr.

Scott¹²⁷ (1912) gives the yield of the Birkeland-Eyde process as 500-550 kg. of nitric acid or 853-938 kg. of calcium nitrate per kw. yr. The best yield at Notodden has been 900 kg. of 100 per cent nitric acid per kw. yr.

The Pauling process guarantees 60 g. of 100 per cent nitric acid per kw. hr. and a cost of 120 francs per kilowatt as cost of the electrochemical plant itself.

Dobbelstein¹⁴⁸ (1912) gives the costs of installation and operation for a plant employing the Häusser method with coke oven gases.

Reference 84 (1914) gives the yields of the Serpek process as 2 tons of alumina and 500 kg. of fixed nitrogen (as ammonia) per kw. yr.

Beckman¹³⁵ (1911) describes the general financial status of the nitrogen fixation industry as being "well paying" and gives income figures. He makes a mistake, however, in stating that the Birkeland-Eyde process has been abandoned. [See Reference 130 (1911).]

Franklin¹⁴⁰ (1911) gives a very general review of the status of nitrogen fixation processes, considering only the Birkeland-Eyde, Schönher, and cyanamide processes, and their relative costs, with data taken from other authors.

Roerber¹⁴⁹ (1910) gives a good general review of the various processes for nitrogen fixation, with costs, and present status of industry.

Voorhees¹⁵⁰ (1910) discusses the relative costs and actual value to the farmer of the various constituents of artificial fertilizers, and shows where economy should be effected.

AMMONIA FROM CALCIUM CYANAMIDE

Landis²⁵ (1916) gives estimates on the plant and operating costs for the production of 30,000 lbs. of ammonia per day, based on designs made by the American Cyanamide Company, in the light of European practice, and after six months' experience in America with a small plant, imported from Germany. These involve the use of an autoclave unit of nine shells requiring a continuous motor load of about 200 h. p.

The plant, without power or pumping plants, equipped to put out as final product an ammonia gas saturated with moisture at the temperature of the condenser water available may be erected for \$120,000. This does not include cost of land, foundations, or sludge disposal. The cost of operation, including the items of power, steam, water, labor, chemicals, repairs, interest, depreciation, etc., comes to \$451.43 per day, or \$0.01505 per pound of ammonia. The detailed items are given in the original.

Laboratory experiments by Manuelli⁷¹ (1914) have shown the yield to be from 90-99 per cent of the theoretical. The cost should be about 20 centimes per kilo of nitrogen.

OXIDATION OF AMMONIA

Zeisberg⁴ (1916) gives costs deduced for American conditions from the costs given in Reference 109 and compares them with estimates from other sources for small and large plants.

He gives the cost of making nitric acid from sodium nitrate as at least 1.75 cents per lb. for labor, repairs, and sulfuric acid and with sodium nitrate at 2.64 cents per lb. the cost of the nitrogen used per lb. of nitric acid would be 3.750 cents compared with 4.280 cents for the Ostwald process. But the Ostwald process will become increasingly more profitable as the price of Chile nitrate and consequently of ammonia becomes less. These estimates are based on an 85 per cent efficiency for the Ostwald process and a 97 per cent efficiency for the retort method of making nitric acid. Zeisberg concludes that ammonia itself is so valuable that there is little hope that the Ostwald process can ever compete successfully with the arc processes for the production of nitric acid.

Kaiser³³ (1916) claims to be able to oxidize ammonia to nitric acid with a 90-95 per cent yield at a cost of 1.25 kg. of coke per kg. of ammonia, besides the power for driving fans.

Diefenbach⁴² (1914) computes that at the selling price existing, oxidation of ammonia to nitric acid is less profitable than conversion to sulfate. But in factories producing dilute nitric acid, absorption by nitric acid should be yet more economical.

In Reference 109 (1913) the cost of manufacture of nitric acid from ammonia from gas liquor is given for a plant capable of producing monthly 148.4 tons of 53 per cent nitric acid from 25 tons of nitrogen in the form of ammonia. The cost of plant is estimated at \$55,000, and the items are given. Operating costs per month should be as follows:

Power, 14,400 h. p. hrs. at 3 cents	\$ 437.50
Steam, 20,000 kg.	137.70
Total operation including above and interest, labor, etc.,	2,187.50
Costs per ton of 100 per cent HNO ₃	39.44

These figures include the plant and cost of production of ammonia gas from gas liquors. Detailed items are given with estimates of profits. The estimates are based on English conditions.

V—APPENDIX

RECOVERY OF NITROGEN COMPOUNDS

BY-PRODUCT COKE OVENS

Christopher⁶⁴ (1913) gives a history of the development of ammonia recovery from coke ovens with the yields at various periods, descriptions of the types of ovens, with comparative working costs and values of the products. A bibliography is included.

The yields obtained in 1870 are given as 10 gallons of tar and 16 lbs. of ammonium sulfate per ton of coal in gas works, and 5 to 11 gallons of tar and 4 to 6 lbs. of ammonium sulfate from coke ovens. This had been increased in 1881 by the Simon-Carves plant to 6.42 gallons of tar and 28 lbs. of ammonium sulfate.

PRODUCER-GAS PLANTS

A further resource for the recovery of nitrogen compounds is the ammonia recovery producer-gas plant. The Lynn apparatus is a recent system based upon the general principles of the Mond process, but with the high and low-pressure reduced by vertical washers. The form and operation is fully described and illustrated. Operating costs are given for a plant producing from 2816 to 2750 kw. hr. per hour, with a consumption of 64.6 to 61.3 tons of coal yielded from 1.5 to 1.44 tons of ammonium sulfate in 24 hours. The ammonia content of the coal used was 0.5 per cent, and the cost \$10.00 to \$12.25 per ton. Including a 10 per cent depreciation charge, the cost of gas is 0.04 per kw. hr. Reference 36 (1914) gives further details.

COAL-GAS MANUFACTURE

Wagner¹⁵ (1914) describes and gives the costs, etc., for recovery of ammonia and other products in coal gas distillation by the Feld system. The raw liquor usually contains from 1 to 2 per cent of ammonia from which all but about 0.005 per cent is recovered.

The operating costs, without depreciation and interest, for the ammonia recovery from a plant carbonizing 300 tons of coal per day should be for a 250-day year:

\$22,530 if aqua ammonia, and
\$12,811 if ammonium sulfate is the final product.

With ammonia at 8 cents per lb., aqua ammonia of 26° at \$102 a ton, and ammonium sulfate at \$60 a ton, the annual profits for the two processes should be \$47,030 and \$30,809, respectively.

If the Bueb process for the extraction of cyanogen be combined with the above Feld process, the operating expenses will be \$11,546 and the profit \$48,039.

Tutwiller⁷⁴ (1914) describes in detail the methods of coal gas manufacture and by-product recovery, giving cuts and diagrams of apparatus. He gives analyses, proximate and ultimate, of a typical coal. He also describes in detail the concentration of ammoniacal solutions, illustrating with cuts and diagrams. His article is very full.

Rittman and Whitaker⁴⁰ (1915) give a bibliography of the chemistry of gas manufacture of 274 references covering the headings:

- Carbonization and distillation of coal.
- Gas producers, water-gas.
- Petroleum oil distillation.
- Oil gas.
- Reactions of hydrocarbons.
- High temperature and high pressure reactions.
- Low temperature carbonization.
- Chemical equilibrium and catalysis.
- General literature.
- Books.

PEAT PRODUCER-GAS PLANTS

Lynn²⁷ (1916) gives an historical résumé of the development of producer-gas by-product recovery in Europe and outlines the latest features of his own system. He mentions the systems and improvements of Young and Beilby, Mond, Duff, Grossley and others, describing each and discussing the advantages of each. The article is very fully illustrated with diagrams, etc. He gives detailed costs of operation and estimates on three different types of installation. He gives the yield of a Lynn plant as 61 lbs. of ammonium sulfate per ton of coal, which is a "nitrogen efficiency of 70 per cent." He also discusses the adaptability of various fuels and states that peat containing 60 per cent of water can be used. Plant burning peat have been in operation in Europe for several years.

Nature¹⁹ (1916) in the course of an article discussing the distillation of peat in producer-gas plants gives figures on the recovery of by-products. Peat contains from 0.5 to 2.5 per cent of nitrogen, almost all of which may be liberated as ammonia by passing steam over the peat at 400° C. The following yields have been obtained from large-scale experiments:

Nitrogen content of peat	Yield of ammonia	Yield of ammonium sulfate
0.5 per cent	1.5 lbs. per ton of peat	1.5 lbs. per ton of peat
1.0 per cent	3.0 lbs. per ton of peat	3.0 lbs. per ton of peat
2.0 per cent	6.0 lbs. per ton of peat	6.0 lbs. per ton of peat

Producer-gas plants in which gas and ammonia are recovered are in operation at Barrow-in-Furness, England, and at the plant near the German border at H. P. and at the plant near the German border at H. P. The first two plants produce ammonia and ammonium sulfate. The ammonia plant produces 1.5 lbs. of ammonia per ton of peat, and the ammonium sulfate plant produces 1.5 lbs. of ammonium sulfate per ton of peat. The third plant produces gas and ammonia. The ammonia content of the peat used is 0.5 per cent. The cost of gas is 0.04 per kw. hr. Reference 36 (1914) gives further details.

MISCELLANEOUS

Ammonia Recovery from Waste Liquors—Knoedler⁴² (1915) has been able to recover 28 per cent ammonia from waste liquors of the Welsbach Company containing about 1 per cent, by a distillation plant which he describes in detail, at a cost of operation of \$2.24 per 1000 lbs. The output of his plant was 3000 lbs. of 26 per cent ammonia per day.

Ammonium Chloride from Recovery Plants—A process has been patented and is being applied by the Berlin-Anhaltische Maschinenbau Aktien-Gesellschaft or the manufacture of ammonium chloride instead of ammonium sulfate from by-product ammonia, with the idea of supplying the market for the pure salt, and also avoiding a future overproduction of sulfate⁷⁹ (1914).

Wagner⁷⁸ (1914), in the course of an illustrated article on coal gas residuals and the Feld system, describes processes and apparatus for the recovery of ammonia gas by continuous stills and its conversion into ammonium sulfate.

The results obtained by slow distillation of coal in vacuum at various temperatures are discussed by Cobb, Burgess and Wheeler⁸⁰ (1914).

A tar scrubber for the direct process¹⁰⁴ (1913) for ammonia recovery from gases, avoiding the customary absorption and redistillation, is described, with cuts, by Strommenger. A good sulfate containing 25 per cent of NH_3 is obtained.

Heck⁸⁰ (1913) describes in some detail the operation of the Brunck direct, and the Koppers semi-direct, processes, with estimates of the relative saving effected by each.

Ohnesorge⁸⁷ (1913) outlines the history and recent development of the direct process for recovery of ammonium sulfate.

The direct process using a Pelouze extractor is briefly described by Pfüdel¹²⁴ (1912).

Brown¹³⁷ (1911) gives working directions for the operation of a waste ammonia recovery plant and for concentration and testing of the product.

Cooper¹³⁸ (1911) has carried out some experiments upon the direct recovery of ammonia, and gives the diagram of his tar extractor.

PRODUCTS MADE FROM CYANAMIDE

Cyanamide is capable of a number of conversions to products, such as urea, dicyanamide, creatinin.

Washburn states that the United States imports annually for the celluloid industry \$50,000 worth of high-grade urea which can now be supplied from this source. Urea is also applicable in the manufacture of explosives, when not prohibitively expensive⁶⁸ (1915). Its nitrogen can be converted almost quantitatively into cyanides by fusion with salt, giving a yield equal to nearly 25 per cent of the weight of the cyanide equivalent.

Clennell¹³⁷ (1915) discusses the chemistry of this reaction, and of others for making cyanides, as given by the literature and patents.

Cyanamide itself is an excellent agent for case-hardening, and hundreds of tons are being used abroad in the manufacture of war materials, and will probably find extensive use here when the peculiarities of the trade have been overcome⁶⁶ (1915).

Sulzer¹³⁰ (1912) makes ammonia and formic acid from calcium cyanamide by fusing with charcoal and sodium carbonate, and then heating with water in an autoclave.

Carlson⁶⁰ (1914) discusses in a general way the use of cyanamide as a raw material for the manufacture of other products such as cyanides, urea, veronal and other drugs. He gives the value of a kilogram in the various forms from element to complex drug.

NOMENCLATURE OF CYANAMID INDUSTRY

The following definitions of terms used in the Cyanamid industry are given by Franke⁹⁹ (1913):

Lime-Nitrogen—Crude calcium cyanamide, ground to a fine powder after removal from the ovens in which it is formed. It contains about 55 per cent calcium cyanamide, CN.NCa , about 2 per cent calcium carbide, and about 20 per cent free calcium oxide.

Cyanamid—This is a trade name for the completely hydrated material prepared for use as a fertilizer in the United States. It contains about 45 per cent calcium cyanamide, 27 per cent calcium hydroxide and no carbide. The name is always capitalized and has no final "e."

Cyanamide—The compound represented by the formula CN.NH_2 . It is sometimes referred to as acid cyanamide, or free cyanamide.

Calcium Cyanamide—The chemical compound of the formula CN.NCa , or CaCN_2 , as it is frequently written.

Calcium Cyanamid—The name used by the United States Department of Agriculture and by some State Departments of Agriculture to designate the commercial Cyanamid. It is sometimes used to indicate the substance represented by the formula CN.NCa , but for the sake of clearness the compound CN.NCa will be called calcium cyanamide in the present paper.

Nitrolim—The trade name for the material sold in England for agricultural purposes. It is a lime-nitrogen to which has been added just enough water to destroy the carbide. Practically all the free lime is present as calcium oxide.

Kalkstickstoff—The commercial material manufactured in Germany for use as a fertilizer. It is similar to nitrolim.

Stickstoffkalk—A crude calcium cyanamide made by nitrifying a calcium carbide which contains about 10 per cent of calcium chloride. Its manufacture in Westergeln, Germany, under the Polzeniusz patents was discontinued in 1910.

Calciocianamide—The Italian commercial product, completely hydrated.

Cyanamide de Calcium—The French commercial product, completely hydrated.

EQUIVALENTS

1 M. (Mark) = \$0.238	1 (centime) = 1/100 franc
1 (pfennig) = 1/100 M.	1 kg. (1000 g.) = 2.205 lbs. (Av.)
1 £ (pound) = \$4.8665	1 kw. hr. = 1.359 H. P.
1 s. (shilling) = 1/20 £	1 long ton = 2240 lbs.
1 fr. (franc) = \$0.193	1 metric ton = 2204.62 lbs.

POWER COSTS

The average coal consumption per kw. hr.³ (1916) was found to be 2.77 lbs. (bituminous) at a modern 18,500 kw. steam turbine plant at Worcester, Mass. The unit cost of production per kw. hr. was 5.3 mills for fuel (\$4.28 per ton) and 1.12 mills for operating labor cost. The cost analysis is given.

Dunn¹⁰ (1916) discusses the relative construction and operation costs of hydro-electric and steam plants for the generation of electricity. He gives comparative unit analyses of cost of operation.

Stillwell¹² (1916) gives similar data and also shows the variation in total cost of power for various costs of coal.

Scheuer²² (1916) gives the cost of power from hard and soft coal at different prices in Germany, with and without by-product recovery. He also gives statistics of coal production and by-product yields of various kinds.

Baekeland¹⁶ (1916) states that at \$1.25 a ton for good steam coal power can be obtained cheaper than the price now paid at Niagara.

In Reference 24 (1916) Washburn discusses the relation of the water power problem to nitrogen fixation, describing the difference between Norwegian and United States water powers. He gives estimated costs of installing plants, etc.

There is considerable interest in the possibility that certain of these processes might be adapted to utilized off-peak and off-season loads⁸² (1915).

In figuring the cost⁴ (1914) of water power, it is the tendency abroad to include only operating costs, and not the investment on the plant, contrary to the practice in the United States. This should be taken into consideration in making comparisons. There are many plants in operation in the chemical industries abroad, whose real costs of power production are no lower than many of the more favored locations in this country.

Scott⁴⁷ (1912) discusses the power question as it affects Great Britain, and goes into comparison and details in regard to the cost of installation of hydro-electric, and steam plants, and the relative advantages of coal and gas-fuel, and of surface combustion. He gives the capital and running costs for a producer-gas engine power station for 3000 brake horse power.

In Norway⁴⁸ (1912) the electric horse-power year costs \$4 to \$6 compared with \$10 to \$15 in the U. S.

Lyon and Keeney⁴⁹ (1913) give the cost of power used for various electrochemical processes in 25 different localities from hydro-electric and steam plants.

VI—REFERENCES

- 1—Martin and Barbour, "Industrial Nitrogen Compounds and Explosives." (D. Appleton & Co., N. Y. 1916.)
- 2—Porter, *Metallurgical and Chemical Engineering*, **15** (1916), 470-5.
- 3—*Electrical World*, **68** (1916), 671.
- 4—Zeisberg, *Metallurgical and Chemical Engineering*, **15** (1916), 299-304.
- 5—Turrentine, *This Journal*, **8** (1916), 923-6.
- 6—Turrentine, *Ibid.*, **8** (1916), 584-5.
- 7—Frankfurter Handelsblatt, May 29, 1916, Abstract, *Engineering* (L.), **101** (1916), 576.
- 8—Harris, *American Fertilizer*, **45** (1916), 32-5.
- 9—Clarke, Abstract, *Metallurgical and Chemical Engineering*, **14** (1916), 601-3.
- 10—Dunn, *Proc. Am. Inst. Elec. Eng.*, **35** (1916), 575-90.
- 11—H. Koppers Co., Pittsburgh, Pa., "By-products of the Coking of Coal in America," **1916**. (Pamphlet issued to oppose government nitrate plant.)
- 12—Stillwell, *Proc. Am. Inst. Elec. Eng.*, **35** (1916), 561-74.
- 13—Washburn, "The Facts in the Nitrogen Case," **1916**.
- 14—Gilbert, "Sources of Nitrogen Compounds in the United States," Smithsonian Publication No. 2421 (1916).
- 15—Backeland, Statement before Senate Committee on Agriculture and Forestry, **1916** (S. 4971).
- 16—Merrill, Statement before Senate Committee on Agriculture and Forestry, **1916** (S. 4971).
- 17—Norton, Statement before Senate Committee on Agriculture and Forestry, **1916** (S. 4971).
- 18—Washburn, Statement before Senate Committee on Agriculture and Forestry, **1916** (S. 4971).
- 19—*Nature*, **97** (1916), 19-23.
- 20—*Scientific American*, **112** (1916), 216.
- 21—Landis, *Metallurgical and Chemical Engineering*, **14** (1916), 260.
- 22—Scheuer, *Elektrotechn. Z.*, **37** (1916), 64-7.
- 23—Skerratt, *Iron Age*, **97** (1916), 359-62.
- 24—Washburn, Statement before House Committee on Military Affairs, Feb. 11, 1916; Statement before House Committee on Agriculture, Feb. 1, 1916.
- 25—Landis, *This Journal*, **8** (1916), 156-60; *American Fertilizer*, **44** (1916), 21-6.
- 26—Cushman, *J. Frank. Inst.*, **181** (1916), 163-90.
- 27—Lynn, *J. Am. Soc. Mech. Eng.*, **37** (1915), 253-66.
- 28—*Nature*, **96** (1916), 537.
- 29—Schluphaus, *Met. und Erz*, **13** (1916), 21-8; Abstract, *Metallurgical and Chemical Engineering*, **14** (1916), 425-6.
- 30—Childs, *Amer. Iron and Steel Institute*, May **1916**; Abstract, *Metallurgical and Chemical Engineering*, **15** (1916), 38-41.
- 31—*Electrical World*, **68** (1916), 10-2, 69-70.
- 32—*Duke, Engineering and Mining Journal*, **101** (1916), 149; *Manufacturers' Record*, **68** (1916), 58.
- 33—Kaiser, *Chem.-Ztg.*, **40** (1916), 14; Abstract, *Chemical Abstracts*, **10** (1916), 806.
- 34—Wagner, "Coal and Coke," **1916** (McGraw Hill Book Co.)
- 35—Vogel, *Chem.-Ztg.*, **40** (1916), 11-3; Abstract, *J. Soc. Chem. Ind.*, **33** (1916), 431.
- 36—Baur, *Schweizerische Wasserwirtschaft*, **7**, Nov. 16 and 17, *Elektrotechn. Z.*, **36** (1915), 694-5.
- 37—Clemmell, *Metallurgical and Chemical Engineering*, **13** (1915), 750-8.
- 38—Cressip, *Iron Age*, **96** (1915), 789-9.
- 39—Dary, *Revue d'Electrotechnique et d'Electrometallurgie*, **8** (1914), 70-2; Abstract, *Elektrochem. Z.*, **31** (1915), 236.
- 40—Dunn, *Scientific American*, **113** (1915), 492-3, 505-6.
- 41—Haber, Maschke, *Z. Elektrochem.*, **21** (1915), 128-30.
- 42—Haber, Tamaru, Oeholm, *Z. Elektrochem.*, **21** (1915), 191-245.
- 43—Haber, Tamaru, Ponnaz, *Z. Elektrochem.*, **21** (1915), 89-106.
- 44—Koenig, *Z. Elektrochem.*, **21** (1915), 267-86.
- 45—Knödel, *This Journal*, **7** (1915), 1061-4.
- 46—Landis, *This Journal*, **7** (1915), 433-8; *Metallurgical and Chemical Engineering*, **13** (1915), 213-8.
- 47—Landis, *Metallurgical and Chemical Engineering*, **13** (1915), 218-20.
- 48—Merrill, Report upon Electric Power Development in the United States, etc., in response to Senate Resolution of Feb. 13, 1915. Part 2, Doc. 316, 485 pp.
- 49—Peacock, *Trans. Am. Electrochem. Soc.*, **27** (1915), 409-17.
- 50—Rittman, Whitaker, "Bibliography of the Chemistry of Gas Manufacture," Bureau of Mines, *Technical Paper*, **130** (1915).
- 51—Scott, *J. Soc. Chem. Ind.*, **34** (1915), 113-26.
- 52—Summers, *Trans. Am. Electrochem. Soc.*, **27** (1915), 339-83; *Proc. Am. Inst. Elec. Eng.*, **34** (1915), 337-81; Abstract, *Metallurgical and Chemical Engineering*, **13** (1915), 241-4.
- 53—Washburn, *Trans. Am. Electrochem. Soc.*, **27** (1915), 385-402; *Metallurgical and Chemical Engineering*, **13** (1915), 309-14.
- 54—*Elektrochem. Z.*, **31** (1915), 211-21.
- 55—*Engineering News*, **78** (1915), 16-21.
- 56—*Metallurgical and Chemical Engineering*, **13** (1915), 456-8.
- 57—*Metallurgical and Chemical Engineering*, **13** (1915), 638-9; *American Fertilizer*, **43** (1915), 37-42.
- 58—Backeland, *This Journal*, **6** (1914), 75-78; *Metallurgical and Chemical Engineering*, **12** (1914), 559-60.
- 59—Carlson, *J. angew. Chem.*, [3] **27** (1914), 724-5.
- 60—Cobb, *J. Gas Lighting*, **126** (1914), 329-31; Abstract, *J. Soc. Chem. Ind.*, **33** (1914), 541; Burgess, Wheeler, *J. Chem. Soc.*, **105** (1914), 131-40.
- 61—Crossley, *J. Soc. Chem. Ind.*, **33** (1914), 1140.
- 62—Dieffenbach, *Chem. Ind.*, **37** (1914), 265-9.
- 63—Haber, *Z. angew. Chem.*, **27** [1] (1914), 473-7.
- 64—Haber, *J. Soc. Chem. Ind.*, **33** (1914), 52-4.
- 65—Perlick, "Die Luftstickstoff Industrie in ihrer volkswirtschaftlichen Bedeutung" (Dr. Werner Klinkhardt, Leipzig, 1913).
- 66—Hene, Dissertation der Berliner Technischen Hochschule **1912**, p. 48; Abstract, *Elektrotechn. Z.*, **35** (1914), 745.
- 67—Knox, "Fixation of Atmospheric Nitrogen" D. Van Nostrand Co. 1914. 110 pp.
- 68—Koenig, *Eldö, Ber.*, **47** (1914), 516-29.
- 69—Kuberschy, *This Journal*, **6** (1914), 692.
- 70—Lowry, *Trans. Faraday Soc.*, **9** (1914), 189-92.
- 71—Mamelli, *Ann. chim. applicata*, **1**, 1914, 388-96; Abstract, *J. Soc. Chem. Ind.*, **33** (1914), 690-1.
- 72—Matignon, *Chem. Z.*, **38** (1914), 894-5; Abstract, *J. Soc. Chem. Ind.*, **33** (1914), 829.
- 73—Serpuk, *Z. angew. Chem.*, [1] **27** (1914), 41-8.
- 74—Tutwiller, *J. Franklin Inst.*, **178** (1914), 383-416.
- 75—Wagner, *Scientific Amer. Supplement*, **80** (1915), 316-9; *Metallurgical and Chemical Engineering*, **13** (1914), 696-702; *Amer. Gas Inst.*, **1914**.
- 76—*Chemical Trade Journal*, May 9, 1914; Abstract, *J. Soc. Chem. Ind.*, **33** (1914), 541.
- 77—*Chem.-Ztg.*, Apr. 23, 1914; Abstract, *J. Soc. Chem. Ind.*, **33** (1914), 590.
- 78—*Chem.-Ztg.*, **38** (1914), 593; Abstract, *This Journal*, **6** (1914), 592.
- 79—*Chem.-Ztg.*, **13** (1914), 117; Abstract, *This Journal*, **6** (1914), 58-9.
- 80—*Engineering* (London), **98** (1914), 267-72, 294-6, 351-3, 465-8.
- 81—*J. Soc. Chem. Ind.*, **33** (1914), 134.
- 82—*Metallurgical and Chemical Engineering*, **12** (1914), 265-8.
- 83—*Z. Ver. deut. Ing.*, **58** (1914), 980.
- 84—*Z. Ver. deut. Ing.*, **58** (1914), 66-7.
- 85—Bradbury, Hirsch, Abstract, *J. Soc. Chem. Ind.*, **33** (1914), 81.
- 86—Christopher, *J. Soc. Chem. Ind.*, **33** (1913), 115-24.
- 87—Fischer, Hene, *Ber.*, **46** (1913), 606-17.
- 88—Frankel, *Z. Elektrochem.*, **19** (1913), 367-5.
- 89—Haber, *Revue d'Electrotechnique et d'Electrometallurgie*, **11** (1913), 111-4; Abstract, *Metallurgical and Chemical Engineering*, **11** (1913), 111-4; *J. Soc. Chem. Ind.*, **32** (1913), 134-5; *This Journal*, **5** (1913), 68-81.
- 90—Heck, *Springer*, **33** (1913), 11-8.
- 91—Koenig, *Ing.*, **46** (1913), 157-9.
- 92—Krocker, *Gas. W.*, **69** (1913), 1-8; Abstract, *Amer. Gas Inst.*, **1913**.
- 93—Laser, *Kunstst. Fabr.*, **3**, 1913, 1-2; Abstract, *This Journal*, **5** (1913), 24.
- 94—Menneghy, *Chem. Abstr.*, **11**, 43 (1913), 81; Abstract, *J. Soc. Chem. Ind.*, **32** (1913), 230.
- 95—Montgomery & Co. Report, Abstract, *J. Soc. Chem. Ind.*, **32** (1913), 84.
- 96—Montgomery & Co. Report, Abstract, *J. Soc. Chem. Ind.*, **32** (1913), 260.
- 97—*Chem. Eng. Prog.*, **12** (1914), 3.
- 98—*Chem. Eng. Prog.*, **12** (1914), 11.
- 99—*Chem. Eng. Prog.*, **12** (1914), 11.
- 100—Richardson, *Chem. Eng. Prog.*, **17** (1915), 100.

- 107—Parr, *Ind. Eng. Chem.*, **5** (1913), 1008.
- 108—R. Z. *Ind. Eng. Chem.*, **19** (1918), 92-5.
- 109—Bühler, *Ind. Eng. Chem.*, **46** (1918), 600-7.
- 110—Greenough, *Stocks Exch.*, **11**, **33** (1913), 1994-5.
- 111—Tucker, *J. Soc. Chem. Ind.*, **32** (1913), 1443-4; *This Journal*, **5** (1913), 191-2.
- 112—*Ann. Intern. Assoc. Ind. Eng. Chem.*, **1** (May 1913), 444-4; *This Journal*, **1** (1913), 476.
- 113—*Engineering Metall.*, **1905**, 20, 600.
- 114—Fourth Annual Report on Alkal. Proceeding, during the year 1912; Abstract, *J. Soc. Chem. Ind.*, **32** (1913), 786-8.
- 115—*Metallurgical and Chemical Engineering*, **11** (1913), 438-42.
- 116—*Time Engineering Supplement*, Oct. 28, 1913; Abstract, *J. Soc. Chem. Ind.*, **32** (1913), 1008.
- 117—*Ann. Intern. Assoc. Ind. Eng. Chem.*, **15** (1913), 1-4; Abstract, *J. Soc. Chem. Ind.*, **31** (1912), 919.
- 118—Berthoulet, *Trans. 8th Intern. Cong. Appl. Chem.*, **28** (1912), 18.
- 119—*This Journal*, **4** (1912), 760-7.
- 120—Bühler, *Ann. Intern. Assoc. Ind. Eng. Chem.*, **1912**, 80-9; Abstract, *J. Soc. Chem. Ind.*, **31** (1912), 919.
- 121—Hirsch, Bradbury, *J. Soc. Chem. Ind.*, **31** (1912), 71, 716.
- 122—Durand, Briner, *Compt. rend.*, **155** (1912), 1495-7.
- 123—Dobbelstein, *Stahl u. Eisen*, **32** (1912), 1571-7; Abstract, *J. Soc. Chem. Ind.*, **31** (1912), 982.
- 124—Eyre, *Trans. Intern. Cong. Appl. Chem.*, **28** (1912), 169-81; Abstracts, *Chemical Engineer*, **16** (1912), 188-91; *This Journal*, **4** (1912), 771-4.
- 125—Fischer, *Hene, Ber.*, **45** (1912), 3652-8.
- 126—Häusser, *Z. Ver. deut. Ing.*, **56** (1912), 1157-64.
- 127—Kochmann, *Arbeit. Pharm. Institut. Berlin*, **8**, 81; Abstracts, *Chem. Zentr.*, [1] **1912**, 169; Chemical Abstracts, **6** (1912), 2295.
- 128—Lowry, *J. Chem. Soc.*, **101** (1912), 1152-8.
- 129—Mangum, *Gas. chem. ind.*, [1] **42** (1912), 126-34; Abstract, *J. Soc. Chem. Ind.*, **31** (1912), 383.
- 130—Norton, "Utilization of Atmospheric Nitrogen," Dept. of Commerce and Labor, Bur. of Manufacturers, Special Agents Series, 52, 1912.
- 131—Pfudel, *J. Gasbel.*, **54** (1911), 1272-3; Abstract, *J. Soc. Chem. Ind.*, **31** (1912), 64-5.
- 132—Reinders, *Cats, Chem. Weekblad*, **9** (1912), 47-58; Abstracts, *Chem. Zentr.*, [1] **83** (1912), 708; *J. Soc. Chem. Ind.*, **31** (1912), 280.
- 133—Ries, *Z. angew. Chem.*, **25** (1912), 586; *J. Soc. Chem. Ind.*, **31** (1912), 383.
- 134—Scott, "Manufacture of Nitrates from the Atmosphere," Smithsonian Report for 1913, pp. 359-84 (1914). (Publication 2291.) Reprinted from *J. Roy. Soc. Arts (London)*, **60** (1912), No. 3104.
- 135—Scott, *Nature*, **89** (1912), 463; Abstract, *This Journal*, **4** (1912), 619.
- 136—Strutt, *Proc. Roy. Soc.*, **1**, **86** (1912), 166-3; Abstract, *J. Soc. Chem. Ind.*, **31** (1912), 70-1.
- 137—Sulzer, *Z. angew. Chem.*, **25** (1912), 108-5; Abstract, *J. Soc. Chem. Ind.*, **31** (1912), 682.
- 138—Tausent, *Z. Elektrochem.*, **18** (1912), 314-9.
- 139—Tucker, *Read. Trans. Am. Electrochem. Soc.*, **22** (1912), 57-66.
- 140—*Metallurgical and Chemical Engineering*, **10** (1912), 126.
- 141—Newspaper clippings, *Eng. Record*, N. C. (June 11, 1912), *This Street Journal*, July 25, 1912.
- 142—Beckman, *Metallurgical and Chemical Engineering*, **9** (1911), 340.
- 143—Birkeland-Eyde, *Metallurgical and Chemical Engineering*, **9** (1911), 436, 485.
- 144—Brown, *Chemical Engineer*, **14** (1911), 456-61.
- 145—Cooper, *Chemical Engineer*, **13** (1911), 111.
- 146—Hühlich, *Russ. Monatsh. Chem.*, **32** (1911), 917-6; Abstract, *J. Soc. Chem. Ind.*, **30** (1911), 1393-4.
- 147—Franklin, *General Electric Review*, **14** (1911), 472-5; *Chemical Engineer*, **14** (1911), 453-6.
- 148—Lamy, *Metallurgical and Chemical Engineering*, **9** (1911), 99-104.
- 149—Edgar, *J. Am. Chem. Soc.*, **33** (1911), 292-9.
- 150—Strutt, *Proc. Roy. Soc.*, **85** (1911), 533-6.
- 151—Tufts, *This Journal*, **3** (1911), 295-9.
- 152—*Ann. Intern. Assoc. Ind. Eng. Chem.*, **9** (1911), 100-1.
- 153—Foerster, *J. Elektrochem.*, **13** (1907), 101-7.
- 154—Habber, Koenig, Platon; Habber, Platon, Holwech, Koenig, Habber, *Z. Elektrochem.*, **16** (1910), 789-813.
- 155—Holwech, *Z. Elektrochem.*, **16** (1910), 369-90.
- 156—Roerber, *Mineral Industry*, **19** (1910), 58-67.
- 157—Vogel, *Proc. Roy. Soc.*, **2** (1910), 1-5.
- 158—Wolokitin, *Z. Elektrochem.*, **16** (1910), 814-26.
- 159—Zenneck, *Physik. Z.*, **11** (1910), 1228-33; Abstract, *Metallurgical and Chemical Engineering*, **9** (1911), 73-5.

ADDITIONAL MATERIAL AND COMMENT

The galley proof of the above article was sent to thirty different libraries, firms and individuals for criticisms and suggestions of further material. The following items were obtained in this way:

F. C. Zeisberg and F. G. Liegenroth, of the E. I. du Pont de Nemours and Company state that the gases from the Birkeland-Eyde furnace are withdrawn at 1100° C. and contain about 1.25 per cent of NO. The concentration of NO in the product of the Schönherr furnace is only about 1.75 per cent and the yield is the same as for the Birkeland-Eyde. The temperature of the escaping gases is 1200° C. for the latter and 800 to 1000° C. for the former. Both of these furnaces, as well as the Pauling, take single-phase current. The Schönherr uses 5000 volts and the Birkeland-Eyde is now built to take as high as 4000 kw. The power factor of the last has been raised to 0.8 in recent developments.

The enrichment of air with oxygen as done in the Kilburn-Scott process is an old idea.

At Notodden the strength rarely rises above 30 per cent HNO₃ by weight in the acid delivered.

The total power in Norway (Rjukanfos and Notodden) used for fixation processes is 350,000 H.P. (250,000 kw.). The Tyn, Matre and Vamma developments will not be so employed for sometime, at least.

H. C. H. Tarr of R. D. Wood and Co. writes: "I feel quite certain that the combination of a by-product gas and steam plant will produce cheaper power than can be attained in any other way. I am preparing an article which will be published in one of the periodicals in the next two or three months, in which I shall go more into detail." This article will appear in the *Metallurgical and Chemical Engineering*. Mr. Tarr has already published in *Power* for November, 1908, comparative analyses of the costs of operating water-power and gas-power plants.

C. W. Andrews of the John Crerar Library supplied the following references to books:

Georg Brion, "Luftsälpeter. seine Gewinnung durch den elektrischen Flammenbogen." Berlin & Leipzig (G. J. Göschen, 1912, 153 pp.).

Theodor Pfeiffer, "Stickstoffsammelnde Bakterien, Brache und Raubbau." (Ed. 2, Berlin, P. Parey, 1912, 100 pp.)

Wilhelm Schneidewind, "Weitere Versuche über die Wirkung verschiedener Stickstoffformen aus den Jahren 1908-1911." (Berlin, Deutsch Landwirtschafts-Gesellschaft, 1912, 171 pp.)

The following books, some of which also were suggested by C. W. Andrews, belong to an earlier period than that covered by this paper, but may be of interest to those who wish to study the earlier phases of the subject:

Robert Huber, "Zur Stickstoff-Frage." (Bern, Stämpfli & Cie., 1908, 116 pp.)

Konrad Wilhelm Jurisch, "Salpeter und sein Ersatz." (Leipzig, Hirzel, 1908, 356 pp.)

Adolf Koenig, "Über die Oxydation des Stickstoffes im gekühlten hochspannungsbogen bei Minderdruck." (Halle, Knapp, 1908, 76 pp.)

This book consists of a brief review of the chemistry of nitrogen oxidation and a detailed report of the author's experiments.

Wilhelm Schneidewind, "Die Stickstoffquellen und die Stickstoffdüngung." (Berlin, P. Parey, 1908, 139 pp.)

P. Vageler, "Die Bindung des atmosphärischen Stickstoffs in Natur und Technik." (Braunschweig, Vieweg, 1908, 132 pp.)

The greater part of this book is devoted to the fixation of nitrogen by bacteria, only 19 pages being given to technical methods. A diagram of the arc chamber of the Bradley and Lovejoy process is shown.

Eduard Donath, "Die technische Ausnutzung des atmosphärischen Stickstoffes." (Leipzig & Wien, F. Deuticke, 1907, 250 pp.)

This book is a good detailed treatment particularly of the chemical aspects of the subject, with descriptions of apparatus and many references to the literature. The Bradley-Lovejoy process is described quite fully.

H. C. H. Tarr, "Über die Oxydation des Stickstoffes in der hochspannungsflamme." (Halle, Knapp, 1905, 63 pp.)

F. Lepel, "Die Bindung des atmosphärischen Stickstoffes, insbesondere durch elektrische Entladungen." (J. Abel Greifswald, 1903, 42 pp.)

NEW PUBLICATIONS

By IRVINS DeMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

Analysis: A System of Qualitative Chemical Analysis. J. A. GIBSON. 12mo. 44 pp. Price, \$0.45. Herald Statesman Publishing Co., Columbia, Mo.

Applied Chemistry. E. B. EMERY and OTHERS. 4to. 212 pp. Price \$1.20. Lyons & Carnahan, Chicago.

Applied Science: Les Sciences physiques et naturelles avec leurs applications à l'agriculture, à l'industrie, etc. I. DUBILET and F. RASÉ. 8vo. 288 pp. Price 1 fr. 50. Librairie Larousse, Paris.

Bauxite: L'industrie de la bauxite dans le département du Var. A. DE KEEFEN. 8vo. 22 pp. Châin, Paris.

Blast Furnace Construction in America. J. E. JOHNSON, JR. 8vo. 410 pp. Price \$4.00. McGraw-Hill Book Co., New York.

Briquetting: A Handbook of Briquetting. Vol. 1. The Briquetting of Coals, Brown Coals and Other Fuels. G. FRANKÉ. 8vo. 651 pp. Price \$9.00. J. B. Lippincott Co., Philadelphia.

Chemical Control in Cane Sugar Factories. H. C. P. GEERLIGS. 8vo. 168 pp. Price 10s. Norman Rodker, London.

Chemical Discovery and Invention in the Twentieth Century. W. A. THOMES. 8vo. 505 pp. Price 7s. 6d.

Chemical Mathematics: Traité de mathématiques générales à l'usage des chimistes, physiciens, ingénieurs, etc. E. FABRY. 8vo. 480 pp. Price 10fr. A. Hermann et fil., Paris.

Chemistry: Cours de chimie. P. BOUGAGUEL. 18mo. 231 pp. Garnier frères, Paris.

Chemistry: Laboratory Manual of General Chemistry. A. G. LAMB. 6to. Price 6s. Oxford University Press, London.

Chemical Directory: The First Annual Chemical Directory of the United States. Ed. by R. F. LEVENE. Williams & Wilkins Co., Baltimore.

Chemists' Yearbook for 1917. F. W. ATACK. 2 vols. 3rd Ed. Price 16s. 6d. Sherratt & Hughes, Manchester.

Chemistry for Photographers. W. R. BLUNT. 12mo. 265 pp. Price \$2.00. American Photographic Publishing Co., Boston.

Coal Mining Kinks. Compiled from COAL AGE. 8vo. 104 pp. Price \$1.50. Hill Publishing Co., New York.

Compressed Air Practice in Mining. DAVID PENMAN. 8vo. 253 pp. Price 5s. Charles Griffin & Co., London.

Electricity: Qu'est-ce que l'électricité? A. DESPAUX. 8vo. 216 pp. Price, 7fr. 50. H. Dunod et E. Pinat, Paris.

Engineering Analysis of a Mining Share. J. C. PICKERING. 8vo. 95 pp. Price \$1.50. McGraw-Hill Book Co., New York.

Engineering Data: The Pocket Diary and Year Book for 1917. A Collection of Useful Engineering Notes. 330 pp. Price, \$0.40. Norman Remington Co., Baltimore.

Engines: The Fitting and Erecting of Engines. C. L. BROWN. 8vo. 175 pp. Price, \$5.00. Emmott & Co., London.

English and Engineering. P. AYDLOTT. 16mo. 390 pp. Price, \$1.50. McGraw-Hill Book Co., New York.

Gasoline and How to Use It. G. A. BIRRELL. 281 pp. Price \$1.50. Oil Statistical Society, Boston.

German-English Dictionary for Chemists. A. M. PATTERSON. 11mo. 332 pp. Price, \$3.00. John Wiley & Sons, New York.

Glass: A Memoir of British Resources of Sands Suitable for Glass Making. G. H. BOWEN. 8vo. Price 1s. 6d. Longmans, Green & Co., London.

Manufacturing Costs and Accounts. A. H. CHURCH. 8vo. 48 pp. Price, \$5.00. McGraw-Hill Book Co., New York.

Mechanical Pocket Book and Diary for 1917. 11mo. 286 pp. Price 1s. 6d. Technical Publishing Co., Manchester.

Mécanique: Précis de mécanique théorique et pratique. F. GÉNOT. 8vo. 244 pp. J. de Gifford, Paris.

Microscopic Examination of Steel. CHAS. E. COOKE. 8 pp. Price \$1.00. John Wiley & Sons, New York.

Minerals: Tables for the Determination of the Common Minerals and Rocks. W. A. TAYLOR. 10mo. 110 pp. Price, \$0.50. Lithological Co., operators Stone, Columbia, Mo.

Operation of Gas Works. W. M. ROBERTS. 8vo. 108 pp. Price, \$5.00. McGraw-Hill Book Co., New York.

Ore: A Study of the Magnesian Sulfid Ore. A. J. THOMAS. 16mo. 100 pp. Price, \$0.60. Ireland, Stanford, E. London.

Organic Chemistry: Leçons de chimie. F. C. SCHUBERT. 10mo. 250 pp. Price, 10fr. 50. G. Masson, Paris.

Organic Chemistry: A Text Book of Organic Chemistry. J. A. Mc. CORMACK. 8vo. Price 5s. 6d. Macmillan Co., London.

Paraffin: The Vaporizing of Paraffin for High Speed Motors. CHAS. BURNETT. 16mo. 20 pp. Price 6s. 6d. J. B. Lippincott Co., Philadelphia.

Refining Industry in the United States. OIL AND GAS JOURNAL. Price, \$5.00. Oil and Gas Journal, Tulsa, Okla.

Saws: Their Care and Treatment. H. W. PITCHAM. 8vo. 7 pp. Price 6s. Wm. Rodker & Son, London.

Steam-Boilers: Their Theory and Design. H. B. BOSWORTH. 4th Ed. 8vo. 377 pp. Price, \$4.00. Longmans, Green & Co., New York.

Ventilation: Some Modern Methods of Ventilation. R. GIBBSON. 8vo. 262 pp. Price 8s. 6d. Archibald Constable & Co., London.

Welding: A Practical Manual of Autogenous Welding. R. ROSEBERRY and R. ROSEBERRY. 8vo. 27 pp. Price 5s. Charles Griffin & Co., London.

Wiring: Standard Wiring for Electric Light and Power. H. C. CUSHING. 7e. 16mo. 360 pp. Price 8s. 6d. The Architectural Press, New York City.

NEW JOURNALS

Abstracts of Bacteriology. Published under the Direction of the SOCIETY OF AMERICAN BACTERIOLOGISTS. Bi-monthly. Price, \$5.00. Williams & Wilkins Co., Baltimore.

The Journal of Dairy Industry. Edited by J. H. FRANKEN. Bi-monthly. Price \$5.00. Williams & Wilkins Co., Baltimore.

The Journal of Urology. Edited by HUGH H. YOUNG. Bi-monthly. Price, \$5.00. Williams & Wilkins Co., Baltimore.

RECENT JOURNAL ARTICLES

Air Drying. CARL HERING. *Mechanical and Chemical Engineering*, Vol. 16 (1917), No. 4, pp. 187-190.

Alloys: A Bibliography of Alloys: Binary, Ternary and Quaternary Systems: CHAS. E. LESTER. *Mechanical and Chemical Engineering*, Vol. 16 (1917), No. 5, pp. 273-282.

Amino Acids: Sur quelques dérivés des amino-acides. J. T. BORNWATER. *Revue de travaux chimiques de France et de la Belgique*, Vol. 36 (1917), No. 5, pp. 281-284.

Analysis of Light Oils. GUSTAV FELDER. *Mechanical and Chemical Engineering*, Vol. 16 (1917), No. 5, pp. 259-263.

Atom: Structure of the Atom. SAUL DUSHMAN. *General Electric Review*, Vol. 20 (1917), No. 3, pp. 186-196.

Bleached Groundwood. OTTO SCHUTZ. *Paper*, Vol. 19 (1917), No. 1, pp. 64-66.

Brick Sewers. J. F. SPRINGER. *Municipal Engineering*, Vol. 52 (1917), No. 2, pp. 47-52.

Carbonization of Kelp for the Recovery of Potash. J. W. TIMMONS. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 4, pp. 196-199.

Cleaning the Blast Furnace Gas. L. BRADLEY and OTHERS. *The Iron Trade Journal*, Vol. 60 (1917), No. 5, pp. 47-50.

Concrete: The Progress of Reinforced Concrete. F. D. ARNOLD. *The Engineering Record*, Vol. 30 (1917), No. 6, pp. 108-110.

Dry Concentration of Gold Ore. LEONARD GOUDAY. *Engineering and Mining Journal*, Vol. 103 (1917), No. 7, pp. 305-306.

Fertilizers: Permanent Soil Fertility. W. F. HANCOCK. *The American Fertilizer*, Vol. 46 (1917), No. 5, pp. 21-25.

Flotation, Past and Present. N. C. BONNEY. *Mining American*, Vol. 74 (1917), No. 18, pp. 8-9.

Flotation's Remarkable Advance in 1916. *The Mining and Metallurgical Engineer*, Vol. 46 (1917), No. 1, pp. 1-11.

Germany's Manganese Supply. *Manganese*, Vol. 13 (1917), No. 3, pp. 4-6.

Graphite Deposits in Burnet and Llano Counties, Texas. W. B. PHILLIPS. *Manufacturing Record*, Vol. 71 (1917), No. 5, pp. 1-4.

Grinding Wheels and Grinding Machines. C. W. HARRIS. *The Engineering Record*, Vol. 32 (1917), No. 1, pp. 10-11.

Hydrocarbons: Sur les points de fusion de quelques hydrocarbures. A. J. LANGE. *Revue de travaux chimiques de France et de la Belgique*, Vol. 36 (1917), No. 5, pp. 285-288.

Hydroelectric Power and Electrochemistry. *Electrochimica Acta*, Vol. 16 (1917), No. 1, pp. 1-11.

Manganese: On the Estimation of Manganese in Hard Steels. *Steel*, Vol. 14 (1917), No. 1, pp. 1-11.

Manganese Significance in Steel Making. *Steel*, Vol. 14 (1917), No. 1, pp. 1-11.

Magnets: The Origin and Growth of Magnets. *Magnetics*, Vol. 14 (1917), No. 1, pp. 1-11.

Magnetic Properties of Sheet Steel. *Magnetics*, Vol. 14 (1917), No. 1, pp. 1-11.

Metal Spraying with Oil Acetylene. *Metal Spraying*, Vol. 14 (1917), No. 1, pp. 1-11.

Metallurgical Problems of the Heat. *Metallurgical Engineering*, Vol. 14 (1917), No. 1, pp. 1-11.

Metric System: The Adoption of the Metric System in the United States. *Metric System*, Vol. 14 (1917), No. 1, pp. 1-11.

Mill and Smelter Construction. *Mill and Smelter Construction*, Vol. 14 (1917), No. 1, pp. 1-11.

MARKET REPORT—MARCH, 1917

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON MARCH 15

INORGANIC CHEMICALS

Acetate of Lime	100 Lbs.	3.25	@	3.50
Alum, lump ammonia	100 Lbs.	4.00	@	4.25
Aluminum Sulfate, high-grade	Ton	65.00	@	70.00
Ammonium Carbonate, domestic	Lb.	10	@	10 1/2
Ammonium Chloride, white	Lb.	18	@	18 1/2
Aqua Ammonia, 26°, drums	Lb.	5 1/2	@	6
Arsenic, white	Lb.	14	@	15
Barium Chloride	Ton	90.00	@	92.00
Barium Nitrate	Lb.	11	@	11 1/4
Barytes, prime white, foreign	Ton	35.00	@	40.00
Bleaching Powder, 35 per cent.	100 Lbs.	3.50	@	3 7/8
Blue Vitriol	Lb.	9 1/4	@	9 1/2
Borax, crystals, in bags	Lb.	7 1/4	@	7 1/2
Boric Acid, powdered crystals	Lb.	12 1/2	@	12 3/4
Brimstone, crude, domestic	Long Ton	45.00		
Bromine, technical, bulk	Lb.	1.30	@	1.40
Calcium Chloride, lump, 70 to 75% fused	Lb.	23.00	@	24.00
Caustic Soda, 76 per cent.	Lb.	4.40	@	4.50
Chalk, light precipitated	Lb.	4 1/4	@	4 1/2
China Clay, imported	Ton	18.00	@	30.00
Feldspar	Ton	8.00	@	15.00
Fuller's Earth, foreign, powdered	Ton	35.00		
Glauber's Salt, in bbls.	100 Lbs.	65	@	70
Green Vitriol, bulk	100 Lbs.	1.15	@	1.20
Hydrochloric Acid, commercial, 18°	Lb.	1 1/4	@	1 1/2
Hydrochloric Acid, C. P., conc. 22°	Lb.	1 1/4	@	1 1/2
Iodine, resublimed	Lb.	3.50	@	3.55
Lead Acetate, white crystals	Lb.	14	@	14 1/2
Lead Nitrate	Lb.	15 1/2	@	15 3/4
Litharge, American	Lb.	8 1/4	@	9 1/2
Lithium Carbonate	Lb.	1.02	@	1.05
Magnesium Carbonate, U. S. P.	Lb.	24	@	26
Magnesite, "Calced" "	Ton	67.50	@	70.00
Nitric Acid, 36°	Lb.	5 1/2	@	5 1/2
Nitric Acid 42°	Lb.	6 1/4	@	6 1/2
Phosphoric Acid, sp. gr. 1.750	Lb.	30	@	32
Phosphorus yellow	Lb.	80	@	90
Plaster of Paris	Bbl.	1.50	@	1.70
Potassium Bichromate, casks	Lb.	37	@	38
Potassium Bromide (granular)	100 Lbs.	1.00	@	1.05
Potassium Carbonate, calcined, 88 @ 92%	Lb.	45	@	75
Potassium Chlorate, crystals, spot	Lb.	61	@	62
Potassium Cyanide, bulk, 98-99 per cent.	Mixture	1.50	@	1.60
Potassium Hydroxide, 88 @ 92%	Lb.	86	@	88
Potassium Iodide, bulk	Lb.	2.90		
Potassium Nitrate	Lb.	30	@	32
Potassium Permanganate, bulk	Lb.	3.80	@	4.00
Quicksilver, flask	75 lbs	115.00	@	120.00
Red Lead, American, dry	Lb.	10 1/2	@	10 1/2
Salt Cake, glass makers	Ton	18.00	@	20.00
Silver Nitrate	Oz.	45 1/2		
Soapstone in bags	Ton	8.00	@	12.00
Soda Ash, 58%	100 Lbs.	3.10	@	3.15
Sodium Acetate	Lb.	9	@	9 1/2
Sodium Bicarbonate, domestic	100 Lbs.	1.95	@	2.05
Sodium Bichromate	Lb.	16	@	16 1/2
Sodium Chlorate	Lb.	24	@	25
Sodium Fluoride, commercial	Lb.	—	@	—
Sodium Hyposulfite	100 Lbs.	1.75	@	1.85
Sodium Nitrate, 95 per cent, spot	100 Lbs.	3.72 1/2	@	3.75
Sodium Silicate, liquid, 40° Bé.	100 Lbs.	1.05	@	1.25
Sodium Sulfide, 30%, crystals, in bbls.	Lb.	2 1/2	@	2 1/2
Sodium Bisulfide, liquid, 32 a. g.	Lb.	.01 1/4	@	.01 1/2
Strontium Nitrate	Lb.	28	@	30
Sulfur, flowers, sublimed	100 Lbs.	2.35	@	2.75
Sulfur, roll	100 Lbs.	2.20	@	2.25
Sulfuric Acid, chamber, 66° Bé.	Ton	29.00	@	30.00
Sulfuric Acid, oleum (fuming)	Ton	38.00	@	40.00
Talc, American white	Ton	10.00	@	11.00
Terra Alba, American, No. 1	100 Lbs.	85	@	90
Tin Bichloride, 50°	100 Lbs.	13.50		
Tin Oxide	Lb.	56	@	58
White Lead, American, dry	Lb.	9 1/4	@	9 1/2
Zinc Carbonate	Lb.	24	@	26
Zinc Chloride, commercial	Lb.	15	@	15 1/2
Zinc Oxide, American process XX	Lb.	12 1/4	@	12 1/2
Zinc Sulfate	Lb.	6 1/4	@	6 1/2

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.	Lb.	45	@	50
Acetic Acid, 56 per cent, in bbls.	Lb.	7 1/2	@	8
Acetic Acid, glacial, 99 1/2% in carboys	Lb.	24	@	26
Acetone, drums	Lb.	22	@	23

Alcohol, denatured, 180 proof	Gal.	66	@	67
Alcohol, grain, 188 proof	Gal.	2.78	@	2.80
Alcohol, wood, 95 per cent, refined	Gal.	1.05	@	1.07
Amyl Acetate	Gal.	3.50	@	4.00
Aniline Oil	Lb.	27 1/2	@	28
Benzoic Acid, ex-toluol	Lb.	8.00	@	8.50
Benzol, 90 per cent	Gal.	59	@	60
Camphor, refined in bulk, bbls.	Lb.	90	@	90 1/2
Carbolic Acid, U. S. P., crystals, drums	Lb.	43	@	45
Carbon Bisulfide	Lb.	5 1/2	@	6 1/4
Carbon Tetrachloride, drums, 100 gals.	Lb.	15 1/2	@	16
Chloroform	Lb.	60	@	61
Citric Acid, domestic, crystals	Lb.	72	@	75
Cresosote, beechwood	Lb.	1.75	@	2.00
Cresol, U. S. P.	Gal.	1.25	@	1.30
Dextrine, corn (carlows, bags)	100 Lbs.	3.45	@	3.50
Dextrine, imported potato	Lb.	12 1/4	@	13
Ether, U. S. P., 1900	Lb.	15	@	20
Formaldehyde, 40 per cent.	Lb.	13	@	13 1/2
Glycerine, dynamite, drums included	Lb.	54 1/2	@	55
Oxalic Acid, in casks	Lb.	45	@	46
Pyrogallie Acid, resublimed bulk	Lb.	3.25		
Salicylic Acid	Lb.	80	@	90
Starch, cassava	Lb.	—		
Starch, corn (carlows, bags) pearl	100 Lbs.	2.45	@	2.50
Starch, potato	Lb.	12 1/2	@	12 3/4
Starch, rice	Lb.	8	@	8 1/2
Flour, sago	Lb.	4 1/4	@	5
Starch, wheat	Lb.	5	@	6
Tannic Acid, commercial	Lb.	65	@	70
Tartaric Acid, crystals	Lb.	85	@	86

OILS, WAXES, ETC.

Beeswax, pure, white	Lb.	52	@	54
Black Mineral Oil, 29 gravity	Gal.	13 1/2	@	14
Castor Oil, No. 3	Lb.	19 1/4	@	20
Ceresein, yellow	Lb.	14	@	18
Corn Oil, crude	100 Lbs.	12.25	@	12.50
Cottonseed Oil, crude, f. o. b. mill	Gal.	89	@	89 1/2
Cottonseed Oil, f. o. b. y.	Lb.	13 1/2	@	14
Menhaden Oil, crude (southern)	Gal.	nominal		
Neat's-foot Oil, 218°	Gal.	1.20	@	1.30
Paraffine, crude, 110 to 120 m. p.	Lb.	6 1/2	@	6 1/2
Paraffine Oil, high viscosity	Gal.	29 1/4	@	30
Rosin, "F" Grade, 280 lbs.	Bbl.	6.15	@	6.25
Rosin Oil, first run	Gal.	37		
Shellac, T. N.	Lb.	52	@	53
Spermacein, cake	Lb.	24	@	25
Sperm Oil, bleached winter, 38°	Gal.	24	@	25
Spindle Oil, No. 200	Gal.	15 1/2	@	16
Stearic Acid, double-pressed	Lb.	1.04	@	1.05
Tallow, acidless	Gal.	30	@	32
Tar Oil, distilled	Gal.	52		
Turpentine, spirits of	Gal.	52		

METALS

Aluminum, No. 1, ingots	Lb.	57	@	59
Antimony, ordinary	Lb.	32	@	33
Bismuth, N. Y.	Lb.	3.05	@	3.10
Copper, electrolytic	Lb.	36		
Copper, lake	Lb.	36		
Lead, N. Y.	100 Lbs.	9.75		
Nickel, electrolytic	Lb.	50	@	53
Platinum, refined, soft	Oz.	105.00		
Silver	Oz.	73		
Tin	Lb.	53 1/2		
Tungsten (W.O.)	Per Unit	17.00	@	17.50
Zinc, N. Y.	100 Lbs.	10.00		

FERTILIZER MATERIALS

Ammonium Sulfate	100 Lbs.	5.25	@	5.50
Blood, dried f. o. b. Chicago	Unit	4.30		
Bone, 4 and 50, ground, raw	Ton	32.00	@	33.00
Calcium Cyanamid	Unit of Ammonia	3.25		
Calcium Nitrate, Norwegian	100 Lbs.	—		
Castor Meal	Unit	—		
Fish Scrap, domestic, dried, f. o. b. works	Unit	nominal		
Phosphate, acid, 16 per cent.	Ton	11.50	@	11.75
Phosphate rock, f. o. b. mine:				
Florida land pebble, 68 per cent.	Ton	2.00	@	2.10
Tennessee, 78-80 per cent.	Ton	5.00	@	5.50
Potassium "muriate", basis 80 per cent.	Ton	415.00	@	425.00
Pyrites, furnace size, imported	Unit	nominal		
Tankage, high-grade, f. o. b. Chicago	Unit	4.25	@	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

AT EASTON, PA.

Volume IX

MAY 1, 1917

No. 5

Editor: CHARLES H. HERTY

Assistant Editor: LEOLA E. MARRS

Advertising Manager: M. A. WILLIAMSON

ADVISORY BOARD

H. E. BARNARD, H. K. BENSON, F. K. CAMERON, B. C. HESSE, A. D. LITTLE, A. V. H. MORY, M. C. WHITAKER

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly; single copy, 60 cents. Price per single copy to American Chemical Society members, 50 cents. Foreign postage, seventy-five cents. Canada, Cuba and Mexico excepted. Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

All communications should be sent to The Journal of Industrial and Engineering Chemistry,

Telephone: Vanderbilt 1930

35 East 41st Street, New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

Spring Meeting American Chemical Society	442
An Appeal to the Wives and Daughters of Chemists	445
Legislation for Electrochemical Industries at Niagara	446
The Bootstrap Method Revived	447
The Ubiquitous Exception	447
Another Phase of Coöperation	448
The Greatest Chemical Library in the World	448

JAPAN STARTS ITS DYESTUFF INDUSTRY

449

ORIGINAL PAPERS

The Incomplete Hydrogenation of Cottonseed Oil. Hugh K. Moore, G. A. Richter and W. B. Van Arsdale	451
The Chemical Composition of the Higher Fractions of Maplewood Creosote. Ernest J. Pieper, S. F. Acree and C. J. Humphrey	462
Preparation of Black Oxide of Uranium (UO ₂). Charles L. Parsons	466
The Extraction of Potash from Silicate Rocks—II. William H. Ross	467
Potash from Incinerator Ash of the Northwest. Curtis W. Thing	472
Aromatic Hydrocarbons from the Thermal Decomposition of Natural Gas Condensate. J. E. Zanetti and G. Egloff	474
The Detection and Determination of Sulfur in Petroleum. C. K. Francis and C. W. Crawford	479
The Theory of Ore Flotation. H. P. Corliss and C. L. Perkins	481
Notes on the Analysis of Cast Nichrome. E. W. Reed	488
A Simplified Inversion Process for the Determination of Sucrose by Double Polarization. Herbert S. Walker	490
The Chemical Changes Which Are Caused by Dehydration of Sorghum Juice for Syrup Manufacture. Arthur K. Anderson	497
The Correction Required in Applying the Babcock Formula to the Estimation of Total Solids in Evaporated Milk. O. L. Evenson	499

Improvements in the Copper Method for Estimating Amino Acids. Philip Adolph Kober	501
A Study of the Determination of Potash Chiefly Concerned with the Lindo-Gladding Method. P. L. Hibbard	504
The Fertilizer Value of City Wastes. P. J. Schroeder	513
The Identification of Emodin-Bearing Drugs. W. S. Hubbard	518
The Determination of Alcohol and Water in Ether for Anaesthesia. R. L. Perkins	521

LABORATORY AND PLANT

The Measurement of the Absolute Viscosity of Very Viscous Media. S. E. Sheppard	523
A Simple Device for the Automatic and Intermittent Washing of Precipitates. Albert C. Lathrop	527
An Improved Compensator for Gas Analysis. E. T. Gregg	528

ADDRESSES

One Billion Gallons of Synthetic Gasoline in 1918. Walter F. Rittman	529
--	-----

CURRENT INDUSTRIAL NEWS

Best Sulfur Industry. New Method of Extracting Vaporous Constituents from Coal Gas; Italian Chemical Industry; Molybdenum; Barium-Radium Carbonates. Status of Potassium Fertilizers. Developing Water Power to Aid Industries. To Promote Cloot Trade Relations with Russia	530
--	-----

SCIENTIFIC SOCIETIES

Fifty Fourth Meeting American Chemical Society. Kansas City, Missouri, April 30 to May 4, 1917. Opening Meeting. Second Annual Technical Conference. Indiana, Washington, D. C., May 6, 1917	531
--	-----

PERSONAL NOTES

Industrial Notes	532
------------------	-----

GOVERNMENT PUBLICATIONS

New Publications	533
------------------	-----

MARKET PRICES

Market Prices	534
---------------	-----

EDITORIALS

SPRING MEETING AMERICAN CHEMICAL SOCIETY

In a spirit of deep gravity and earnestness of purpose, clearly reflective of the new era into which this nation has been ushered by the declaration of a state of war with the German Empire, the Fifty-fourth Meeting of the American Chemical Society was held at Kansas City, Missouri, from April 10th to 14th, 1917, with an attendance of 382 registered members and guests.

On the evening of April 10th a complimentary dinner was tendered the members of the Council by the Kansas City Section in the rooms of the Kansas City University Club. During the meeting of the Council, held at the Hotel Muehlebach immediately following the dinner, President Stieglitz summarized the reports of the various committees, following which many points of importance in connection with the policies of the Society were discussed, a number of these being embodied in definite legislation.

The Committee on Foreign Commerce in Chemicals was discontinued and the President authorized to appoint a committee to cooperate with the Bureau of Foreign and Domestic Commerce in compiling detailed statistics of chemical imports other than dyestuffs provided adequate funds are obtained from the chemical industries by the committee previously appointed for that purpose.

The Council voted that the Society should become a member of the American Metric Association, and recommended to the directors an appropriation of funds for membership dues.

The Committee on Government Specifications of Food and Toilet Articles reported that no scheme of certification or guaranteeing of food products is practicable, but recommended that the Society use its influence in urging more effective legislation in order to bring about better organization for enforcement of existing national and state legislation.

As a result of the recommendations embraced in the report of the special committee on Analyzed Reagents, the following resolutions were passed:

Resolved, That in pursuance of a recommendation of the Committee on "Analyzed Reagents," the President of the Society be instructed to appoint a committee of three to act in an advisory capacity with the Bureau of Standards and the manufacturers of analyzed reagents, in accordance with the duties assigned to the proposed advisory committee in the report of the Committee on "Analyzed Reagents."

Resolved further, That the first duty of this Committee shall be to address the Secretary of Commerce on behalf of the American Chemical Society in a letter signed by the President, urging upon him the very great desirability of obtaining at the earliest possible moment a fund to enable the Bureau of Standards to test reagents in conformity with the plans recommended by the Committee on "Analyzed Reagents."

New local sections were authorized as follows: Southeastern Texas Section, Central Texas Section, Toledo Section and Michigan Agricultural College Section.

Invitations for the 1918 Fall Meeting were received from the Cleveland Section and from the Philadelphia

Section. These invitations were placed on file until the Boston Meeting in September.

The proposed formation of a Division of Metallurgy was not deemed wise at this time, but the Division of Industrial Chemists and Chemical Engineers was requested to arrange for special symposiums in metallurgy, from the results of which it can be determined whether the demand for a separate division on this subject is sufficient to authorize its organization.

The President and Secretary were authorized to take up with the authorities in Washington the question of the advisability of the adoption of some military unit by the Society.

The matter of amendment of the constitution to create a Board of Control of the National Policies of the American Chemical Society, along the lines suggested by Dr. B. C. Hesse in his article, "The American Chemical Society and the Nation," in the April issue of *THIS JOURNAL*, was referred to a committee for consideration and for recommendation to the members of the Society. Pending the completion of this legislation a committee consisting of the President, the Secretary, the two most recent Past Presidents, and two Councilors-at-Large (to be elected by the Council) was authorized to act with the full power of the Council on all matters of national import until the September Meeting of the Society. On ballot of the Council, Drs. B. C. Hesse and W. D. Bigelow were elected the councilors-at-large to serve on this committee. The committee therefore consists of: Julius Stieglitz, Charles L. Parsons, T. W. Richards, Chas. H. Herty, B. C. Hesse, W. D. Bigelow. In connection with this matter the following resolution was unanimously passed:

Be it Resolved, That it is the sense of the Council of the American Chemical Society that local sections and divisions have no authority to publish or issue any resolution or official action on matters of national import. That this resolution shall not be interpreted to discourage the discussion of such matters but that any action taken as the result of such discussion shall be reported to the President and Secretary for submission to the Council or Advisory Committee.

On Wednesday morning the General Meeting of the Society was held. The general session was opened by a brief address of welcome by Prof. W. A. Whitaker of the University of Kansas, chairman of the local executive committee. In the absence of Mayor Edwards, the address of welcome, in behalf of Kansas City, was given by Mr. George H. Edwards, Jr. This was followed by a stirring address by President Frank Strong of the University of Kansas. President Strong expressed the opinion that the war would last at least two and possibly four years longer, and that a period of from ten to twelve years must then elapse before universities would again return to normal conditions. He also expressed the conviction that just as at present federal control of armies, food, etc., is necessary, so, after the war, there will probably be great changes in our public policies, including the practical elimina-



AMERICAN CHEMICAL SOCIETY BANQUET AT THE MUEHLBACH HOTEL, KANSAS CITY, APRIL 12TH

tion of party politics and the accentuation of federal administrative powers. In the hands of democracy, he predicted that this would lead to the most efficient of all governments in history.

In response to these addresses of welcome, President Stieglitz expressed the thanks and appreciation of the Society and spoke as follows:

ADDRESS AT OPENING SESSION

KANSAS CITY MEETING, AMERICAN CHEMICAL SOCIETY

By PRESIDENT JULIUS STIEGLITZ

MR. EDWARDS CHANCELLOR STRONG, DR. WHITAKER:

On behalf of the American Chemical Society, I gratefully accept your courteous and hospitable welcome to this thriving city, and to your famous State University. We shall carry away with us grateful memories of our stay and experiences here, instructive impressions of a wonderfully active and growing section of our country, happy recollections of the entertainments your local committee have been at great efforts to provide for us. We appreciate this hearty welcome none the less because we have come more serious in thought and more conscious of momentous duties than we anticipated when the plans were made to hold our Spring Meeting here. We thought of coming simply to have our minds broadened by listening to lectures, reports and the conversation of our fellow-chemists, to enjoy the hospitality of a part of the country famous for its welcome to its guests, to learn from, and wonder at, the thriving industries of Kansas City, to inspect one of our State Universities which is developing the cult of the sciences, and especially of chemistry, with amazing speed. We expected to come to have a good time, intellectually and socially. None of us dreamed that we should meet, carrying the burden of a tremendous responsibility, shared with our millions of fellow citizens and overshadowing everything else in our every thought.

It is fitting, fellow-chemists, that we, meeting in Convention, should take counsel in regard to our share in this mighty problem. Uppermost in your minds, as in my own, must be this

question: What can we do collectively and individually to help our country in this her hour of need of the help of her every son?

Collectively, we can express once more our supreme devotion to her cause, we can express our satisfaction that we have set ourselves sternly to the task of safeguarding, we hope for all time, the ideals of our country, the insuring of life, liberty and the pursuit of happiness to one and all. But as chemists, as scientists, I believe the greatest service we can at this moment render in our collective capacity is to emphasize with all the weight of our influence that our preparation for war, for defense, as well as for attack, be a *thoroughly scientific preparation*—scientific in such military branches as ordnance, munitions, aviation, range-finding; scientific in the preparation of the bodies and minds of our brave soldiers for the great task before them; scientific from the outset in our provisions to protect them against disease, which in the Spanish War took a far greater toll than all our fighting did! We must be prepared to cure them of their inevitable wounds, to reach the standard set abroad of restoring ninety per cent of the wounded to health! Where so many are preparing for the material side of war, let us throw the weight of our influence in insisting that scientific preparation be not neglected in a single respect. Let us warn the country too—the authorities in Washington already realize this—that there shall be no needless waste of our scientifically trained young men, trained in chemistry, in physics and in medicine. Here is where the temptation to err at the outset is greatest. England learned the lesson at a heavy cost and fortunately our authorities have been warned. These young men, chemists in the industrial laboratories, scientific students in our universities and colleges, have trained brains and hands which are needed to multiply the output of our factories, needed to multiply the working power of our matured scientists, to develop into original investigators themselves. Nations are being called upon to solve in one year the problems of ten or twenty years. In no other way could England and France have gained their present superiority in game in aviation, in all the munitions of warfare, in the wonderfully short time of two years, against a country which had been the

paring for war intensely for many years. This increased speed in output of scientific results, can only be attained by multiplication of the minds devoted to the scientific problems involved. Let me add, too, that the scientists' rôle is not without its hazard. The British medical corps has lost proportionately more men than any other branch of the service excepting the infantry alone! That is the price paid in the succor of the wounded. Chemistry is not quite as hazardous as medicine, but the frequent reports of loss of life by explosions, the articles in medical journals recording the loss of life and health through the injurious action of the chemicals used in munition plants, reports of the disease-breeding conditions in the localities where munition plants have sprung up like mushrooms, show that our science also has its risks. And, furthermore, chemistry is at all times a hazardous occupation, as is proved by the fact that we must pay increased premiums on accident policies. But above all, in urging that the scientific men be assigned to scientific service and that the young chemists, physicists and medical students be reserved for scientific work we have in mind above all else the fact that *we are in this war to win*, to establish once and for all the principle of democracy, to live and let live, against the most powerful military nation in the world. To succeed we must put every man where he is most useful and where he gives his best service.

Many thoughtful observers believe the war may last two to four years longer! There is now a shortage of chemists, as a result of the great industrial expansion of the last two years. We must keep the sources of supply carefully guarded and active if we wish to prepare for any eventuality—our "crops" of science men are almost as valuable as our food crops.

And now pertaining to the question, what we can do as individuals, each anxious to assist our government, let me say that it seems to me that our first duty is to carry out our present duties with all the power and strength we have. We must accelerate in the steel plants the production of steel and iron of every kind, we must accelerate in the food plants the production of food to the highest point of speed possible, we must assist as chemists to make the soil as productive as possible, we must multiply the units for the production of explosives, we must keep up the sources of supplies of young trained chemists, physicists and medical men. Our further duty, as I see it, is to put our individual affairs into such shape that if a special call for service comes, we can respond with the least possible delay. And then, like the units of a great army, we must wait for orders!

When the first alarm sounded early in February, your executive officers, as the result of a suggestion of Dr. Baekeland, took immediate steps to obtain the cooperation of the Government in preparing an exhaustive census of American chemists. The Society owes to its Secretary, Dr. Parsons, a special vote of thanks for the great skill and speed with which this project has been put into effect. I would also suggest here that in each local section, chemists notify the secretary of the section or the government chemists in the section, whether they can spare any men for days of emergency work. The Government laboratories occasionally are overwhelmed for short periods of time. Here again the students in chemistry can be of greatest service.

And finally, let me assure you that in the completion of this census, the central organization for the working out of problems, for the calling of special men for special service is in splendid shape. We have Doctors Baekeland and Whitney representing the Society on the Naval Defense Board, we have Dr. A. A. Noyes, Dr. T. W. Richards, Dr. Bogert and others on the National Research Council, which is working in closest cooperation with the National Defense Council in Washington. Dr. Bogert is Chairman of the Committee on Chemistry in the National Research Council and this Committee is fully organized so as to take up any problem without loss of time. Prof. Millikan,

one of my colleagues at the University of Chicago, is in Washington, as Director of Research to organize investigations on some of the most important problems before the Government. The Bureau of Mines is becoming a great research laboratory of the Government on war problems and Dr. Parsons, your Secretary, is organizing the work. The National Defense Council is in heartiest sympathy with the men in control of the lines of scientific effort, which have just been described.

Your President is in frequent communication with most of these leaders in Washington and New York.

Let me summarize my remarks by urging you to recognize that the routine work of the chemists is in itself essential for the country, that the research work on special problems has been organized and is being organized as effectively as possible, and that we, the rank and file of the Society, must await marching orders as patiently as we can.

In conclusion, I wish to present now resolutions drawn up by your Council, bearing on the questions touched upon.

"Resolved, That we reaffirm the tender to the President of the United States of the services of the members of our Society in all fields in which we are qualified to act."

"Resolved, That the security and welfare of the country demand the organization of all men and facilities of the United States so as to insure the greatest possible service and value from each. The progress of the war thus far principally teaches us that modern warfare makes extraordinary demands upon science, food supply and finance. For the protection and success of our men under arms, we recommend the use, in their respective fields, of all trained chemists, physicists and medical men, including advanced students of these subjects. To this end, in collaboration with the United States Bureau of Mines, we are preparing a census of chemists. With no desire to avoid field service for men of training in the professions named, we urge that those of ability be held to the work they can best perform. Thus we may avoid unnecessary loss from lack of control of the tools and requirements of war."

In explanation of the next resolution, I need hardly remind you as chemists of the supreme value of platinum for chemical and industrial purposes. It has seemed best to protect the supplies of this precious metal for scientific purposes, by sending out the following appeal to our citizens.

"Resolved, That the attention of the National Council of Defense be called to the scarcity of platinum under existing conditions and to the great need of the metal, more particularly in the prosecution of the war. We hold that its use at this time in the production of articles of ornament is contrary to public welfare. Therefore we recommend that an appeal be made to the women of the United States to discourage the use of platinum in jewelry and that all citizens be urged to avoid its use for jewelry, for photographic paper and for any other purpose whatever, save in scientific research and in the making of articles for industrial needs."

At the conclusion of the President's address, the above resolutions were, on motion, unanimously passed.

Following the business session, Mr. Arthur J. Boynton presented a paper on the economic resources of the Kansas City zone. He depicted the rapid growth of Kansas City in population and wealth, pointing out the fact that it is the natural gateway of the great Southwest. He emphasized the great resources in agriculture and live stock of the territory tributary to Kansas City, calling especial attention to the fact that the extensive farming previously so characteristic of this section is being replaced by the intensive system and consequently calls for increased use of artificial

fertilizers. Kansas City is in the heart of the corn belt and of the grass section. Natural gas and crude oil constitute a great source of wealth, the oil being rich in kerosene and gasoline. He further called attention to the large zinc industry, especially as typified in the Joplin, Missouri, region, the abundance of coal, extensive Portland cement manufacture, glass factories, deposits of gypsum, salt, etc. Kansas City has remarkable railroad facilities and its freight tariffs are based on Missouri River rates.

On Wednesday afternoon there was held an interesting and largely attended symposium on the subject of "Petroleum and Natural Gas," under the chairmanship of Dr. H. P. Cady. In the evening a complimentary smoker was tendered, at which the members were entertained by an interesting program presented by local talent and by the students of the University of Kansas and the University of Missouri.

On Thursday divisional meetings were held. In the Division of Industrial Chemists and Chemical Engineers interest centered in the symposium on the "Chemistry and Metallurgy of Zinc," presided over by Dr. John Johnston. The divisional meetings were continued in the afternoon until 4.30, at which time an automobile trip was taken over the famous boulevard system of Kansas City. This remarkable civic development of a young western city, embracing a system of more than seventy miles of city boulevards, proved an eye-opener to all and was especially instructive in the methods of its financing and in its effect on the upbuilding of the city.

In the evening the annual subscription banquet was given in the Hotel Muehlebach. Many novel and delightful features characterized the menu and its service, while the after-dinner speeches varied markedly from the usual type and served to stir the patriotism of all present by their high appeal. This was especially true of the stirring address of Mr. J. H. Atwood of Kansas City, who received an ovation at its conclusion. Dr. Chas. H. Herty acted as toastmaster. The speakers and their subjects were as follows:

President Julius Stieglitz "The Chemist in the Role of National Defense."

Vice Chancellor W. L. Burdick, of the University of Kansas: "Patriotism."

Dr. E. W. Washburn, of the University of Illinois "What England's Chemists Have Done in the Service of Their Country during the European War."

Mr. J. H. Atwood: "America's Role in the Present Crisis."

Mr. Ellwood Hendrick "The Press and Publicity Work of the Society."

Col. Kealy, of the 3rd Mo. Regiment (now mobilized): "The Army."

On Friday morning the divisional programs were completed, and in the afternoon the members divided into groups for excursions. One group visited the plant of the National Zinc Company, at which the roasting of zinc blende and the manufacture of sulfuric, nitric and hydrochloric acids were inspected. Another excursion was to the Soap and Glycerine Works of the Peet Bros. Manufacturing Company. The plant of the Southwest Milling Company was of interest to those concerned with the manufacture of flour. The ex-

cursion to the Armour Packing Company attracted many who were unfamiliar with this great industry, while the Standard Oil Company's refinery at Sugar Creek, in addition to the usual methods of petroleum refining, gave opportunity for seeing in operation the Burton process for cracking petroleum.

Saturday was set apart by the University of Kansas at Lawrence, Kansas, for the inspection of its grounds and buildings.

A somewhat novel feature of the meeting was the attendance of a number of members of the Society at a luncheon given by the Engineers' Club at which a number of addresses were made emphasizing the necessity of close cooperation by engineers and chemists. At a luncheon with the City Club, an organization composed of the business men of Kansas City, stress was laid upon the rôle of the chemist in commercial development.

The visiting ladies were entertained by a committee of ladies of Kansas City and of the University of Kansas at an afternoon tea and a theatre party on Wednesday. They also participated in the automobile drive on Thursday.

A fine spirit was developed at the meeting, partly as a result of the wise provision of the local committees in arranging for all meetings to be held at the Hotel Muehlebach, which was headquarters for the meeting.

The thanks of the Society were expressed both formally by the Council and informally by the individual members for the generous and delightful hospitality shown throughout the meeting by the Local Section, the industrial plants and the University of Kansas.—[EDITOR.]

AN APPEAL TO THE WIVES AND DAUGHTERS OF CHEMISTS

"Can I not help you in some direct way in your work?" This question, asked by a feminine voice in all earnestness, is doubtless familiar in all families where chemistry constitutes the means of livelihood. The affirmative answer is now at hand—the woman and the opportunity are met.

Among the many substances made use of by the chemist, one of the most important is the element platinum. In the laboratory it is indispensable for many operations, particularly in the advancement of the science through the medium of chemical research; in the plant it is of fundamental importance in many processes, especially in the manufacture of sulfuric acid by the contact process. On the continued growth of the output of sulfuric acid the welfare of many other chemical industries directly depends. So too, in the modern method of making sulfuric acid by oxidation of ammonia, platinum is the all-important factor. These two acids, sulfuric and nitric, are the most reagents in the production of concentrated acid and in high explosives which are essential in modern warfare.

Unquestionably the properties of platinum together with its unusually high price have set it on a large scale in jewelry manufacture with increasing attention of the ancient available for chemical use. The

is not necessary as cheap alloys are now known which will answer every requirement of jewelry as to luster, hardness and durability.

Moreover, the chief sources of supply of this metal, Russia and Brazil, have severely restricted its output owing to the exigencies of the war in which both of these countries are now engaged.

The resolution contained in President Stieglitz's address, in this issue, points out clearly the necessity of conserving our present limited supply of platinum and of avoiding its use in jewelry.

The National Academy of Sciences has passed a resolution similar to that of the American Chemical Society, while the delegates to the convention of the Daughters of the American Revolution, held this week in Washington, D. C., pledged themselves by formal vote "to refuse to purchase or accept as gifts for the duration of the war, jewelry and other articles made in whole or part of platinum, so that all the available supplies of this precious metal shall be available for employment where they can do the greatest good in the service of our country."

Lend a strong hand to this important movement, wives and daughters of our chemists, in conversations with your friends, through club addresses, through your publications, and by public appeals wherever gatherings are held. You will thus aid directly those who are now charged with the additional responsibility of supplying the products essential for the defense of our country and the triumph of the noble ideals which led us into the World War!

LEGISLATION FOR ELECTROCHEMICAL INDUSTRIES AT NIAGARA

During the closing week of the last Congress, Senator Wadsworth of New York on three consecutive days, February 27, 28 and March 1, asked unanimous consent for consideration of his Joint Resolution (S. J. Res. 218) giving relief to the industries dependent on power derived from the Niagara River by extending the time of the extra withdrawal of 4400 cu. ft. of water per second (discussed in our February issue) from July 1, 1917, to July 1, 1918. On each occasion Senator Husting of Wisconsin objected. Further consideration of the matter was thus prevented.

On March 9th Senator Wadsworth wrote *THIS JOURNAL*: "As soon as the Congress convenes in extra session, I shall renew my efforts to have the permit for the diversion of the forty-four hundred cubic feet of water extended." The Senator has promptly carried out his determination in this matter, for, on April 4, 1917, among the very earliest joint resolutions introduced in the Senate during the present session was his Joint Resolution, S. J. Res. 13, as follows:

Resolved, etc., That public resolution No. 45 of the Sixty-fourth Congress, approved January 19, 1917, entitled a "Joint resolution authorizing the Secretary of War to issue temporary permits for additional diversions of water from the Niagara River" is continued in full force and effect, and under the same conditions, restrictions and limitations, until July 1, 1918.

This Joint Resolution was immediately referred to the Committee on Foreign Relations and was

favorably and without amendment reported back to the Senate by Senator Hitchcock on April 18, 1917, and immediately passed by the Senate. On the following day it was taken from the table of the Speaker of the House and referred to the Committee on Foreign Affairs. It is sincerely and confidently hoped that this Committee and the House of Representatives will act with the promptness and unanimity which characterized the Senate action on this important emergency legislation.

Whatever divergent views may exist as to the details of regulation or control of power development from the waters of the Niagara River, it should be remembered that the electrochemical industries are not concerned with power development except as purchasers of power from the power companies. On the other hand, these industries play a rôle of the very highest importance in the war program which is now being formulated by the President and the Congress. They do not constitute any experimental phase of the development of chemical industries, for already at Niagara Falls, through the brilliant achievements of its chemists and engineers, there exists the greatest electrochemical industry in the world. How closely the efficiency of our Army and Navy is dependent upon the maximum output of this industry cannot be more clearly stated than by an extract from a letter we have recently received.

Niagara power has a very close relation to "preparedness" and the best example perhaps is the dependency of the steel industry on ferro alloys. The steel industry would be quickly paralyzed if there should be any failure in the supply of ferro silicon, the major portion of which is produced at Niagara. The present situation on ferro silicon is very acute and steel works not having contracts are practically unable to obtain this alloy at any price. Three-fourths of all the open hearth steel requires ferro silicon in its manufacture and when we further consider that specifications for shell steel for shrapnel and high projectiles call for high percentages of silicon we see what a shortage of this alloy would mean in the program of "preparedness."

Ferro chromium is another alloy which has its seat at Niagara. It is absolutely essential in the manufacture of armour plate, armour piercing projectiles, not to mention its indirect bearing on "preparedness" because of its use in high speed steel and special castings.

Silicon metal is necessary in making electrical steel for alternating current apparatus. The latest type of dreadnaught is the electrically propelled battleship. Each ship has an electric power plant of 18,000 horse power and silicon steel is required in all this apparatus. Silicon metal is an important preparedness product in the generation of hydrogen for dirigible balloons. The Allies are using large quantities of this product and it is of such importance that the British Government is now erecting a plant to insure a regular supply.

Niagara Falls has become the seat of the electrode industry of the United States and three of the largest works are located here. Electrodes either of the graphitized or amorphous type are basic elements in the manufacture of products in the electrolytic cell as well as in electric furnace products such as ferro alloys, calcium carbide and abrasives. Artificial abrasives are an essential element in the metal working operations of arsenals, navy yards and all munition manufacturing. Shells, rifles and bayonets call for enormous quantities of grinding wheels.

Aluminum is a structural material of great importance in engines for aeroplanes and automobiles as well as many articles of military equipment. Of course aside from the direct uses of products of Niagara Falls bearing on munition work they all have more or less of an indirect bearing on many of the basic industries of the country.

The total output of these Niagara plants was required for normal needs previous to 1916. Since that time there have been withdrawn or will soon have been

withdrawn, for use by the Canadian industries, 125,000 horse power previously available for the industries on the American side. Meanwhile our entry into the war will necessitate still greater use of the products of these plants in the rapid expansion of our navy and army; nevertheless all are agreed that there must be no diminution in the supply of munitions to the entente allies, now our allies.

May we not therefore respectfully suggest to the International Conference, now deliberating in Washington, that an important subject for their most serious consideration would be the question of definite arrangements for largely increased output of the American electrochemical industries. If power is provided, the American electrochemists will promptly respond to the increased demand upon them.

THE BOOTSTRAP METHOD REVIVED

Like a bolt from the blue sky came the suggestion from the Secretary of the Treasury, as announced in the daily press recently that a tax of 25 cents a gallon on denatured alcohol, at present tax-free, be levied as a partial means for raising revenue to meet war appropriations.

Certainly mature consideration will lead our national legislators to disregard this suggestion, for it is evident that confusion has arisen as to the purpose of Congress in 1906 in relieving denatured alcohol of any tax. Ten years of careful study of this industry, especially in Germany, convinced our people that the lack of such a provision in our laws was chiefly responsible for the non-existence of many needed chemical industries here. Since 1906 the denatured alcohol industry has grown and with its growth the lacking industries have been gradually supplied.

Of particular import at this time is the fact that denatured alcohol enters so largely into the manufacture of many products whose purchase it is sought to provide for, either for our own military forces or for those of our allies, by the \$7,000,000,000 appropriation. Denatured alcohol is used in the manufacture of many lines of explosives such as smokeless power and detonators; of hospital supplies such as ether, chloroform, iodoform, alkaloids, tincture of iodine; and of general supplies needed by our military forces such as artificial leather, aeroplane wing coatings, disinfectants, photographic material, etc.

Are we to tax ourselves in other lines by the amount necessary to enable the purchase by the Government of such materials at prices increased by just the amount of the suggested tax? This is the old vain endeavor to raise one's self by one's bootstraps. Furthermore, it is proposed to aid our allies by financial loans needed partly for the purchase of just such supplies as have been mentioned above. Shall we then require them to help finance the loan by meeting the increased cost of material due to the levying of such a tax? We do not believe that Congress has any such intention.

Aside from such considerations, however, it is an admitted fact that the chemical industries play a great

rôle in modern warfare. The function of tax-free denatured alcohol has been an extremely important one in the rapid development of our chemical industries during the past decade. This is especially true of the rapidly developing but still youthful American dyestuff industry. It has had much subtle opposition to contend with during its brief two years of existence, which opposition could be plainly traceable to that country with which we are now at war. Shall we now play directly into the hands of our enemies who wish to preserve for the future their previous monopoly in this line? It is not difficult to imagine their grim satisfaction that such a disastrous blow should be dealt the chemical industries of this country, without effort on their part and with so little real return to ourselves.

Sometimes we fret over delay in legislation, but deliberation has its advantages. Full consideration of the disastrous effects of this suggested levy will doubtless lead to its rejection, leaving the chemical industries free to continue that rapid expansion and development along new lines which are immediately necessary if this country is to attain its maximum strength for the prosecution of the war in which we are now engaged.

THE UBIQUITOUS EXCEPTION

In some way or other German interests have in the past been pretty successful either in shaping our revenue legislation to suit their ends or in very keen ability to find loopholes through which to escape damage to their products and therefore to their pockets. To provide funds for the conduct of the Spanish-American War, our government enacted a War Revenue Bill on June 13, 1898. Among the articles selected for special taxation, collected by the affixing of tax stamps, were proprietary medicinals protected by patent or trade-mark (Section 20). This tax was paid by American manufacturers of such products; but in the *Federal Reporter* (Volume 91, page 608) record is made of a case, *United States vs. Stubbs*, District Court S. D. N. Y. Nov. 22, 1898, concerning the alleged forfeiture of a quantity of Aristol, Phenacetin and ten other articles, products of the German coal-tar synthetic medicinals industry. The *Federal Reporter* states, "It was admitted that all the articles in question are covered by patents and a trade-mark and that all are proprietary medicinal articles." However, there was an exception in Section 20, namely, "uncompounded medicinal drugs or chemicals" were not subject to the tax. After full argument the court ruled that this meant mixing or compounding in a pharmaceutical sense and that therefore the above products, admittedly covered by patents and a trade-mark and admittedly proprietary medicinal articles, need not be stamped!

Prof. John Uri Lloyd, of Cincinnati, commented strongly upon this situation in the March, 1899, number of the *Bulletin of Pharmacy*. He wrote:

If the lawmakers proposed to tax medicines that are protected by patent and trademark, they failed so to do for the

most notoriously protected and monopolistic remedies, both patented and trade-marked, escape the tax. I refer to the European patented remedies that have no competition in the United States because our Government's protective laws forbid their manufacture here; and yet these remedies pass free according to the courts' decision. I am not criticizing our European friends who adroitly found a flaw in our law, big enough to let them sell their patent medicines free of tax while most American patents must be stamped. I simply say, a law that was intended to tax all alike, foreigner and American, whoever makes a patent medicine, and every style of patent or trade-marked medicine, and yet is so defective as to let either class escape, does the other class a wrong. No proprietary or patent medicine, simple or compound, foreign or home-made, should escape. Justice to those concerned demands that if the intent of the law cannot now be carried out by the Commissioner of Internal Revenue, the defective law should be promptly amended so as to correct its defects. As it stands now it is faulty.

There is a sequel to this story which would prove extremely interesting to the members of the Division of Pharmaceutical Chemistry, and perhaps some day Prof. Lloyd will consent to our publishing it, or, better still, perhaps we can persuade the author of "Stringtown on the Pike" to write it himself in his own inimitable style.

Meanwhile, we would again urge our congressmen to consider from all angles any legislation adversely affecting the developing American coal-tar chemical industries, which are now rapidly supplying our country with those products for which we have so long been dependent upon Germany. In doing this they are "doing their bit" in the program of national self-containedness.

ANOTHER PHASE OF COOPERATION

Many of our universities and colleges have already adopted the policy of granting immediate graduation, without further examination, to those of their graduating classes who have enlisted in the government service and whose enlistments have been accepted.

There is another class of service, however, connected indirectly with the government, namely in those industries which are furnishing war supplies and whose present forces are now utterly inadequate for the demands made upon them.

The call from the industries for the immediate service of the graduating class of engineers of Lehigh University has been so insistent that, upon recommendation of its Faculty, approved by this Board of Trustees, all senior students so desiring will have their examinations advanced one month so that they may be enabled promptly to give relief in those overtaxed industries for which they have been especially trained.

THE GREATEST CHEMICAL LIBRARY IN THE WORLD

Why should we not have such? The basis of true progress in the chemical industries is a complete chemical literature on which active brains can with courage, confidence, wise forethought and adequate financial support continue to enlarge the great

structure of the applications of the science of chemistry. The skill and genius of American chemists and chemical engineers have proved themselves to our people. The financial returns from such efforts have been abundant. It must not be forgotten, however, that such returns have been obtained under conditions practically free from foreign competition. In the coming struggle to maintain and improve present advances, wise preparedness will not neglect this important foundation of the industrial structure.

What have we of this nature now? Many partial libraries, housed in many institutions, educational and industrial, and more or less accessible to chemists in the various sections of the country, but nowhere under one roof have we a complete literature, readily available, to which a chemist could go in the certainty that there he would find everything published bearing on the problem whose correct solution is his responsibility.

We thought, at one time, that America possessed in the Chemists' Club library a literature at least approaching that ideal, but we were mistaken in that conception as examination has proved. The laudable ambition of the club to supply such a need failed, even though its volumes were increased by the addition of those belonging to the American Chemical Society, an addition authorized by the unanimous vote of the Council of the Society. The reason for the failure was not far to seek: the financial tax upon the resources of the Club was too great; consequently the bibliographic service had to be discontinued; the hope of a duplicate library which could be used as a circulating library for the benefit of chemists at a distance had to be abandoned, though partially attained; and funds for subscriptions to current literature were so inadequate that it was necessary to resort to receipt of many, many journals through the American Chemical Society, through various publishing houses and through the courtesy of individuals. A list of the current periodicals, compiled by the kindness of the librarian, showed 16 journals received from our office and 96 journals received from *Chemical Abstracts*. If a chemist therefore is depending upon this library to keep completely up-to-date in the developments in any field covered by these 112 periodicals, not to mention many others, he must wait until this office has finished the perusal of its 16 periodicals (a number of which, by the way, we have never yet seen in the office), or in the case of those received through *Chemical Abstracts*, he must wait until these have been allotted by the editor to the various abstractors, have been by them abstracted, and have been returned to the editor after being retained for purposes of correction and reference until publication of the abstract—if even then.

No criticism is intended or implied in this outline of conditions in the library of the Chemists' Club. Our purpose is to point out that such shortcomings can be overcome by one method and by one method only; and that is by a generous endowment of that library. If some individual wishes to confer a lasting blessing upon chemistry in America, or if all those who have profited by the financial gains of this

remarkable period in the history of American chemical industry would unite, there might be forthcoming an endowment of a half million dollars. The interest on this amount wisely invested by an expert and representative committee would enable the collection of a complete library in duplicate which would include complete sets of all journals, complete files of all current issues, trade journals, all editions of books published (so important as shown by a recent experience of our own), consular reports, government reports, all patent files, especially those of Germany and Belgium, dissertations, etc.; it would provide ample accommodation for the convenient housing of this material; it would furnish sufficient clerical force to administer the circulating library feature; it would

assure the revival of the bibliographic service which was at one time so valuable a feature in the operation of the library.

The very presence in our midst of such a library would prove a stimulating influence wherever problems in chemistry await intelligent solution.

These are days of great things: days when the imagination is often astounded by actual accomplishment. The genius of our people is to do things in a big way; the endowments for educational institutions, for public libraries, for special lines of research—all attest this national trait. May we not hope, therefore, that generous impulse and broad-minded vision will lay such a foundation-stone for our chemical structure as is worthy of the highest American ideals?

JAPAN STARTS ITS DYESTUFF INDUSTRY

By ALCAN HIRSCH, Consulting Chemical Engineer to the Japan Dyestuff Manufacturing Company, Ltd.

When the world's production of dyestuffs and intermediates was cut off from Germany by the World War, countries other than the United States suffered tremendously from the dyestuff famine. Among these countries was Japan, whose consumption of dyestuffs is less than one-sixth of that of the United States, but whose textile, paper, leather and other allied industries were dependent upon German dyestuffs and intermediates. The Japanese Government decided that it wished to be in an independent position

Nakaya, formerly Vice Minister of the Department of Communications. The Board of Directors consists of Messrs. Nakaya, Uyemura, Fujiyama, Ohashi, Inahata, Watanabe, Hori, Ito, and Kubo. The Honorary Councillors are: Baron Shibusawa, Baron Okura, Dr. Jokichi Takamine, and Messrs. Kataoka and Nakano. The Works Director is Dr. Kotaro Shimomura.

LOCATION AND BUILDING OF PLANT

In June 1916, the Company purchased 30,000 tsubo of land (1,080,000 sq. ft.), and leased an additional quantity. This land is situated at Kawakishicho, Nishiku, Osaka, where the main plant is located. The plant is situated adjacent to the Ajikawa River, which gives it water connection through Kobe Bay to the Pacific Ocean, and also water connection to the Inland Sea. Most of the raw materials are transported by water directly to the plant.

This land, as late as last June, consisted of high-grade rice land, which means that it was submerged. Filling in began last June, and the land had to be drained, and also had to be filled in with dirt to a height of six feet. When it is understood that all of this filling in had to be done by hand, and that piles had to be driven by manual labor for the foundation of each of the buildings, some idea of the stupendous task can be obtained. At the present writing, twenty large buildings are completed, and a number of smaller ones are in course of construction.

WORKS DIRECTOR EDUCATED IN THE UNITED STATES

Great credit is due to Dr. Kotaro Shimomura, Works Director of the Company. Dr. Shimomura was educated at the Worcester Polytechnic Institute in this country, and was for many years Professor in the School of Science at Kyoto. Some twenty years ago, he introduced the first soda ash in Japan, and for the last twenty-five years has been intimately connected with the industrial chemical development of that country. Being a man of broad viewpoint and true vision, he at that time foresaw the working



DR. HIRSCH AND SOME OF THE RESEARCH LABORATORY STAFF, JAPAN DYESTUFF MANUFACTURING COMPANY, LTD.

regarding the manufacture of dyestuffs, and that it would do all in its power to encourage, foster and assist in the development of this new industry.

ORGANIZATION OF COMPANY

Accordingly, on the 24th of December, 1913, the Japanese Government authorized the formation of the Nippon Senryo Seizo Kaisha, or the Japan Dyestuff Manufacturing Company, Ltd., capitalized at 8,000,000 yen (\$4,000,000), and subsidized by the Government. The President of the Company is Mr. H.



VIEWS OF THE PLANT OF THE JAPAN DYESTUFF MANUFACTURING COMPANY, LTD.

up the coal tar into the refined benzol, toluol, xylol, naphthalene, anthracene, etc.; thence into the intermediates, and finally into the different colors. This dream is being realized to-day.

Dr. Shimomura brings to his work the enthusiasm and energy of a scientist and deep thinker combined in rare degree with the judgment and practicality of an experienced technician and operating manufacturer. He has surrounded himself with a large, varied and very competent staff of highly trained men, of whom Mr. Gompei Kuwada is Chief Engineer.

RESEARCH FACILITIES AND STAFF

The Company maintains a large research laboratory, which is equipped in the most modern manner, and also a technical laboratory, where the processes may be tried on a semi-commercial scale. There is also maintained an experimental plant which serves the purpose of providing a place where the small scale manufacture can be carried out, and where the new processes can be installed on a commercial basis. It also serves as a school for training the men. The Company has a system of apprenticeships where it trains new employees in actual plant experience.

COMMERCIAL PRODUCTION

The Company has been producing commercially for some time aniline oil, aniline salt, phenol, Orange No. 2, Fast Red A, Benzo Purpurine 4B and Congo Red. By July it will be turning out daily large quantities of the standard shades of basic colors—blues, violets and greens; sulfur colors—blues and dark blues (Kon); and direct colors—blacks, blues and reds. In addition, the experimental work on synthetic indigo has been completed, and this important dyestuff will be produced on a large scale.

PLANT MANAGEMENT AND WELFARE METHODS

The plants are run on a three-shift, 8-hour basis, which proves to be most efficient, and gives the best results from the standpoint of employer and employee. It is believed that this is the first time this has been adopted in Japan. This method supersedes the old method of having a large number of men working

together with frequent stops for tea drinking and smoking, and a general attitude of taking it easy because they knew they had to work from twelve to fourteen to sixteen hours. By the new method, the highest scale of wage is paid, the best type of workmen attracted to the industry, and the ratio of production to labor is greater than it was in the former case.

There is also a bonus system, and a profit-sharing system in force, whereby methods for saving and elimination of waste products are encouraged and rewarded. The Company is providing up-to-date wash rooms, lockers and showers for its employees, and is adopting ventilation systems and safety-first methods for the protection of its men, as well as educating the men to protect themselves. A system of special rewards for new processes and improvements is being adopted, so as to encourage the men and inspire them to exert their best energies in their work.

PROSPECTS OF THE COMPANY

The Japan Dyestuff Manufacturing Company, Ltd., is in an excellent position to enter this field on a scientific basis, and on an equal footing with the rest of the world. This is due to the utilization of waste products, and the coordination of its different manufacturing plants, as well as favorable conditions of labor, so that this Company should be able to produce in normal times as efficiently as any company in the world. When it is remembered that one of the large English dyestuff firms paid a dividend of 10 per cent for the five years previous to the war in the face of severe German competition, it is seen that the future of the Japan Dyestuff Manufacturing Company, favored as it is with the cooperation of the Government, is exceedingly bright.

The Japanese appreciate highly the efforts of American chemists to help them, and the friendly feeling of the American chemists is expressed by the action of Dr. Charles F. Chandler, the Dean of American Chemists, who was kind enough to donate his collection of fifty years of books, pamphlets, and patents on dyestuffs to the Company as a nucleus for their chemical library.

50 EAST 41ST STREET, NEW YORK CITY
April 12, 1917

ORIGINAL PAPERS

THE INCOMPLETE HYDROGENATION OF COTTONSEED OIL

By HUGH K. MOORE, G. A. RICHTER AND W. B. VAN ARSDEL

Received April 12, 1917

The hardening of liquid oils by means of the addition of hydrogen is a process of vital importance. Hardened fats are employed in the manufacture of lard substitutes, artificial waxes, confectionery, butters, lubricants, candle material and soap. The present outlook for still wider fields of application lends great significance to any new data or results achieved by investigation.

The purpose of this article is to publish certain interesting experimental results obtained during an investigation on the hydrogenation of vegetable oils. This investigation is still under way at the Research Laboratory of the Berlin Mills Company and more complete and detailed results will be presented in book form in the near future.

Most of the references on catalytic hydrogenation which are obtainable at present, deal either with the purely theoretical phase of the reaction or with a rather superficial description of patent literature. Sabatier and his co-workers carried out a splendid research, demonstrating the theoretical possibilities in the field of hydrogenating organic compounds. Their work, however, was confined primarily to reactions involving single organic compounds. The modern problem of hardening oils is concerned with materials which consist of a number of unsaturated compounds, each one of which must be considered in the catalysis. The greater the number of unsaturated components present, the more difficult becomes the problem of studying the course of the reaction. Previous investigators have avoided this complication by combining the unsaturated components as one whole and measuring the course of hydrogenation by iodine number determination or hydrogen absorption. Such a method does not give much information regarding the changes actually occurring in the oil.

Normann, Ipatiev, Bömer, Fokin¹ and others neglect entirely the possibility that, depending on the conditions of the operation, the glyceride components of a partially hydrogenated oil may differ materially from those of a second partially hydrogenated product which is obtained from the same original oil and reduced to the same iodine number. Other investigators have likewise measured the hydrogenation by considering the unsaturated components as a whole rather than as individual units.

The object of our investigation was to study the physical and chemical changes which take place in an oil during the process of hydrogenation and the work was limited chiefly to partially hydrogenated products. The only oil used in obtaining data for this article was

cottonseed oil. During the experimentation other oils have yielded very similar results although no complete series of results is as yet ready for publication.

SCOPE OF WORK

Our work has led in several different directions in the general field of oil hydrogenation, so that the results to be reported may be conveniently grouped in five sections, which may be briefly described as follows:

I—Changes in the amount and character of the various fatty glycerides of oils during the course of hydrogenation, especially as affected by experimentally variable factors such as temperature, pressure, etc.

II—Changes in the chemical characteristics of the oil (especially its iodine number) during hydrogenation.

III—Changes in the physical characteristics of the oil (e. g., titer and melting point) during hydrogenation.

IV—Other changes in properties due to hydrogenation, such as response to Halphen test.

V—The preparation of catalyzers, and their resistance to poisons.

METHODS OF STUDY

The methods of study were in part the analytical procedures in common use for the investigation of oils and fats, but other useful lines of approach were developed in this laboratory with a special view to the nature of the work in hand. Such, for instance, is the graphical method of following compositions described in a later paragraph.

I—PHYSICAL CONSTANTS

The physical constants occurring in our work, viz., melting point and titer, were determined by methods in common use. Titer, especially, is a well-defined and standard determination much used in the soap, candle and lard-compound industries; briefly, it is the solidification point of the fatty acids liberated from an oil by saponification, or the temperature at which the heat of crystallization of these acids balances radiation loss during solidification. The Official Method¹ was followed, using the modern glycerol saponification. Melting point, as is well known,² is a very indefinite "constant," whose value is greatly affected by slight changes in manipulation, and for which there does not exist, as yet, a well-defined, standard method. We have adopted for the greater part of our work the "open capillary" method mentioned briefly in Tewkesworth³ and used as a practical test by a large proportion of the industries handling solid fats. According to this method, which must be quite rigidly

¹ Wm. Normann, British Patent No. 1315, 1903; LePrince (N) Sveske, German Patent No. 141,029, 1902; S. Fokin, *J. Russ. Phys. Chem. Soc.*, **35** (1906), 419-446; **38** (1910), 885-888; **39** (1911), 605-609; **40** (1912), 304-321; *Z. anorg. Chem.*, **23**, 1341-9, 1492-1502; Ipatiev, *J. Russ. Phys. Chem. Soc.*, **40** (1908), 1-60; Bömer, *Z. Nahr. Genussm.*, **24**, 103-113.

² *J. Assoc. Oil and Fat Chemists*, No. 1, 2 (1916), 394.

³ Chemical Technology of Oils, Fats and Waxes, 5th Ed., Tewkesworth, L. p. 315.

⁴ *Anal.*, 1, p. 318.

standardized for results of any value,¹ the melting point is the temperature at which a column of fat, chilled in a capillary tube and immersed in water which is slowly heated, softens sufficiently to be started upward in the tube due to the hydrostatic pressure of the water.

CHEMICAL CONSTANTS

Some of the chemical constants are as standard as the titer; for instance saponification value and acid value² which indicate the amount of alkali which will combine with a fat or fatty acid, and hence give indirectly the molecular weight of the fat or acid. Others, however, are not so fully standardized—for instance the iodine number of the fat and of the liquid fatty acids—so that there is not only some leeway in choice of method, but there is even opportunity for improvement through certain modifications. For determining the iodine number, which is intended to represent the degree of unsaturation of the oil or acid as a whole in terms of the percentage of iodine which it will absorb under specified conditions, three iodine solutions are in fairly common use, and the details of manipulation are different for each one; more than that, the results are not identical within several per cent. For convenience of manipulation and general reliability we have chosen the Hanus method³ which we have found to compare as follows with the Hübl method in the case of several different fats and fatty acids:

SUBSTANCE	HANUS IODINE No.	HÜBL IODINE No.
Fat No. 1.....	65.1	67.3
Fat No. 2.....	86.2	87.8
Oil No. 3.....	106.2	107.7
Fatty Acid No. 1.....	102.5	104.5
Fatty Acid No. 2.....	121.6	123.6

According to Meigen and Winogradoff⁴ the iodine number cannot be used for the purpose of calculating the degree of unsaturation directly because either an appreciable amount of substitution takes place in the saturated part of the molecule, or if this is guarded against the addition of halogen to the unsaturated part is incomplete; McIlhiney⁵ proposes to determine the sum of addition and substitution separately, arriving at the true addition by difference. Investigation showed the addition value so obtained to be always somewhat higher than the result of the Hanus method, especially in the case of fatty acids, but the difference was not sufficiently significant to

warrant the extra labor and complication; for present purposes comparative results, given by the simpler methods, are quite as interesting as absolute results.

For a more thoroughgoing study of the nature of or changes in oils, it is necessary to use other methods than those outlined above; for instance, some of the many components may be separated from the mixture and then studied separately by the known methods. Many such methods of separation have been proposed, but the only one that has proved to be of any great value is that known as the Gusserow-Varrentrapp lead-salt-ether method, which has been variously modified by Muter, Lane, Tortelli and Ruggieri, and many others, and which is in principle a separation of two groups of lead salts of fatty acids based on the difference in solubility of the two groups in ethyl ether. For convenience the acids of the soluble group are called liquid fatty acids, the insoluble ones solid fatty acids. The detailed procedure of the separation is not by any means agreed upon, five different sets of directions being given by as many different texts on oil analysis; the variation arises partly from the fact that not all investigators have made this separation with the same purpose in view. An attempt may either be made to separate the groups completely and quantitatively from one another, or else a "sample" of the liquid acids may be isolated, in relatively small amount, but quite free of contamination with acids of the other group. The latter course, which we have thought preferable, has been fairly well mapped out by Tortelli and Ruggieri¹ and others. The sample of liquid acids which results from the separation is examined by the usual methods, iodine number and acid value being especially important.

The detailed procedure for separating a sample of liquid fatty acids is as follows:

METHOD—Weigh out 20 g. of the fat into a 300 cc. Erlenmeyer flask. Add 180 cc. of alcoholic potash (40 g. KOH per liter of ethyl alcohol which has been digested with NaOH and redistilled) and boil until completely saponified, then until three-fourths of the alcohol is gone. Add 100 cc. water, and neutralize with glacial acetic acid, using phenolphthalein as an indicator; come back to end-point with $N/2$ NaOH solution.

Measure out into a 500 or 600-cc. Erlenmeyer flask 100 cc. of 20 per cent lead acetate solution and 100 cc. of distilled water, and bring to boiling. If the neutralized soap solution has by this time crystallized out, warm the flask until contents are liquid, then add carefully to the boiling lead acetate solution; after boiling cautiously for about two minutes, remove the flask from source of heat and when cooled to a safe temperature cool in running water.

Prepare a 4-in. funnel with 25 cm. paper and pour the liquid contents of the flask into the filter paper; when the liquid has run out of the filter paper, wash the flask twice with 50 cc. each time of distilled water, filtering the washings, then twice with 25 cc. each time of 95 per cent alcohol, filtering the washings and taking care to wash the sides of the paper with alcohol.

When the alcohol has entirely drained from the funnel, dry the filter paper free from alcohol and return the loosely adhering precipitate to the flask, which has been allowed to drain free from alcohol for 10 minutes. Add 220 cc. of ether (prepared by washing U. S. P. ether five times with 10 per cent portions of distilled water, drying with calcium chloride, and distilling).

¹ The procedure followed in this laboratory is as follows: thin walled glass tubes of inside diameter between 0.09 and 0.11 in. are cut to about 8-in. lengths. With the finger over one end of the tube, the other end is inserted in the melted fat (about 60° C.) and a plug of the liquid from 1.25 to 1.50 in. long is withdrawn in the tube. A small drop is allowed to collect on the lower end, and the fat is then chilled in the tube in an ice-water bath for thirty minutes. The outside and lower end are then wiped free of excess fat. The melting-point apparatus is a 500 cc. beaker, with a stirring device and separate support for the glass tubes and thermometer. Air-free water (about 400 cc.) is put in the beaker, the tubes are placed vertically in it with the upper surface of the plug of fat just one inch below the water level, and heat is applied to raise the temperature 3 to 4° F. per minute. The melting point is taken as that temperature at which the plug of fat just starts to slip up the tube. This procedure gives results which are from 1 to 10° C. lower than those of the "closed capillary" method and 2 to 4° C. lower than those of the Wiley method, both given in *J. A. O. A. C.*, 2 (1916), No. 3, 301-302.

² *J. A. O. A. C.*, 2 (1916), No. 3, 306.

³ *Ibid.*, 304.

⁴ *Z. angew. Chem.*, 1914, Aufsatzteil, 241.

⁵ "Chemical Technology of Oils, Fats and Waxes," Lewkowitsch, 1, p. 394.

¹ Lewkowitsch, 1, p. 549.

Boil the ether and lead soaps under a reflux condenser for one hour. After cooling, cork well and allow to stand from 16 to 18 hours at a temperature of 7 to 10° C.

At the end of this time, filter off the insoluble soaps in a 4-in. water-jacketed funnel kept covered with a watch-glass. Wash the flask and soaps once with 25 cc. of cold ether, and add washings to filtrate. Pour this ether solution of soluble soap into 150 cc. of a hydrochloric acid solution (made by adding one part of concentrated hydrochloric acid, sp. gr. 1.2, to 4 parts of water) in a 500-cc. separatory funnel. Cork the separatory funnel and shake until the ether layer becomes practically clear and colorless. If the first treatment does not accomplish this result, repeat the washing with acid. Draw off the acid solution containing the lead chloride, and wash the ether first with 100-cc. portions of sodium chloride solution (125 g. per liter), then with 100-cc. portions of distilled water, until 3 drops of $N/2$ alkali will neutralize the last washing using phenolphthalein. Separate the water layer as completely as possible, and pour the ether solution of liquid fatty acids into a clean flask.

Place the flask in a water bath and connect it with a hydrogen generator and a condenser. Pass a gentle stream of dry hydrogen, free from oxygen, below the surface of the solution, and distil off the ether. Finally, boil the water bath until no odor of ether can be detected in the liquid fatty acids. Cool the acids, filter through a $5\frac{1}{2}$ cm. paper in an atmosphere of dry hydrogen, free from oxygen, and dry by exposing the liquid fatty acids in a Petri dish over concentrated sulfuric acid in an atmosphere of hydrogen for 24 hours. Determine the iodine number of the acids with as little delay as possible.

REMARKS—Early in our study persistent failure to obtain consistent results on duplicate separations impressed us with the importance of some apparently small details, and as a final conclusion we adopted the following precautions, which are embodied in the above method:

(1) The alcohol used in saponification should be purified by treatment with caustic alkali and by redistillation.

(2) The washed cake of lead salts should be freed as completely as possible from adhering water or alcohol, so that the purity of the ether used for the separation will not be lowered.

(3) Commercial "anesthesia" ether should be purified of all but traces of alcohol and water by washing with water and drying with calcium chloride, since its solvent action is considerably modified by the presence of either impurity. Treatment with metallic sodium is, however, unnecessary.

(4) In order to secure uniform treatment of the cake of lead salts, it should be boiled for one hour with the ether, although in many cases it will be completely disintegrated in less time.

(5) The lead salt-ether mixture should be held at a definite temperature for a definite length of time so that crystallization of the solid salts will take place under uniform conditions and to a uniform extent. The temperature should be quite low and the duration fairly long, so that the solids will separate as completely as possible. A tolerance of 3° C. in temperature (7 to 10°) and two hours in time (16-18) has been found reasonable.

(6) The contents of the funnel should be kept cool during filtration of the insoluble lead salts from the ether solution, since an appreciable amount of the solids will redissolve if the temperature is allowed to rise more than a few degrees.

(7) The solid salts should not be thoroughly washed with ether, since such washing would increase the relative amount of solids carried into the ether-soluble portion. One small portion of ether is used, however, the object being to displace some of the solution left adherent to the solid, and thus increase the yield of liquid acids, rather than to wash the solid portion free from liquid salts. As a matter of fact, the acids liberated from the solid portion washed in this manner are found to have an iodine number ranging from 20 to 30, instead of zero.

(8) The operations subsequent to liberation of the acids in ether solution should be carried out in an indifferent atmosphere, preferably hydrogen, since the usual products contain notable quantities of linolic acid, easily oxidized by the air at room temperature.

(9) The isolated liquid acids should be filtered, to separate droplets of water, and then dried in a sulfuric acid desiccator, since small amounts of moisture affect the iodine number determination greatly.

(10) The liquid acids should be examined without undue delay, to minimize the effects of oxidation.

The liquid fatty acid separation has been used with a considerable degree of success and certainty; it is usually possible to check duplicate determinations within 1 or 2 per cent, and different laboratories have agreed almost as closely. The chief limitation is imposed by the decrease in amount of liquid acids present as an oil approaches saturation; the relative amount of contamination of the isolated liquid acids with solid acids becomes finally quite large, so that the practical limit to the method is found to have been reached by the time the iodine number has dropped to 50 or 40; its field of greatest usefulness, therefore, is in the examination of oils and semi-solid fats—the materials with which this paper is especially concerned.

If a fat which is too hard to be analyzed directly (below iodine number 40-50) is mixed with an appropriate amount of an oil whose liquid fatty acids have already been examined, the mixture may be analyzed and from the result the composition of the hard fat may be calculated. The iodine number of liquid fatty acids thus calculated is always somewhat higher than that found by direct analysis of the fat itself, as would be expected. This procedure we have followed in several cases, with promising results, and further work is under way. The chief drawback of the method is the very considerable loss in accuracy which it entails.

3. THE GLYCERIDES OF COTTONSEED OIL

Investigation of cottonseed-oil acids has shown in the hands of several investigators¹ that the unsaturated acids present are oleic and linolic acids, practically to the exclusion of all others and further, that these two are the components of the "liquid fatty acids." Our own work, which is not reported in this article, confirms this conclusion. Oleic acid, $C_{17}H_{33}COOH$, contains one double bond (molecular weight 282.5), two double bonds, since each one of these substances has a definite known (calculated, not experimentally) iodine number. The iodine number of the liquid fatty acid mixture affords a means of determining the percentage of each in the mixture according to the well known formula:

$$\text{iodine number} = 184.4 \frac{x}{100} + 256.8 \frac{y}{100} \quad (1)$$

where x is the percentage of oleic acid, y the iodine number of the mixture, and 184.4 the iodine number of oleic acid and 256.8 the iodine number of linolic acid.

¹W. A. Pryor, *Transactions of the American Chemical Society*, **39**, pp. 184-191, 1917; *Journal of the American Chemical Society*, **39**, pp. 184-191, 1917.

²Id., **41**, p. 100.

³Id., **41**, p. 100. The authors of these papers have also shown that the iodine number of the mixture is a function of the iodine number of the components and is not a function of the iodine number of the components alone. This is in agreement with the results of the present investigation.

It has been known for some time that oleic, linolic, palmitic and the other "fatty" acids do not occur in natural oils and fats wholly combined in the form of simple triglycerides—esters in which all three of the glyceryl bonds hold the same kind of acid radical, as in tripalmitin, trilinolin, triolein, etc.—but are to a large extent combined in the "mixed" glycerides, such as palmito-diolein. At present there is no satisfactory method available for the study or estimation of the mixed glycerides, of which a very large number may exist; valuable information may be obtained, however, if the problem is simplified by assuming the oil to be a mixture of simple glycerides. Under that assumption, for instance, three mols of palmito-diolein might be considered a mixture of one mol of tripalmitin with two mols of triolein; or the combination of one-third of a glyceryl radical with one acid radical might be taken as a unit, such units being called simply "palmitin," "olein," etc. This method of study finds many precedents in other fields of chemistry.

Cottonseed oil, then, may be said to contain "linolin" and "olein" as its unsaturated constituents, and because of molecular weight relations they are present in the same relative proportions (within a few hundredths of 1 per cent) as are the linolic and oleic acids in the liquid acids. Linolin and olein have definite iodine numbers—173.6, and 86.2, respectively—so that it is possible to calculate what iodine number the "liquid glycerides" of the oil would have if they were unmixed with other substances; this iodine number is always higher than the actual iodine number of the oil, which is reduced in proportion to the amount of saturated material present, irrespective of the molecular weight of the latter material. The data are all available, therefore, for calculating the actual percentages of olein, linolin, and saturated material, given only the iodine numbers of the oil and of the liquid fatty acids obtained from it. A simple algebraic process reduces this work to the following three equations:

$$\text{Per cent Saturated Glycerides} = 100 - 104.5 A/B \dots\dots\dots (2)$$

$$\text{Per cent Olein} = 207.6 A/B - 1.144 A \dots\dots\dots (3)$$

$$\text{Per cent Linolin} = 100 - (\% \text{ Sat. Glycer.} + \% \text{ Olein}) \dots\dots\dots (4)$$

in which A is the iodine number of the fat and B the iodine number of the liquid fatty acids.

It will be noted in the above paragraph that all substances having zero iodine number have been grouped together as "saturated glycerides." In the case of cottonseed oil this material is nearly all palmitin, and in hydrogenated cottonseed oil it is a mixture of palmitin and stearin (the latter derived from the olein and linolin by hydrogenation); the relative proportions are not especially important in the present work.² In other oils and fats different saturated glycerides may be found, but they do not affect the calculation; the

necessary condition is that the unsaturated glycerides should be olein and linolin. Other unsaturated bodies, if present, would introduce a certain error, since the iodine numbers would differ from those used in the calculation.

4—GRAPHICAL REPRESENTATION

An oil or fat of the nature of hydrogenated cottonseed oil may therefore be studied as a three-component system, counting the saturated glycerides together as one component; and the convenience of graphical methods is available through the use of Roozeboom's triangular diagram. This diagram, well known in work with alloys, slags, ceramics, etc.,¹ is so constructed that one, and only one, point on the equilateral triangle represents any possible mixture of the three components. The diagram is drawn as in Fig. 1, where

P is any point within the triangle, ABC ,

PD is parallel to AC , PF to BC and PE to AB .

It follows in a simple manner that

$$BE + CF + AD = BC, \text{ a constant.}$$

When each side is divided into 100 parts it is obvious that BE represents the percentage of one component in the mixture represented by P , CF is the percentage of a second component, and AD is the third, and the sum of these three percentages is 100. It has been our custom to measure saturated glycerides as BE , linolin as CF and olein as AD , so that point C represents pure saturated glyceride, A pure linolin and B pure

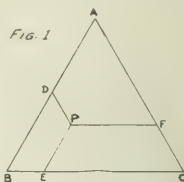
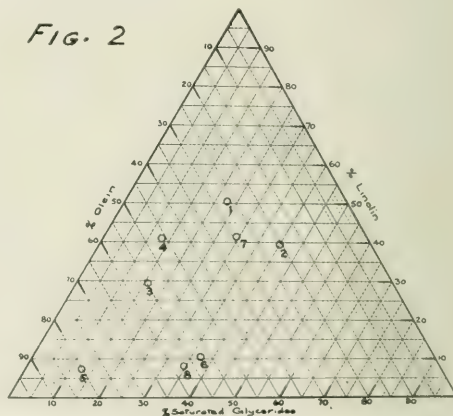


FIG. 2



olein. The following typical examples may be given to illustrate the method, the figures being first summarized in the table, and then plotted on the diagram as shown in Fig. 2.²

Evidently the tendency is for liquid oils to appear near the left-hand side of the triangle, solid and semi-

¹ Triangular-ruled paper may be purchased from dealers in draftsmen's supplies.

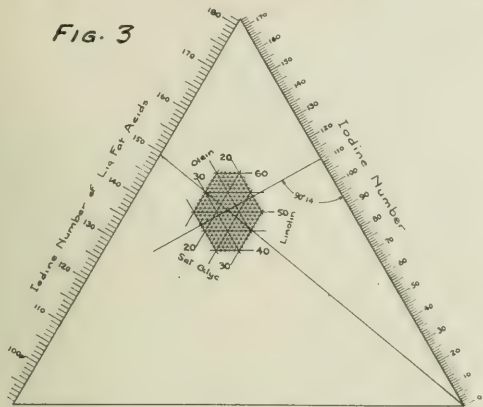
² For obvious reasons we have refrained from including in this list any of the trade-marked fats now on the market.

¹ "Chemical Technology of Oils, Fats and Waxes," Lewkowitsch, 1, p. 406.

² Dr. W. D. Richardson, of Swift & Co., Chicago, has suggested to us that the proportions of palmitin and stearin in the saturated glycerides may be calculated from the neutralization value of the solid fatty acids liberated from the insoluble lead soaps, making correction for the unsaturated acids remaining in the mixture. By this method he has found a sample of cottonseed oil to contain 2.0 per cent stearin and 22.9 per cent palmitin.

solid fats being shifted toward the opposite vertex. Any oil when completely hydrogenated would obviously end up at that vertex (saturated glycerides)

FIG. 3



but as to the compositions it would pass through during the progress of saturation, represented graphically by a curve connecting the starting-point with the right-hand vertex, there is no published information; with that problem our experimental work is largely concerned.

Certain properties of the triangular diagram are of great assistance in connection with the problem. In the first place, all possible mixtures of two substances *P* and *Q* lie on the straight line *PQ*, which is divided in inverse proportion to the amounts of *P* and *Q* mixed. In consequence, all points of equal iodine number lie on a straight line, and likewise all points of equal iodine number of liquid fatty acids lie on a straight line. Lines of equal iodine number are found to be parallel, all making an angle of $90^\circ 14'$ (on the lower

TABLE I

No.	MATERIAL	IODINE NUMBER				
		Original Material	Liquid Fatty Acids	Saturated Glycerides	Calculated Olein	Calculated Linolin
1	Cottonseed oil.....	110.7	149.5	22.6	26.9	50.5
2	Cottonseed stearine....	86.0	149.8	40.0	20.5	39.5
3	Peanut oil.....	98.0	121.7	15.85	54.9	29.25
4	Corn oil.....	110.6	133.0	13.0	46.0	41.0
5	Olive oil.....	82.0	97.8	12.4	80.1	7.5
6	Leaf lard.....	63.5	105.3	37.0	52.4	10.6
7	Compound lard.....	97.0	143.3	29.3	29.1	41.6
8	A semi-solid hydrogenated cottonseed oil...	63.0	101.0	34.75	57.2	8.05

side) with the right-hand side of the triangle; this differs so little from 90° that it can easily be estimated with the aid of a draftsman's triangle. By graduating the right-hand edge uniformly from zero to 173.6 the line representing any given iodine number may be drawn on the triangle. Lines of equal iodine number of liquid fatty acids all pass through the right-hand vertex, hence if the opposite side of the triangle is graduated uniformly from 90.07 to 181.4, any given iodine number of liquid fatty acids (provided the liquid acids contain oleic and linolic only) may be represented. Then by drawing these two lines the position of a point on the triangle may be found graphically, given only the iodine number of the oil and of the liquid fatty acids, without making any numerical calculation. For instance in Fig. 3 cotton-

oil, of iodine number 110.9 and of iodine number of liquid fatty acids 149.5 is found graphically to have the same proportion of components as was calculated in Table I.

EXPERIMENTAL PART

GENERAL—For the experimental work two types of hydrogenation apparatus have been used: (1) a simple glass flask heated by an oil-bath and containing the oil-catalyzer mixture, through which hydrogen is bubbled vigorously, and (2) an iron container, electrically heated, in which the oil-catalyzer mixture is mechanically agitated with hydrogen. That is, all of the work herein reported refers particularly to the "batch" processes, in which a given quantity of oil is gradually hardened, but we believe our conclusions also apply in principle to the more complicated continuous processes. In the first apparatus the procedure was to weigh in the desired amounts of oil and catalyzer, heat to the desired temperature, and then start bubbling the hydrogen vigorously. The hydrogen was taken from I. O. C. cylinders and was not purified. Its volume was regulated by means of a small constant-speed blower and a gasometer. In the other apparatus the oil was brought up to temperature in an atmosphere of hydrogen, the catalyzer was added, air again driven out with hydrogen, and finally agitation started. In either case samples were taken at intervals, the catalyzer was filtered out, and the desired tests made. Times were counted beginning at the moment of starting agitation with hydrogen.

I.—HYDROGENATION CURVES

For the study of the glyceride changes during hydrogenation, the tests made on samples included iodine number and iodine number of liquid fatty acids, calculation giving the "component glycerides" (olein, linolin and saturated glycerides) of each sample. The smooth curves drawn through the points plotted on the triangular diagram always, in the cases studied, had the same general shape—suggestive of the hyperbola, concave toward the right-hand side of the triangle. The linolin is always found to decrease from that present in the original oil and the saturated glycerides always increase, while the olein rises to a maximum and then falls continuously. These changes are what would be expected, since hydrogenation must cause linolin to disappear, forming olein, while olein, hydrogenated more slowly, would at first increase and then eventually disappear forming stearin, a saturated glyceride. The shape of the curve depends upon the relative velocity of these two actions, and it appears from our work that this relative velocity must be subject to important variation, according to the experimental conditions. The actual experimental graph invariably crosses the base-line of the triangle before reaching the right-hand vertex, owing to the limitations of the lead-salt-ether method below iodine number 20 or 30. On this account we have not attempted to locate exactly in the region of very hard fats and have made assumptions only in the region where the method gives trustworthy figures. The conditions which we have varied experimentally are, (1) temperature, (2) pressure, (3) amount of catalyzer,

TABLE II—TESTS FOR HYDROGENATION CURVES
Cottonseed Oil used in all cases with Nickel Catalyst prepared as described under "Catalyzers," page 32
Abbreviations: LFA, Liquid Fatty Acids; SG, Saturated Glycerides; Ol, Olein; Lin, Linolin

EXPERIMENTAL CONDITIONS DURING RUNS																			
Apparatus	Run	Temp	Pres	Catalyzer	Agitation	Oil Used	Sample	Iodine No.	PERCENTAGES	Sample	Iodine No.	PERCENTAGES	Sample	Iodine No.	PERCENTAGES	Sample	Iodine No.	PERCENTAGES	Sample
								Fat	LFA		Fat	LFA		Fat	LFA		Fat	LFA	
Glass	A	155°	Atmos	5% No. 1	Bubbling	100	1	107.8	138.9	21.7	32.3	46.0	1	107.8	138.9	21.7	32.3	46.0	1
	B	100	Atmos	5% No. 1	Bubbling	100	1	84.8	134.6	29.0	44.2	26.8	1	92.8	138.2	24.4	43.9	31.7	1
						100	2	70.8	110.2	33.1	52.2	14.7	2	82.3	117.9	27.0	50.8	22.2	2
						100	3	61.9	103.4	37.5	53.1	9.4	3	68.5	101.1	29.2	62.2	8.6	3
						100	4	48.8	87.7	46.9	53.1		4	50.7	143.9	21.7	32.3	46.0	4
Iron	C	155	20 lbs.	2% No. 1	135 R. P. M.	100	1	79.7	108.7	23.4	60.7	15.9	1	70.2	107.6	31.7	55.0	13.3	1
	D	155	40 lbs.	2% No. 1	135 R. P. M.	100	2	59.8	92.3	32.4	65.9	1.7	2	52.8	91.0	39.4	59.9	0.7	2
						100	3	60.3	88.0	41.6	58.4	46.0	3	42.2	87.1	51.0	49.9	0.7	3
						100	4	107.7	143.9	21.7	32.3	46.0	4	107.7	143.9	21.7	32.3	46.0	4
						100	5	72.2	112.0	27.9	54.4	17.7	5	87.3	120.4	24.3	50.4	25.3	5
Iron	E	155°	20 lbs.	4% No. 1	135 R. P. M.	100	1	57.6	92.4	34.8	63.3	1.9	1	52.1	108.5	31.1	54.9	14.0	1
	F	155°	20 lbs.	4% No. 1	250 R. P. M.	100	2	42.9	86.4	50.3	49.7		2	59.7	97.1	35.7	59.3	5.0	2
						100	3						3	47.1	91.3	40.3	59.0	0.7	3
						100	4						4	47.1	90.2	54.6	45.3	0.1	4
						100	5						5	110.9	149.1	22.4	27.2	50.4	5
Glass	G	160°	Atmos	No. 1	Bubbling	GO	1	88.4	125.1	22.4	27.2	50.4	1	74.9	126.9	38.4	36.6	25.0	1
	H	160°	Atmos	No. 2	Grate doubled	GO	2	79.6	118.8	29.8	48.2	22.0	2	71.5	124.9	40.1	37.0	22.9	2
						GO	3	75.0	113.3	30.8	51.4	17.8	3	66.8	119.3	41.6	39.5	18.9	3
						GO	4	71.7	108.8	31.0	54.9	14.1	4	63.5	117.1	43.4	39.8	16.8	4
						GO	5	68.8	104.7	31.3	52.7	11.0	5	60.6	114.2	44.6	40.6	14.8	5
Iron	I	155°	40 lbs.	2% No. 1	135 R. P. M.	10 lbs	6	61.6	97.1	33.8	60.9	5.3	6	57.2	112.6	46.9	40.4	13.1	6
	J	155°	40 lbs.	2% No. 1	135 R. P. M.	20 lbs	7	52.2	90.5	39.7	60.0	0.3	7	108.4	142.8	20.6	33.5	45.9	7
						20 lbs	8	97.4	130.6	22.1	43.4	34.5	8	77.1	110.5	27.0	56.6	16.4	8
						20 lbs	9	78.9	91.1	31.2	60.3	8.5	9	63.7	100.4	33.6	58.9	7.5	9
						20 lbs	10	66.8	101.3	31.2	60.3	8.5	10	42.1	87.5	51.1	48.9	10

(4) agitation, and (5) size of apparatus; these variations are noted in Table II, along with the analytical results, and in Figs. 4 to 10.

TEMPERATURE—The ease with which these points, located in Fig. 4, fit smooth curves, such as those drawn, is one indication of the trustworthiness of the lead salt-ether method when used with care, and the fact that the two curves differ by much more than the deviation of any of the single points from its own curve is assurance that the difference is not due to freaks of analysis—the more so as all of the seven samples reported were analyzed at once, and not in two groups.

The result may be interpreted as follows: while both linolin and olein were hydrogenated faster at the high temperature than at the low temperature, relatively linolin was hydrogenated much faster at the high temperature, so that the olein had a greater tendency to accumulate under the latter conditions. In other words, both unsaturated radicals are acted upon in both cases, but at the higher temperature the more highly unsaturated one comes nearer to being singled out for hydrogenation than at the lower temperature—the action is more "selective." This would be the case if, for instance, the temperature coefficient of the reaction linolin-olein is greater than that of the reaction olein-stearin, but in view of the complicated nature of the glycerides which are actually present that explanation is doubtless too superficial to be the entire truth.

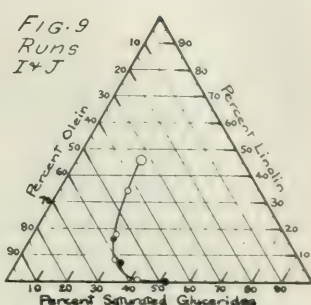
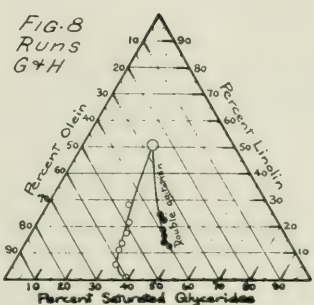
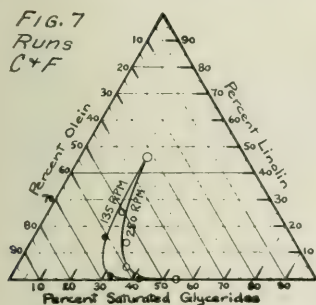
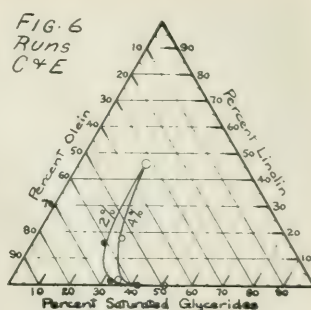
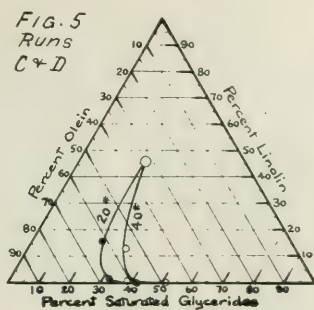
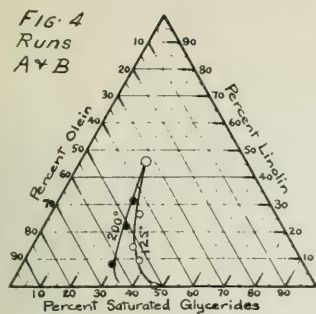
PRESSURE—The influence of the hydrogen pressure upon the course of the hydrogenation may be illustrated by Runs C and D (Fig. 5) which were both carried out in the apparatus with mechanical agitation.

Increasing the pressure is here seen to have the opposite effect to increasing the temperature, so that at a high pressure the action is less "selective" than at a low pressure. An obvious corollary of this conclusion is that it would appear to be possible to duplicate at high pressure and high temperature a curve obtained at low pressure and low temperature, while the reaction as a whole might be made to proceed many times as fast in the former experiment as in the latter.

In this case again a tentative "mechanism" may be put forward. It should first be noted that the occasional hydrogenation of a linolin chain clear to stearin instead of only to olein would have the same apparent effect as would an increase in the relative velocity of the olein-stearin reaction. Now if an increase in hydrogen concentration at the catalyzing surface (such as would be produced by increased pressure) caused an increase in the number of linolin chains to which four atoms of hydrogen were added at once, the observed effect would follow.

INFLUENCE OF PERCENTAGE OF CATALYZER—The influence of percentage of catalyst was illustrated in Experiments C and E (Fig. 6). In this case the observed result, which shows a divergence in the same direction for increased percentage of catalyst as for increased pressure, seems to be at variance with what is commonly understood to be a law of catalytic reactions, namely that if the amount (or surface) of the catalyst be increased, all of the reactions involved will be speeded up by exactly proportional amounts. In this case, one reaction (olein-stearin) appears to be accelerated more than the other. The scheme advanced in the preceding section may be made to give a satisfactory explanation; in that section the concentration of hydrogen at the catalyzing surface was taken to be the controlling factor. Now increasing the percentage of catalyst must increase this concentration, for the average distance between a catalyst particle and the hydrogen bubble-surfaces is made smaller, thereby decreasing the lag between the "demand" for hydrogen at the catalyst surface, and the "supply," which must be kept up by the processes of solution and diffusion. Thus an increase in percentage of catalyst would cause an increase in the formation of stearin relative to the change in linolin, as in the two curves reproduced above.

AGITATION—The influence of degree of agitation on the path of hydrogenation was determined first by comparing Experiments C and F (Fig. 7), in which the iron apparatus, mechanical agitator, was used.



FIGS. 4 TO 9. CHANGES IN GLYCERIDES OF COTTONSEED OIL DURING HYDROGENATION

"Degree of Agitation" is a magnitude which is not easily expressed in quantitative form, but the R. P. M. of an agitating device may serve as an index of the agitation, at least for moderate speeds.

Another pair of experiments carried out in the glass flask, bubbling hydrogen, conditions were identical in both experiments except that in Run H, the hydrogen was bubbled through the flask at approximately twice the rate used in Run G (Fig. 8).

In both pairs of experiments the influence of increased agitation is shown to be the same as that of increased pressure or per cent catalyst, and in the case of Runs G and H the variation in the curves is striking. The effect of doubling the volume of gas supplied, when the bubbling is already vigorous, may well be to increase the true "agitation" many times. On the other hand, doubling the R. P. M. of a mechanical agitator possibly does not even double the agitation, since at high speeds there is a strong tendency for the whole body of oil to rotate without much disturbance.

It may readily be seen that the "mechanism" suggested in the preceding section applies to the present case just as well, since the effect of increasing the agitation is to increase the number and surface of hydrogen bubbles and also to decrease their average distance from catalyst particles.

SIZE OF APPARATUS. The size of the apparatus in which the hydrogenation is carried out apparently does not affect the path of the hydrogenation, as appears from the data of Runs I and J (Fig. 9). It is

of course, not certain that 135 R. P. M. produces the same "degree of agitation" in both cases; if the agitation is really better at this speed in the large machine, the effect of the increase in size on the path of hydrogenation is in the opposite direction to the effect of increased agitation.

INFLUENCE OF MATERIAL OF CATALYZER

When some other catalyst than nickel is used, as in Experiment K, in which 1 per cent palladium in PdCl_2 method of Paul patent¹ acted as catalyst (Table III), the hydrogenation curve is found to have

TABLE III—EXPERIMENT WITH PALLADIUM AS CATALYZER (FIG. 10)

Run Sample	IODINE NUMBER		PERCENTAGES CALCULATED		
	Fat	Liquid Fatty Acid	Saturated Glycerides	Olein	Linolin
K 0	108.1	117.8	36.5	53.5	10.0
1	80.1	118.0	78.3	20.7	0.0
2	70.6	113.2	79.2	20.8	0.0
3	64.5	97.1	30.6	69.4	0.0
4	53.0	90.5	38.6	61.4	0.0

the same general characteristics as those described before (Fig. 10). Bubbling apparatus was used, a temperature of 135° C. and atmospheric pressure. No experiment using nickel catalyst is available to compare directly with it.

SUMMARY OF HYDROGENATION CURVES

To summarize the conclusions from the preceding experiments, it appears that the chemical character of a partially hydrogenated oil is determined by the conditions of the hydrogenation. That to obtain a product of the same linolein number at another time

¹ U. S. Pat. 1,414,414, issued Nov. 19, 1922. A convenient amount of solid Nickel is used in a corresponding experiment.

TABLE IV—CHANGES IN CHEMICAL CONSTANTS

EXPERIMENTAL CONDITIONS DURING RUNS									
APPA- RATUS	RUN	Temp.	Pres- sure	CATA- LYZER	AGITATION	Sam- ple	—RUN I— Time I No.	—RUN II— Time I No.	—RUN I— Time I No.
Iron	1a	155°	20 lbs.	2% No. 1	135 R. P. M.	0	0:00 107.7	0:00 107.7	
	1b	155°	40 lbs.	2% No. 1	1	0:05 79.7	0:05 70.2	
						2	0:15 59.8	0:10 52.8	
						3	0:25 50.3	0:15 42.2	
						4	0:35 41.4	0:20 34.9	
						5	0:45 37.0	...	
Glass	Ic	35°	Atmos.	5% No. 1	Bubbling	0	0:00 111.0	0:00 111.0	0:00 111.0
	d	87°	Atmos.	5% No. 1	Bubbling	1	13:40 101.1	2:35 93.2	1:40 90.3
	e	125°	Atmos.	5% No. 1	Bubbling	2	27:00 96.7	5:50 83.0	2:55 79.5
	f	160°	Atmos.	5% No. 1	Bubbling	3	...	10:30 68.0	4:10 72.6
	g	200°	Atmos.	5% No. 1	Bubbling	4	...	12:25 62.4	6:10 58.9
	h	240°	Atmos.	5% No. 1	Bubbling	5	...	18:55 53.7	3:15 52.1
						6	...	25:55 40.5	...
							—RUN I— Time I No.	—RUN II— Time I No.	—RUN I— Time I No.
							0:00 110.9	0:00 110.0	0:00 111.0
							1:35 88.4	0:25 74.9	0:15 96.3
Glass	Ii	150-160°	Atmos.	54% No. 2	Bubbling	0	0:00 110.9	0:00 110.0	0:00 111.0
	j	150-160°	Atmos.	54% No. 2	Rate > doubled	1	2:22 79.6	0:35 71.5	0:15 96.3
						2	3:10 75.0	0:50 66.8	0:25 88.6
						3	3:58 71.7	1:05 63.5	0:36 82.6
						4	5:00 68.8	1:20 60.6	0:56 75.3
						5	6:35 66.5	1:35 60.6	1:26 65.0
						6	12:00 61.6	1:50 58.5	1:26 62.8
						8	28:20 52.2	2:20 57.2	1:56 60.3
Iron							—RUN I— Time I No.	—RUN II— Time I No.	—RUN I— Time I No.
	24 in. × 12 in. diam. Ik	155°	20 lbs.	2% No. 1	67 R. P. M.	0	0:00 110.9	0:00 110.9	0:00 108.4
	24 in. × 12 in. diam. l	155°	20 lbs.	2% No. 1	135 R. P. M.	1	0:45 82.7	0:10 95.3	0:04 101.3
	24 in. × 12 in. diam. m	155°	20 lbs.	2% No. 1	270 R. P. M.	2	1:00 74.4	0:20 81.4	0:07 96.8
	40 in. × 18 in. diam. n	155°	20 lbs.	2% No. 1	270 R. P. M.	3	1:30 62.9	0:30 70.3	0:12 91.3
						4	1:45 59.8	0:35 64.9	0:27 78.3
						5	2:15 54.3	0:40 60.5	0:37 73.3
						6	...	0:45 54.6	1:17 56.0
						7	1:57 50.0
							—RUN I— Time I No.	—RUN II— Time I No.	—RUN I— Time I No.
Iron	Io	155°	20 lbs.	2% No. 1	135 R. P. M.	0	0:00 107.7	0:00 107.7	
	p	155°	20 lbs.	4% No. 1	135 R. P. M.	1	0:05 79.7	0:04 77.2	
						2	0:15 59.8	0:08 57.6	
						3	0:25 50.3	0:12 42.9	
						4	0:35 41.4	...	
						5	0:45 37.0	...	

relatively higher in saturated glycerides and linolin, the operating conditions should compare as follows with those in the other case: temperature lower, pressure higher, agitation more violent and percentage catalyzer greater. It is interesting to note that it is possible to hydrogenate the linolin to olein with only the slightest increase in saturated glycerides by operating at a high

Meissl number and percentage of free fatty acids change either not at all, or only slightly.

It is evident that the saponification value could not be expected to change greatly, for the molecular weight of the mixture of stearin and palmitin corresponding to completely hydrogenated cottonseed oil is 873, while that of the original oil is about 865, a difference of less than 1 per cent. It is worth noting here that this 1 per cent represents all the hydrogen that is necessary to saturate the oil completely, a fact which partly accounts for the commercial attractiveness of the process.

The drop in iodine number, however, is one of the most striking effects of hydrogenation, and it has been commonly used in the past to indicate the progress of the reaction.^{1,2} Fokin concludes, from a study of the hydrogen absorption, that "the reduction procedure is included in the category of monomolecular reactions," but notices that the curves "often show a straightening out toward the abscissa axis." He comes to the conclusion that the conditions which determine the shape of the curve are: (a) the velocity of diffusion of the gas (presumably through the oil); (b) the condition of the catalyzing surface; and (c) the presence of catalyzer poisons. Very similar conclusions were published recently by Boeseken,³ but most of his work was on organic compounds of lower

FIG. 10

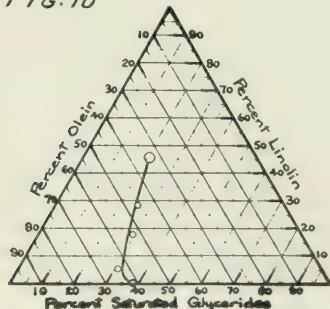


FIG. 10—HYDROGENATION CURVE: PALLADIUM CATALYZER

temperature, low pressure and low agitation, and using only a small amount of catalyzer.

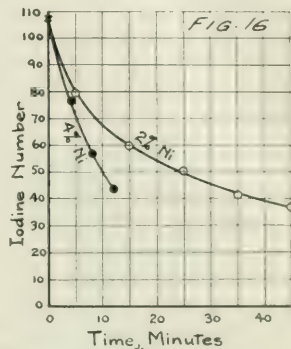
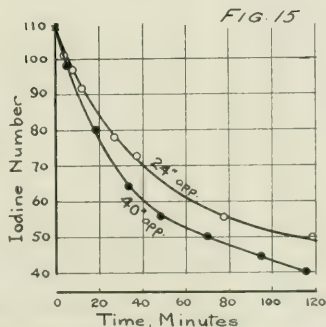
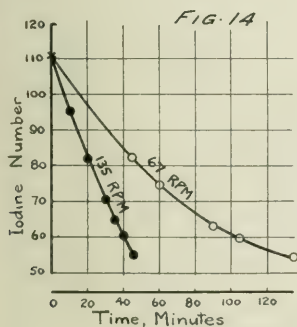
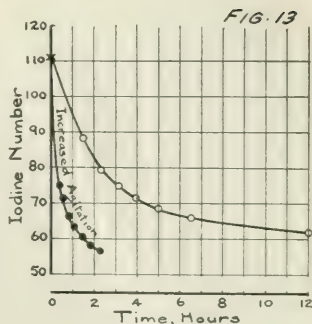
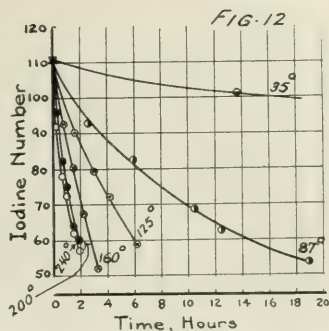
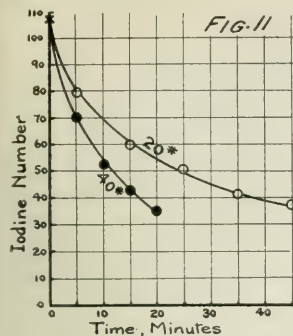
II—CHANGES IN CHEMICAL CONSTANTS OF OIL DURING HYDROGENATION

Of all the "chemical constants" of cottonseed oil, the iodine number (with its variations, the "hydrogen number," Mauméné number and heat of bromination), is the only one which is changed markedly by hydrogenation. Saponification value, acetyl value, Reichert-

¹ Paal-Roth, *Ber.*, **41**, pp. 2282-2291; Fokin, *J. angew. Chem.*, **23**, 1451-9, 1492-1502; Bömer, *J. Nahr. Genussm.*, **24**, 104-113.

² Paal and his co-workers, and Fokin recorded the volume of hydrogen absorbed at various stages of the process, thereby determining directly the amount of saturation which had taken place, instead of indirectly by means of the iodine number.

³ *Rec. trav. chim.*, **35** (1916), 260-287.



FIGS. 11 TO 16—CHANGES IN IODINE NUMBERS OF COTTONSEED OIL DURING HYDROGENATION

molecular weight than the oils. So far as we know, the effect produced in the iodine number time curve by varying experimental conditions has not heretofore been investigated. The factors we have considered have been (1) pressure; (2) temperature; (3) agitation, as affected either by changing the rate of bubbling hydrogen, changing the R. P. M. of a mechanical agitator, or changing the size of a machine at given R. P. M.; and (4) amount of catalyst. The experimental conditions and results appear in Table IV and in Figs. 11 to 16.

PRESSURE—Early investigators appreciated the fact that the hydrogenation reaction is accelerated by pressure, and so far as is known, all of the commercial oil-hardening processes are carried out at gas pressures ranging from 20 to 150 lbs. or even higher. This influence may be illustrated by Experiments Ia and b. Samples were withdrawn from time to time and iodine numbers were determined after filtering out the catalyst. In Fig. 11 the results are presented, the two curves of iodine-number vs. time being drawn on the same coordinates.

Comparison of the two curves of Fig. 11 shows that the time required to reduce the iodine number of the oil to any specified figure is roughly cut in half by doubling the pressure—i. e., in these experiments the rate of hydrogenation was approximately proportional to the hydrogen pressure.

TEMPERATURE—It is likewise well known that the

hydrogenation reactions in oil have a positive temperature coefficient—i. e., the rate is greater the higher the temperature, although the thermal decomposition of the oil sets an upper limit to the available range at about 250° C. The following Runs Ic, d, e, f, g, and h made under conditions identical except as to temperature (Fig. 12).

The hydrogenation reactions in oil have a positive temperature coefficient in the range between 35° and somewhat above 200° C.—possibly up to 240° C., but as may be seen from a study of the curves of Fig. 12, this coefficient drops consistently as the temperature rises. Thus for the range of temperatures 35–125° the time required to reach a certain iodine number is on the average decreased about 35 per cent for each 10° rise in temperature, while for the range 160–200° this coefficient is less than 20 per cent. Since the commercial processes nearly all operate at temperatures of 160–180°, it is evident that no material gain in time could be made by the use of higher temperatures, and the point of maximum economy is probably being realized.

AGITATION—The increase in velocity of reaction due to increased agitation of oil and catalyst with hydrogen may be illustrated for the bubbling apparatus by Runs If and i, which were made at 140–160° C. with cotton oil and 34 per cent of its weight of nickel reduced from the green oxide, and not on a carrier. In the second case the hydrogen was passed through the

flask at a little more than twice the rate obtaining in the first case (Fig. 13).

In this case an increase of about 100 per cent in the volume of hydrogen supplied increased the velocity of the reaction 800–1000 per cent. In apparatus of this type handling charges of commercial size it is not usual to cause such violent agitation as is easily brought about in a 2-liter flask, and it is doubtful whether doubling the hydrogen supply would on a large scale more than double the reaction-rate. The importance of efficient agitation, or of intimate commixture of the oil, catalyzer and hydrogen, has apparently been realized by nearly all of the workers in this field, as witness the patent files, but there is no observation recording such a great increase in agitation as the above, brought about by such simple means.

For the mechanical agitation Runs *Ik, l, m* and *n* may serve to show the effect of either changing the R. P. M. of the agitator (Fig. 14) or of changing the size of the apparatus without either altering the type of agitation or the R. P. M. of the agitator (Fig. 15).

Increasing the R. P. M. of a mechanical agitator is shown in Fig. 14 to produce a considerable increase in velocity. In this case the speed of rotation is changed from what might be called a "low" figure, 67, to a "moderate" figure, 135; doubling the speed again has been found in other experiments to give only a slight increase in agitation.

If the machine is increased in size, but not in type of agitation, Fig. 15 indicates that the agitation is more thorough at the same R. P. M. resulting in this case in the small machine requiring about 50 per cent longer time to reach a given iodine number.

CATALYZER—As in practically all catalytic reactions, the speed of hydrogenation is increased as the percentage catalyzer is raised. The quantitative relation will appear from Runs *Io* and *p* (Fig. 16).

The time required to reach a given iodine number in Curve *Ip* is seen to be approximately half of that required in *Io*, so that the reaction velocity is roughly proportional to the percentage of catalyzer. Considerations of outlay required for catalyzer preparation and recovery limit the amount used in commercial batch processes, however, to 1, or at most, 2 per cent. When a very good grade of refined oil is used, as little as 0.1 per cent nickel is common practice, high pressure and agitation being relied upon to reduce the time consumed.

SUMMARY OF IODINE NUMBER-TIME CURVES

To summarize, increasing the pressure, temperature, agitation or amount of catalyzer will increase the rate at which cottonseed oil is hydrogenated. This increase in rate is roughly proportional to the increase in pressure or amount of catalyzer, while raising the temperature 10° in the region of common practice, 160 to 180°, increases the rate only about 20 per cent. Increase in agitation (difficult to measure quantitatively) produces a marked increase in the reaction-rate.

It will be noted that all of these curves show a general similarity to the logarithmic curve which represents a monomolecular reaction, as Fokin pointed out.

As a matter of fact, however, in every case the curve flattens out sooner than would be expected, as though the catalyzer was losing its activity as the experiment progressed. It should be remembered, moreover, that even if all of the different reactions involved took place monomolecularly, it would by no means follow that the resultant iodine number-time curve would have the same characteristic. The relative rates of the reactions would determine the shape of the curve. It should be possible, then, by studying the iodine number time-curves mathematically, to draw some conclusions as to the relative velocities of the reactions involved; this would give indirectly a check on the results of the component glyceride analysis, as explained under "Hydrogenation Curves." We hope to report the results of such a study in a future communication.

III CHANGES IN PHYSICAL CONSTANTS OF OIL DURING HYDROGENATION

The most striking effect of the hydrogenation of an oil is, of course, the gradual increase in solidity, with the accompanying change in such physical constants as melting-point and titer. We are not aware that any quantitative investigation of these physical changes has yet been published.

MELTING-POINT—The change of melting-point was studied in an experiment in which the oil was hydrogenated with mechanical agitation of 108 R. P. M., temp. 160° C., pressure 20 lbs., catalyzer 5 per cent. nickel on a carrier. The melting-point and iodine number were among the constants determined on each sample, and these constants compared as follows (Fig. 17) (the last sample was in reality made in another experiment, but the product is identically the same as would be made under the above conditions):

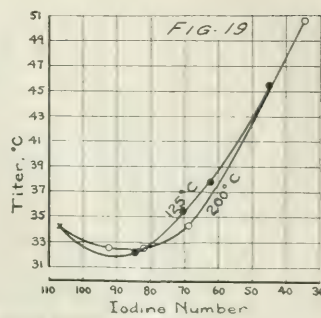
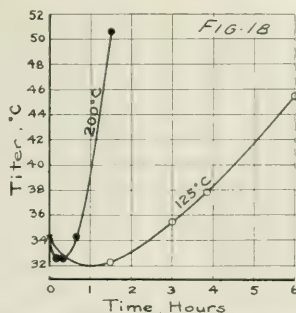
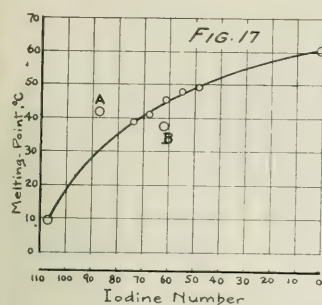
	M ₀	M ₁	M ₂	M ₃	M ₄	M ₅	M ₆
Melting point, ° C.	9.0 ¹	39.4	40.8	45.8	48.0	48.9	60.5
Iodine number	107	74.3	66.7	61.0	54.5	48.5	0.4

There can be no doubt that while the two ends of this curve remain fixed, the intermediate points are capable of considerable variation from the curve, depending on the conditions of hydrogenation. We have, for instance, the points *A* and *B* on Fig. 17. Sample *A* was made by one of the "continuous" processes from the same kind of cotton-oil, while Sample *B* was made at a very high temperature.

TITER—The titer of an oil or fat, being the solidification-point of its fatty acids, might be expected to share the characteristic of the melting-point of the fat, namely, a gradual increase on hydrogenation. It is found, however, to show the peculiarity of first decreasing, passing through a minimum, and then increasing steadily, as appears from the data from Runs¹ *Ta* to *b*.

Cotton-oil was hydrogenated in the bubbling apparatus with 5 per cent of nickel, on a carrier, in one case at 125° C., and in the other at 200° C. Titer and iodine number were among the determinations made on each sample. Time (from the beginning of the experiment), iodine number and titer are tabulated

¹ We have seen the results of experiments made under the direction of Dr. W. D. Richardson which, while conceived and carried out independently of us, confirm our conclusions in every respect.



FIGS. 17 TO 19—CHANGES IN PHYSICAL CONSTANTS OF COTTONSEED OIL DURING HYDROGENATION

below; in Fig. 18 titer is plotted against time and in Fig. 19 against iodine number.

Run Ta (125° C.)	Ta ₀	Ta ₁	Ta ₂	Ta ₃	Ta ₄
Time.....	1: 30	3: 00	3: 50	6: 00	
Iodine No.....	107.7	84.4	70.5	61.8	45.7
Titer, °C.....	34.26	32.35	35.50	37.80	45.50

Run Tb (200° C.)	Tb ₀	Tb ₁	Tb ₂	Tb ₃	Tb ₄
Time.....	0: 10	0: 20	0: 40	1: 30	
Iodine No.....	107.7	92.4	82.1	68.5	34.5
Titer, °C.....	34.26	32.60	32.65	34.35	50.7

The apparently anomalous fact that the addition of more saturated, higher melting acids at first lowers, instead of raising the solidification point is evidently due to the existence of a eutectic, or low-melting mixture of the components. According as the path of hydrogenation carries the composition close to or far from this point the minimum attained will be lower or higher. From Fig. 19 it is evident that the low-temperature run passed closer to the eutectic point than did the high-temperature run. Below iodine number 50 the two runs were practically identical, as would be expected from the fact that since linolin has largely disappeared the two hydrogenation curves of component glycerides cannot differ very greatly. Variation of other experimental conditions than temperature would probably bring about corresponding variations in the iodine number-titer curve.

From the curves of Fig. 18 it may be seen that to reach a given titer at 125° requires about four times as long as at 200°, an average coefficient of about 20 per cent for every 10° C.

IV. RESPONSE TO HALPHEN TEST

Hydrogenated cottonseed oil was first stated by Paal and Roth¹ to give no coloration when subjected to the characteristic Halphen test² and the same statement has been made by later investigators. The amount of hydrogenation which is required to render the oil just incapable of responding to the test has not to our knowledge, been investigated. To determine that point a quantity of oil was hydrogenated in the bubbling apparatus, temperature 150–160° C., 2 per cent nickel on a carrier acting as catalyst. Samples were taken (a) of the original oil, (b) of the mixed oil and catalyst before heating, (c) of the mixed oil and catalyst when heated to 150° C., 5 minutes being required to reach this temperature, (d) after 5 min. hydrogenation, (e) after 9 min. hydrogenation, and (f)

after 15-min. hydrogenation. A similar sample of oil was heated to 150–160° for 20 minutes in the absence of any hydrogen or catalyst, and was then found to give the same intensity of Halphen test as Sample a. The other samples gave tests as follows:

Sample	Iodine Number	RESULT
b.....	104.9	Not noticeably diminished
c.....	103.7	Distinctly weaker test
d.....	102.7	Faint test in 3 minutes
e.....	101.3	Faint test after heating 1½ hours
f.....	97.6	Negative even after heating 1½ hours

A drop of four units in iodine number may be said to have destroyed the chromogenetic substance.

V—CATALYZERS

Our observations in the field of catalyzers are principally of interest as showing the effect of various poisons on the activity of the material. The powerful poisoning effect of certain gases has been known ever since the researches of Sabatier and Senderens, but the influence exerted by solid and liquid impurities does not seem to have been determined.

The mode of preparation of the catalyzers used in experiments described in this article was as follows:

1—Green nickel oxide was ground to pass a 150-mesh sieve, and was reduced in a current of hydrogen for about 4 hours, temperature 320 to 340° C., pressure 30 to 60 lbs. It was mixed with a certain amount of cottonseed oil before exposing to the air.

2—Basic nickel carbonate precipitated from the sulfate in the presence of finely divided infusorial earth was calcined to nickel oxide and then reduced in hydrogen at 400 to 500° C., atmospheric pressure, for periods ranging from 4 to 11 hours. The product was also mixed with oil before exposing to the air.

The experiments on poisons were carried out in the bubbling apparatus, a mixture of oil with 1 per cent nickel on a carrier being hydrogenated first for one hour to ascertain the original activity of the catalyst. At the end of the hour, 2 per cent of the finely powdered solid substance in question was added, and the hydrogenation continued. Samples were then taken at intervals to determine the further loss of the iodine number, and the poisoning effect was judged by the shape of the iodine number-time curve compared to one in which no poison was present. The results may be summarized as follows:

¹ Paal and Roth, *Ber.*, **42**, 1909, 1541–1553.

² *J. O. A. C.*, No. 3, 1916, 313.

SUBSTANCE	EFFECT ON ACTIVITY
Sulfur.....	Destroyed immediately
$\text{Na}_2\text{S}_2\text{O}_3$	Gradually destroyed
NaCl	No effect
Na_2SO_4	No effect
NaNO_3	No effect
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	No effect
Reduced iron.....	No effect

The three gases H_2S , SO_2 , and Cl_2 were also tried. In each case the activity was destroyed immediately. A small amount of water vapor in the hydrogen was found gradually to destroy the activity of the catalyzer.

GENERAL SUMMARY

I—The lead-salt-ether method for separating the liquid fatty acids of oils and fats has been studied, and certain important precautions are noted.

II—The triangular diagram has been applied to the study of oil hydrogenation.

III—It has been shown that the conditions of hydrogenation, namely, pressure, temperature, per cent catalyzer and degree of agitation, affect the proportions of "saturated glycerides," "olein," and "linolin" in partially hydrogenated cottonseed oil.

IV—By studying iodine number-time curves the effects within certain limits of pressure, temperature, per cent catalyzer and degree of agitation upon the velocity of hydrogenation have been determined.

V—The changes undergone by melting-point and titer during hydrogenation are studied by means of curves against iodine number and time as the other variables. The titer is shown to pass through a minimum before beginning its increase.

VI—The degree of hydrogenation necessary to destroy the response of cottonseed oil to the Halphen test has been shown to be a drop of about four units in iodine number.

VII—A number of solid inorganic materials are shown to have no effect on the activity of a catalyzer; sulfur and sodium sulfide, on the other hand, are found to destroy the activity.

We wish to acknowledge with thanks the many valuable suggestions made by Messrs. R. S. Pease, E. B. Sebben and H. C. Fuller of this laboratory, who have in addition carried out most of the experimental work described in this article.

RESEARCH LABORATORY
BERLIN MILLS COMPANY
BERLIN, NEW HAMPSHIRE

THE CHEMICAL COMPOSITION OF THE HIGHER FRACTIONS OF MAPLEWOOD CREOSOTE¹

By ERNEST J. PIRPER, S. F. ACREH and C. J. HUMPHREY

Received March 7, 1917

Investigators² both in Europe and this country have studied the constituents of the creosote oil obtained from beechwood tar, and in some cases from oakwood tar, but no one, as far as is known to the writers, has ever before attempted the study of maplewood creosote. The fact that different species of hardwoods show a considerable difference in analysis might lead

¹ The present paper is one of four prepared by the junior author in partial fulfillment of requirements for the degree of Doctor of Philosophy in the University of Wisconsin.

² Hofmann, *Ber.*, 8, 67; 11, 329; 13, 1371; Liebermann, *Ann.*, 169, 23; Tiemann and Koppe, *Ber.*, 14, 2005; Behal and Chao, *Compt. rend.*, 116, 197; 119, 166; Kebler, *Am. Jour. Pharm.*, 1889, 409; *J. Soc. Chem. Ind.*, 1894, 1087, 1187; 1897, 367, Abstracts.

one to suppose that there would possibly be a decided difference in the composition of the wood tars obtained in destructive distillation.

A commercial sample of maplewood creosote¹ was obtained by the Forest Products Laboratory. This creosote was heated in an iron retort, and 15 liters were distilled in three separate runs, the fractions reported in Table I being collected and their volumes and weights determined.

TABLE I—FRACTIONS OF MAPLEWOOD CREOSOTE

Fraction °C.	Volume Cc.	Weight Grams	Per cent by volume of entire distillate
93–115	760	709.46	6.23
115–195	840	844.20	7.40
195–210	815	811.84	7.10
210–215	445	443.22	3.89
215–220	840	867.72	7.72
220–225	590	605.34	5.40
225–230	805	821.50	7.20
230–235	1000	1,029.60	9.06
235–240	1000	1,029.50	9.04
240–245	480	496.80	4.36
245–250	740	771.82	6.77
250–255	515	532.51	4.67
255–265	1375	1,442.38	12.66
265–280	950	979.93	8.60
TOTAL.....	11,155	11,385.62	100.00
Loss.....	95		
11,250 cc. = Total Distillate = 75 per cent of Wood Creosote			
3,750 cc. = Pitch = 25 per cent of Wood Creosote			
15,000 cc. = Total Wood Creosote			

The percentages of total distillate contained in the three fractions 93–195° C., 195–230° C., and 230–280° C. are shown in Table II. The first fraction consists principally of water and some pyrolygous acid; the second principally of the mono- and di-hydroxy phenols, especially guaiacol and cresol; and the third mainly of the tri-hydroxy phenols, especially pyrogallol-dimethyl-ether and its homologues. The pitch residue is being thoroughly investigated.

TABLE II—FRACTIONS OF MAPLEWOOD CREOSOTE

Fraction °C.	Volume Cc.	Per cent of Total Distillate
93–195	1600	13.63
195–230	3495	31.21
230–280	6060	55.16

Just as in the case of other wood creosotes, the relation shown in Table II is not absolutely constant, but depends upon a number of factors, such as the method of distilling the raw material, etc.

A liter of the crude wood creosote was then distilled from the iron retort, and the distillate fractionated from a glass vessel connected with a Hempel column. The fraction above 195° C., which we will term the creosote oil, was a light yellow oil with a specific gravity of 1.04 at 20° C. When well shaken in a separatory funnel with an equal volume of 15 per cent NaOH solution to dissolve and separate the acid oil from the neutral oil, the latter floated to the top of the mixture and was removed and shaken with more alkali to dissolve any remaining acid oil. One treatment of the refined creosote with an equal volume of 15 per cent NaOH solution is usually sufficient to dissolve practically all the acid oil. The neutral oil obtained was washed with water until free from alkali, and distilled from a glass vessel connected with a Hempel column.

The alkali extract was then treated with dilute sulfuric acid until slightly acid. The acid oil which

¹ After standing several months the sample showed a gradual and partial change into pitch.

separated was washed with water until free of sulfuric acid and was then distilled in the same manner as the neutral oil.

The entire creosote oil (above 195° C.) gave 24 per cent neutral oil, and 68 per cent acid oil. Evidently 8 per cent was lost in the process of separation.

Table III shows the percentage of acid and neutral oils found in the fractions above 230° C.

TABLE III—ACID OIL AND NEUTRAL OIL IN MAPLEWOOD CREOSOTE

Fraction ° C.	Per cent Acid Oil	Per cent Neutral Oil	Per cent Loss
230–240	70	23	7
240–250	86	8	6
250–255	79	13	8
255–265	84	8	8
265–280	85	6	9

In the separation of the neutral oil from the acid oil in the fractions boiling above 230° C. a crystalline sodium salt was precipitated in the presence of an excess of a 15 per cent NaOH solution. Hofmann,¹ Liebermann, and other investigators also obtained a sodium salt in the same manner in their investigation of the oils of beechwood creosote. The identification of this sodium salt from maplewood creosote was, therefore, undertaken and the results compared with those obtained from beechwood creosote.

FRACTION 230–240° C.

This fraction was redistilled and 1700 cc. (1785 grams) were treated with an equal volume of 15 per cent NaOH whereupon the neutral oil immediately separated. A white crystalline sodium salt precipitated from the alkaline solution and was filtered by suction and washed with a mixture of alcohol and ether: 20 g. of an apparently pure white substance were obtained in this way. The material is easily soluble in water, less soluble in ethyl alcohol and methyl alcohol, and insoluble in ether, benzene, acetone or chloroform. On standing in the air, or more quickly on heating, the sodium salt turned blue. This color change was due to an oxidation and will be explained later in detail.

The salt was treated with dilute sulfuric acid until the solution was slightly acid: 15 g. of a heavy oil were precipitated out and were washed with water in a separatory funnel until free of sulfuric acid. It was taken up in ether, separated from the aqueous solution, and after evaporation of the ether was distilled under reduced pressure. In this manner a very pale yellow, almost colorless oil was obtained which boiled between 253–275° C. The oil had a spicy peppermint odor and gave a brownish-red coloration with ferric chloride.

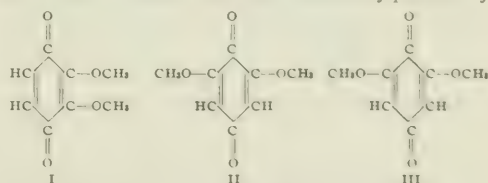
Treating 2 g. of the oil with benzoyl chloride in a strongly alkaline solution gave 2.9 g. of the benzoyl derivative after the first crystallization from alcohol. It was very difficult to obtain a substance which melted sharply. It was found that part of the benzoyl derivative was soluble in petroleum ether at room temperature. The solution was filtered by suction from the insoluble portion, and from the filtrate a fraction was obtained which on six crystallizations from alcohol had the melting point 90–91° C. The portion insoluble in cold petroleum ether was treated

with fresh petroleum ether and heated on a steam bath for a few minutes and quickly filtered. This operation was repeated several times and from the filtrates a benzoyl derivative was obtained which on 10 crystallizations from alcohol had the melting point 110–111° C. The residue insoluble in warm petroleum ether was recrystallized from alcohol and after 6 crystallizations showed a melting point of 117–118° C. It is evident, therefore, that the oil consists of a mixture of substances which gave three definite benzoyl derivatives.

On oxidation with potassium bichromate and dilute acetic acid the oil gave a mixture of coerulignone and dimethoxyquinone, whose constitutions are discussed below. On heating the mixture with warm glacial acetic acid the dimethoxyquinone was dissolved while the coerulignone was unaffected. On recrystallizing the dimethoxyquinone from glacial acetic acid a sharp melting point of 246° C. was obtained.

Hofmann¹ obtained dimethoxyquinone by oxidizing propyl-pyrogallol-dimethyl-ether. Later, Will² obtained dimethoxyquinone, together with mononitropyrogallol-trimethyl-ether by oxidizing the trimethyl-ether of pyrogallol with concentrated nitric acid. At the same time he obtained dimethoxyquinone by oxidizing the trimethyl-ether of propyl-pyrogallol which he obtained by treating the propyl-pyrogallol-dimethyl-ether with methyl iodide and potassium hydroxide.

Will considered that there are two possible structures (I and II) for this dimethoxyquinone. Ciamician and Silber³ obtained the same dimethoxyquinone by



oxidizing the trimethyl-ether of phloroglucin and considered the structure to be as shown in III.

The coerulignone obtained is insoluble in the ordinary solvents. It can be obtained very pure by dissolving it in phenol at 30° C. and treating the solution with alcohol or ether. In this way deep violet-blue needles are formed. Hofmann⁴ obtained coerulignone by the oxidation of the dimethyl-ether of pyrogallol obtained from beechwood tar. Alkalies and acids decompose coerulignone, giving a violet-blue color with acids. Coerulignone is easily reduced to hydrocoerulignone. Liebermann and Flatau⁵ showed that coerulignone condenses with primary amines to give blue dyes containing only two methoxy groups.

Hofmann believed coerulignone to have the constitution I (shown above) while Liebermann and Flatau showed that there were in addition two possibilities II and III.

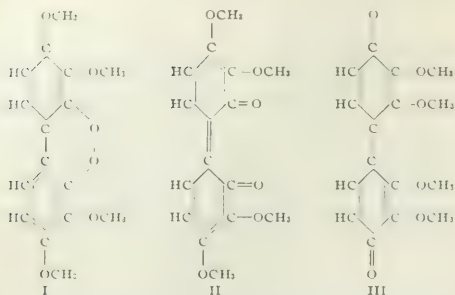
¹ Ber. 11, 1185, 1186.

² Ber. 21, 1888, 1889.

³ Ber. 26, 1888, 1889.

⁴ Ber. 11, 1185, 1186.

⁵ Ber. 30, 1897, 1898.



It should also be noted that there is a possibility of having the methoxy groups in the following positions with respect to the C=O group: (1) *ortho-ortho-ortho-ortho*; (2) *ortho-ortho-meta-meta*; and (3) *meta-meta-meta-meta*.

FRACTION 240-250° C.

From 1189 g. of this fraction 106 g. of a sodium salt were obtained as in the previous fraction. The oil obtained, 52.7 g., boiled between 255-269° C. On benzylation two derivatives were obtained with the melting points 110-112° C. and 116-117° C. On oxidation the oil gave a mixture of coerulignone and dimethoxyquinone. On treating a chloroform solution of the oil with bromine a crystalline derivative was obtained after the solution had stood for a week. After 3 crystallizations from alcohol the derivative showed a melting point of 125-126° C.

On treating the oil with methyl alcohol saturated with HCl gas and heating in a sealed tube at 125-130° C. for 5 hours, a charred residue was obtained which was dissolved in absolute alcohol. A few crystals which had the melting point 127-128° C. separated on standing. The amount was too small for purification.

FRACTION 250-255° C.

The sodium salt, 34 g., obtained from 501 g. of this fraction was treated as in the previous fractions, and 17 g. of an oil were obtained which distilled between 249-258° C. On oxidation the oil gave only coerulignone. On benzylation a derivative was obtained which gave a melting point of 111-112° C. after 8 crystallizations. No crystalline derivative was obtained on treating the oil with a saturated alcoholic solution of hydrochloric acid.

FRACTION 255-265° C.

The sodium salt, 221 g., secured from 1123 g. of this fraction was treated as in the previous fractions and 92.5 g. of an oil¹ distilling between 251-269° C. was obtained. On benzylation a derivative was obtained which had the melting point 110-111° C. On oxidation coerulignone was obtained. When treated with alcohol saturated with HCl gas, as in the previous fractions, a pronounced odor of methyl chloride was observed, but no crystalline compound was obtained.

Five grams of oil were then treated in a methyl alcoholic solution with an excess of 25 per cent NaOH

¹ It is advisable to centrifuge the oil in the higher fractions when suspended in water. This will separate any paraffin that is present.

solution and dimethyl sulfate was added drop by drop until an excess was present. The solution was then heated on the steam bath until the excess of dimethyl sulfate was decomposed. The sodium sulfate was removed by treating the solution with alcohol, and the filtrate was shaken with ether. On evaporation an oily residue was obtained which from alcohol gave a few crystals with the melting point 43-46° C.¹ The mother liquor obtained from the crystals above gave dimethoxyquinone on oxidation with cold concentrated nitric acid, and therefore contained pyrogallol-trimethyl-ether but no appreciable amount of pyrogallol-dimethyl-ether.

The remaining methylated oil was boiled with a concentrated solution of potassium permanganate until all the oil had been decomposed. The excess of permanganate was decomposed with warm alcohol, the solution filtered and the filtrate acidified with dilute sulfuric acid. The solution was treated with ether and an oily residue was obtained from the extract. When this oil was kept in a refrigerator for several days a few crystals were formed which, without crystallization, melted at 92-96° C.

Will² obtained a trimethyl-ether of pyrogallol carboxylic acid which melted at 99° C. By the use of potassium permanganate he first oxidized the methyl pyrogallol to the pyrogallol carboxylic acid and then methylated the methyl ester with potassium hydroxide and methyl iodide. The ester was afterwards converted into the free acid melting at 99° C.

FRACTION 265-280° C.

The sodium salt, 135 g., from 642 g. of this fraction gave 78 g. of oil which distilled between 256-271° C. On benzylation a derivative was obtained which had the melting point 111-112° C. On oxidation, coerulignone, together with a possible trace of dimethoxyquinone, were obtained.

On methylation with dimethyl-sulfate an oily residue was secured which gave dimethoxyquinone on oxidation with concentrated nitric acid. The oily residue was oxidized with potassium permanganate but no crystalline product was obtained. Equal parts of the oil from this fraction and phenyl mustard oil, together with a trace of solid sodium hydroxide, were heated in a sealed tube immersed in a steam bath for three days. The crystals that separated on cooling were filtered by suction and recrystallized several times from alcohol. Crystalline leaflets were obtained with a melting point 156-157° C. In a similar manner a compound with the same melting point was obtained from the oil of the sodium salt of fraction 255-265° C. The sulfur was determined according to the Carius method:

0.1493 g. gave 0.1283 g. BaSO₄ or S, 11.61 per cent.
Calculated for C₆H₃(OCH₃)₂OSCNC₆H₅: S, 10.99 per cent.

This reaction with phenyl mustard oil will be further investigated to see if it offers a method of isolating crystalline derivatives of the different phenolic compounds present in the wood creosotes.

¹ Will obtained a trimethyl-ether of pyrogallol, which melted at 47° C., by treating pyrogallol with methyl iodide and potassium hydroxide in methyl alcohol.

² Ber., 21 (1888), 607.

The percentage of methoxyl groups in the oil of this fraction was determined according to the Zeisel¹ method. In the apparatus (Fig. 1) all connections were made by means of ground-glass joints, and specially modified washing bottles containing the red phosphorus and silver nitrate, respectively, were used:

0.1063 g. oil gave 0.2839 g. AgI or CH_3O , 35.25 per cent.
Calculated for $\text{C}_8\text{H}_8(\text{OCH}_3)_2(\text{OH}) : \text{CH}_3\text{O}$, 40.26 per cent.

The difference arises because the oil is probably a mixture. This will be further studied.

In the same manner methoxyl determinations were made on the benzoyl derivatives melting at 110–

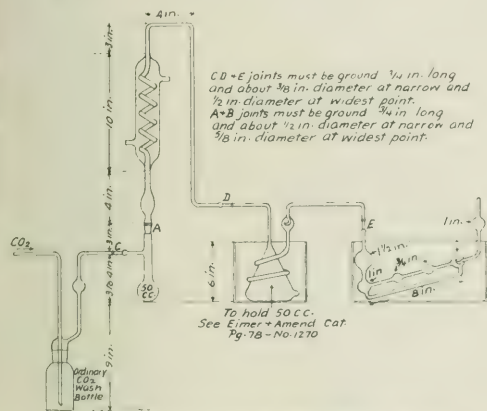


FIG. 1—ZEISEL APPARATUS FOR DETERMINING CH_3O GROUP

111° C., and 116–117° C., respectively, but not enough of the derivative melting at 90–91° C. was obtained to determine the percentage of methoxyl group.

BENZOYL DERIVATIVE M. P. 110–111° C.

0.1347 g. gave 0.2377 g. AgI, 0.03137 g. $\text{CH}_3\text{O} = 23.29$ per cent.
Calculated for $\text{C}_8\text{H}_8(\text{OCH}_3)_2\text{OCOC}_6\text{H}_5$: 24.02 per cent.

BENZOYL DERIVATIVE M. P. 116–117° C.

0.0918 g. gave 0.1531 g. AgI, 0.02021 g. $\text{CH}_3\text{O} = 22.01$ per cent.
Calculated for $\text{CH}_3\text{C}_6\text{H}_5(\text{OCH}_3)_2\text{OCOC}_6\text{H}_5$: 22.79 per cent.

The following methoxyl determinations were also made:

Crude tar, 6.81 per cent CH_3O , acid oil (195–255° C.), 11.06 per cent, neutral oil (195–260° C.), 5.14 per cent, pitch, 5.10 per cent.

The results secured from the study of the sodium salt obtained from the higher boiling fractions of maplewood creosote are summarized in Table IV. In the first and second columns are given the names of the compound or compounds identified and the corresponding characteristic oxidation product which was obtained. In the third column is given the melting point of the characteristic benzoyl derivative.

From these results it is evident that the oil obtained from the sodium salts of the fractions above 230° C. consists primarily of a mixture of pyrogallol-dimethyl-ether and methyl-pyrogallol-dimethyl-ether, together with a trace of propyl-pyrogallol-dimethyl-ether.

It was previously mentioned that the sodium salt

TABLE IV—PRODUCTS OBTAINED FROM THE OIL PRODUCED FROM THE SODIUM SALT

Fraction °C.	Compound identified	Oxidation Product	M. P. Benzoyl Derivative
230–240	I. Pyrogallol - dimethyl-ether.....	Coerulignone	110–111° C.
	II. Methyl - pyrogallol-dimethyl-ether.....	Dimethoxyquinone	117–118° C.
	III. Propyl - pyrogallol-dimethyl-ether.....	Dimethoxyquinone	90–91° C.
240–250	I.	Coerulignone	110–112° C.
(a)	II.	Dimethoxyquinone	117–118° C.
250–255	I.	Coerulignone	111–112° C.
255–265	I.(b)	Coerulignone	110–111° C.
	II.	Dimethoxyquinone	111–112° C.
265–280	I.(b)	Coerulignone	111–112° C.
	II. or III.	Dimethoxyquinone (trace)	

(a) This oil gave a brom derivative m. p. 125–6°. A compound melting at 127–8° was obtained by treatment with alcoholic hydrochloric acid.

(b) We also obtained a phenyl mustard oil addition product melting at 156–157° C.

(c) The pyrogallol-dimethyl-ether in this fraction was converted into the 43–6° m. p. trimethyl-ether and the 92–96° m. p. trimethyl-ether carboxylic acid was obtained from the methyl-pyrogallol-dimethyl-ether.

turned blue in the air or more quickly on heating. Hofmann¹ also found that the sodium salt obtained from the higher fractions of beechwood creosote turned blue, and showed that the color was due to the formation of euphonic acid or hexamethoxyaurine $[\text{C}_{19}\text{H}_8\text{O}_3(\text{OCH}_3)_6]$, from the oxidation of two molecules of pyrogallol-dimethyl-ether and one molecule of methyl-pyrogallol-dimethyl-ether in the presence of an alkali. We have isolated this dye and find that the aqueous solutions of its alkali salts are deep indigo-blue. Acids change it to a carmine-red solution.

The sodium salt obtained from the higher fractions of maplewood creosote was in general about the same as was found by Hofmann in beechwood creosote. One decided difference is apparent in the amounts of these constituents present. The higher boiling fractions of beechwood creosote contained a considerable quantity of propyl-pyrogallol-dimethyl-ether, while in maplewood creosote there was only a small quantity of this substance present, the principal constituents being pyrogallol-dimethyl-ether and methyl-pyrogallol-dimethyl-ether.

SUMMARY

I—A commercial sample of maplewood creosote gave 75 per cent of wood creosote and 25 per cent pitch. About 14 per cent of the creosote boiled at 93–105°, 31 per cent at 195–230°, and 55 per cent at 230–280°.

II—When the different fractions of creosote were extracted with alkalies, from 70 to 85 per cent was found to be phenolic compounds.

III—The sodium salts of some of the phenols were isolated and found to consist chiefly of pyrogallol-dimethyl-ether, methyl-pyrogallol-dimethyl-ether, and propyl-pyrogallol-dimethyl-ether. These substances were identified by their oxidation products and benzoyl derivatives. These sodium salts are therefore identical with those found by others in beechwood creosote, but differ in the amount present. These and other substances present in a number of commercial hard wood tars are being further investigated in the laboratory.

INVESTIGATION IN THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, IN CO-OPERATION WITH THE FOREST PRODUCTS LABORATORY, MADISON, WISCONSIN

PREPARATION OF BLACK OXIDE OF URANIUM (UO_2)¹

By CHARLES L. PARSONS

Received April 6, 1917

In the extraction of uranium from its ores, the uranium is almost invariably obtained in the form of sodium uranate, $\text{Na}_2\text{U}_2\text{O}_7$. This material is sold to the trade as "yellow oxide of uranium" and is used chiefly to give to glass the rich, yellow tint characteristic of uranium and its salts.

Sodium uranate of course does not lend itself readily to the production of alloys of uranium and for this purpose it is desirable to obtain the material in the form of oxide. Indeed, there can be little doubt that the more concentrated form which the pure oxide offers would render this material more desirable even for use in glass works.

There have been rumors of some two years' standing that uranium steel is being used in Germany in some of the larger cannon. These rumors have recently been corroborated and there appears to be no question that in Germany uranium steel has been developed which softens at a temperature higher than any steel heretofore used in cannon. Some of the larger guns have a rigidity under repeated fire and high temperature which allows them to be used through a longer period of intense firing without impairing their accuracy than was formerly possible.

Uranium has also been proposed and, indeed, used to replace tungsten in tool steel—the claim being that 1 per cent uranium can successfully replace from 6 to 12 per cent tungsten. It has accordingly become important to be able to procure uranium oxide cheaply, in order that ferro-uranium might be readily produced. A report on the production of ferro-uranium has already appeared² in THIS JOURNAL.

Uranium oxide has now been prepared to the amount of several tons in the Denver plant of the National Radium Institute. The details of its early production have already been explained.³ The method first used to make it was by precipitating as ammonium uranate. This required too many precipitations to separate the sodium entirely, and, accordingly, on ignition of the ammonium uranate a considerable amount of sodium uranate remained with the uranium oxide. As the method was also very costly, it was abandoned. In like manner the attempt to volatilize sodium oxide from the uranium oxide at the high temperature of the electric arc was not successful commercially owing to the dangerous explosions that took place. The cause of these explosions was never satisfactorily explained but they were probably due to the production of metallic sodium. Fortunately, some simple experiments which I carried out in the laboratory led to an immediate and easy solution of the problem. These experiments were suggested by a reaction first mentioned by Wohler⁴ and made use of analytically by

Hillebrand,¹ when, in a study of uranium compounds, he fused uranyl chloride with a mixture of ammonium and sodium chlorides, obtaining thereby a reduction of the uranium chloride to uranyl oxide.

It is of course evident at once that sodium uranate, if treated with hydrochloric acid, would give a mixture of salt and uranyl chloride and if this were fused with more salt and ammonium chloride, uranium oxide would probably result. This was found to be true, but the process worked successfully only in small quantities with a large excess of ammonium chloride and could not be applied commercially. Based, however, on the principle that a reducing agent acting on uranyl chloride should give, in a fused salt bath, uranium oxide, a series of experiments led to the final simple result that it was necessary only to fuse sodium uranate itself in a salt bath in the presence of carbon to yield the desired product. As soon as this was determined the method was applied on a plant scale. For some months now, the production of uranium oxide has been going on almost daily in the plant of the National Radium Institute and a purer uranium oxide than has ever been made in quantity heretofore has been turned out in lots of several tons. The method first adopted and still used is as follows:

A cast steel pot, made of pure low-carbon steel, 19 in. deep by 16 in. wide with walls $\frac{3}{4}$ in. thick, is filled with a mixture containing 35 parts salt, 20 parts sodium uranate and 1 part ground charcoal. The whole is heated by an oil burner in a crucible furnace. In first starting the run the pot is filled with a carefully mixed charge. Under the influence of the heat, reaction begins on the bottom and sides and the carbon monoxide bubbles up through the thick, pasty melt. The material should not be stirred during the operation but the reaction should be allowed to continue to completion, more charge being added from the pot from time to time as it settles down under the reaction. In this manner about one-third more material than the pot would ordinarily hold can be added and the melt when finished leaves the pot approximately four-fifths full.

Reaction takes place at a red heat and is allowed to continue until no more gas escapes from the mass. The oxide should then be dipped (not poured) from the bottom of the pot with a long-handled iron ladle and ladeled together with the salt melt into an iron pot or trough where the mixture can cool. Approximately 4 runs per day per furnace can be made. The following figures represent the quantities used during a month's run with two furnaces:

NO. OF CHARGES	SODIUM URANATE	SODIUM CHLORIDE	CARBON
174	9680 lbs.	17,776 lbs.	495 lbs.

The steel pot is but little attacked on the inside but scales off on the outside from the action of the flame and accordingly lasts for only 35 to 40 charges.

The reaction is practically quantitative and no uranium oxide is lost in the flux. Owing to the light

¹ Published by permission of the Director of the Bureau of Mines.

² H. W. Gillett and E. L. Mack, "Ferro-Uranium," THIS JOURNAL, 9 (1917), 342.

³ Parsons, Moore, Lind and Schaefer, "Extraction and Recovery of Radium, Uranium and Vanadium from Carnotite," Bull. Bur. Mines, 104.

⁴ Gmelin Kraut, 6 Ed., Vol. 2, Part 2, p. 372.

¹ W. D. Hillebrand, Z. anorg. Chem., 3 (1893), 243.

character of the charge a small amount of sodium uranate is apparently lost in the flues. After cooling, the salt mass containing the uranium oxide is readily broken with a hammer and easily dissolves in water. In practice the material for the day's run is put, at the end of the day, in a large box with an iron sieve bottom and placed in the top of a tank containing water. During the night the salt dissolves and the fine powdered uranium oxide passes through the sieve and settles in the bottom of the tank. By bringing the water to the boiling temperature with steam and stirring the contents of the tank, the uranium oxide is quickly and thoroughly washed and, as it is very heavy, it can be almost immediately separated by decantation. The oxide so obtained generally contains some iron and some aluminum. These can, for the main part, be separated by washing the uranyl oxide with a 5 per cent solution of hydrochloric acid, in which it is not soluble. The acid dissolves the main part of the iron and aluminum compounds. In this way it is a simple matter to obtain uranyl oxide almost pure. In commercial practice a purity equivalent to 97 per cent U_3O_8 is obtained, no attempt being made to separate all of the iron as its presence is not deleterious in the production of ferro-uranium.

One of the advantages of the process is that vanadium, if present, is easily separated and recovered at the same time. Sodium uranate made from carnotite always contains vanadium in some quantity. In the procedure described above the vanadium stays in the salt as sodium vanadate, dissolves with the salt, and can be readily precipitated therefrom, in a high degree of purity, by iron sulfate. Indeed, the recovery of the vanadium will about half pay for the whole operation.

The cost of producing "black oxide" of uranium from sodium uranate by this method varies with conditions. The average cost of conversion during the last 4 months of operation has been slightly less than 11 cents per lb. This might be made considerably lower by running the furnace continuously, or it might be increased if the furnace were run more intermittently. It will, of course, also vary with the cost of fuel oil.

In the operations of the National Radium Institute the cost of conversion has varied from around 9 to 13 cents per lb., depending upon conditions.

BUREAU OF MINES, WASHINGTON

THE EXTRACTION OF POTASH FROM SILICATE ROCKS—II

By WILLIAM H. ROSS

Received March 5, 1917

In a previous publication¹ an account has been given of a preliminary investigation on the possibilities of recovering potash from insoluble silicates. It was shown that when 1 part of feldspar and 3 parts of calcium carbonate were ignited for about an hour at a temperature of 1300–1400°, the potash in the feldspar was completely volatilized and the clinker which remained had a composition which fell between the limits required for Portland cement.

It was also observed that when part of the lime was replaced with a quantity of calcium chloride equivalent to the alkalies in the feldspar, volatilization took place in about half the time required when the ignition was made with lime alone. As a result of these experiments it was concluded that potash could be set free from feldspar by substituting the latter for clay in the manufacture of cement; that the potash would be volatilized to a greater or less extent, and could be recovered in the flue dust; and that it should be possible to obtain raw materials which on ignition would form a residue of the composition required for Portland cement clinker.

Since potash silicates occur in the raw materials used in the manufacture of cement and as the temperature of clinkering is equal to that used in the feldspar experiments, it might be expected that complete volatilization of the potash would also take place in the burning of cement. The heating zone of a rotary kiln constitutes, however, only a comparatively short proportion of its length and while the charge occupies more than an hour in passing through the kiln, the time that it is subjected to a clinkering temperature is less than that required to bring about complete volatilization of the potash. The length of the kilns has also a retarding effect on the evolution of the potash. While complete volatilization for these reasons does not take place in any case, it is now known that the escape of potash from cement plants is considerable and from analyses which have recently been made in this laboratory it has been found that the percentage of the total potash in the raw mix which is volatilized in different cement plants in this country varies from about 25 to 95 per cent. In several cement plants this potash is now being collected with the flue dust by electrical precipitation and is used directly in the manufacture of fertilizers, or the potash is leached from the dust and disposed of separately. Recent developments have thus confirmed the conclusions previously reached that one of the most promising methods of recovering potash from potash silicates was by the use of the latter in the manufacture of cement.

Since the publication of the preliminary report referred to, a great deal of attention has been given in this laboratory to the further investigation of this subject, particularly along the lines suggested in the numerous patents which have been granted on processes for the extraction of potash from insoluble silicates. It was soon concluded that owing to the limited percentage of potash occurring in any insoluble potash silicate, no process for recovering potash from these silicates can prove economical unless there is recovered at the same time some other product of value in addition to the potash.

The patented processes which relate to this subject now exceed 100 in number. Almost one-third of the total number make no claims to recover any product other than the potash.¹ In the remaining processes,

¹ U. S. Patents 5,384, 49,943, 511,001, 641,406, 772,536, 789,074, 831,922, 910,662, 952,278, 959,841, 987,436, 993,463, 1,011,172, 1,029,378, 1,056,808, 1,068,853, 1,091,044, 1,091,240, 1,148,890, 1,189,805, 1,199,604, 1,176,613, 1,194,464, 1,197,556, 1,201,396, 1,209,201, 1,217,880, 1,217,990; British Patents 1,211 (1885), 4,750 (1908); French Patent 409,513 (1910).

¹ Eighth Intern. Congress of Applied Chemistry, 18 (1912), 217.

specifications are given for recovering various other products, as aluminum compounds,¹ compounds of aluminum and silicon,² cement,³ raw materials for the manufacture of glass or of pottery,⁴ various miscellaneous materials,⁵ and by using a reagent in the treatment of the feldspar, which in itself contains a fertilizing element, there is claimed a product containing two or more fertilizing elements in soluble form.⁶

The by-product cited in the largest number of patents is alumina or a compound of aluminum. It happens, however, that in many of the processes the potash and alumina require in a large measure a separate treatment for their preparation and purification, and consequently the recovery of one does not contribute very greatly toward meeting the expense of recovering the other. With regard to the utilization of the by-products obtained in these various processes, it may be pointed out that the percentage of silica in feldspar is usually about double the combined percentages of the potash and alumina present. When consideration is taken of the other reagents added in any treatment of the feldspar, it follows that the insoluble residue remaining at the end of the process will amount to several times the quantity of potash, or potash and alumina present; consequently, in order that the residual material may find a market when any considerable amount of potash is produced, it must be of such a nature that it can be used on a very large scale. Such may be said to be the case of the raw materials used in the manufacture of glass, of which upwards of one and a half million tons are produced annually, but the process which produces cement as a product in the extraction of potash from feldspar has the advantage in that the quantity of cement used in this country is more than 10 times as great.

In addition to the work described in the patent literature investigations on the possibilities of recovering potash from feldspar have also been made by Rhodin,⁷ Cushman and Hubbard,⁸ Foote and Scholes,⁹ Hart,¹⁰ and Cushman and Coggeshall.¹¹

It is possible that a number of the processes which have been proposed for the extraction of potash and

other products from potash silicates may yet prove to be of economic application, but our experiments so far only give support to this contention in the case of those processes in which these silicates are used in industries, as the cement industry, where the potash is recovered not as the principal product, but more or less incidentally as a by-product.

The present paper is descriptive of one phase of the work that has been undertaken, as already stated, on the possibility of recovering potash from feldspar and other silicates. It has been found that when feldspar and lime in the proper proportions to make cement are digested with water under a pressure of 10-15 atmospheres, about 90 per cent of the potash passes into solution in the form of the hydroxide and the residue on ignition gives a clinker of the same composition as that obtained when the same feldspar and lime are ignited directly.

TREATMENT OF FELDSPAR WITH STEAM AT HIGH PRESSURE

This work developed from an investigation undertaken by Dr. Patten, formerly of this Bureau, on the action of steam at high pressure on insoluble potash silicates. The pressure under which the experiments were made was obtained by heating the material to be treated in a steel bomb with a known volume of water.

The bomb in these experiments was devised by H. Bryan, of this laboratory, and constructed of nickel steel in the Washington Navy Yard. The shape and dimensions of the bomb are given in Fig. 1. Its capacity was 150 cubic centimeters.

The internal pressure which a bomb of these dimensions is able to withstand with safety may be calculated¹ from the equation:

$$P = H \frac{R_1^2 - R^2}{R_1^2 + R^2}$$

where P is the pressure in lbs. per sq. in. on the internal surface of the bomb, R_1 the outside radius, R the inside radius, and H the maximum hoop tension at the interior of the bomb. In order that the bomb may be used with safety it should not be subjected to repeated stresses beyond the elastic limit of the material used in its construction. In the case of nickel steel the elastic limit is

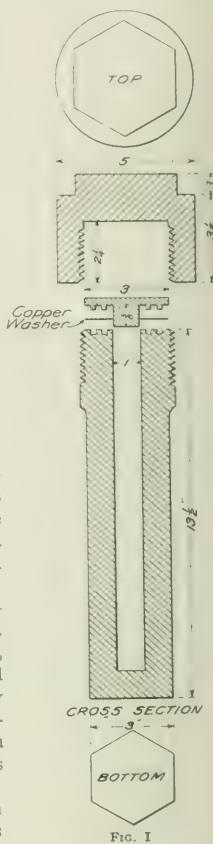


FIG. 1

¹ U. S. Patents 772,612, 772,657, 847,856, 862,676, 869,011, 1,035,812, 1,036,897, 1,054,518, 1,083,691, 1,111,881, 1,151,498, 1,151,533, 1,165,154, 1,202,215, 1,214,003; British Patents 9,486 (1842), 17,985 (1904), 2,463 (1905); French Patent 344,296 (1904); German Patent 1,289,909 (1914); Norwegian Patent 27,039 (1916).

² U. S. Patents 1,030,122, 1,034,281, 1,062,278, 1,095,306, 1,106,984, 1,125,007, 1,148,156, 1,174,795, 1,196,734, 1,215,517, 1,215,518; British Patents 5,559 (1902), 28,970 (1912), French Patents 466,952, 468,527 (1914).

³ U. S. Patents 46,979, 912,266, 1,041,327, 1,058,686, 1,078,495, 1,078,496, 1,089,716, 1,123,841, 1,124,238, 1,160,171, 1,160,172, 1,186,522, 1,194,344, 1,200,887, 1,202,327, 1,209,135, 1,209,219, 1,209,222; British Patent 3,185 (1837).

⁴ U. S. Patents 1,072,686, 1,087,132.

⁵ U. S. Patents 995,105, 997,671, 1,011,173, 1,083,287, 1,146,532, 1,157,437, 1,182,668; British Patents 2,050 (1862), 4,403 (1913).

⁶ U. S. Patents 16,111, 49,891, 947,795, 999,494, 1,018,186, 1,099,151, 1,103,910, 1,111,490, 1,126,408, 1,129,224, 1,129,505, 1,129,506, 1,129,721, 1,134,413, 1,144,405, 1,156,108, 1,172,420, 1,214,346, 1,217,389.

⁷ J. Soc. Chem. Ind., 20 (1901), 439.

⁸ J. Am. Chem. Soc., 30 (1908), 779.

⁹ In the case of patents issued in foreign countries as well as in the United States, the numbers to the latter patents alone are given.

¹⁰ This Journal, 4 (1912), 377.

¹¹ Ibid., 4 (1912), 827; 7 (1915), 670.

¹² Ibid., 4 (1912), 821; 7 (1915), 145.

¹ Lanza, "Applied Mechanics," p. 897.

usually placed at about 40,000 lbs. per sq. in., which, therefore, is the value to be given to H in the equation. R_1 and R were respectively $1\frac{1}{4}$ and $\frac{1}{2}$ in.

The value of P , the maximum pressure per sq. in. which could safely be generated in the bomb without going beyond its elastic limit, is thus calculated to be 29,000 lbs., or about 1,970 atmospheres.

This limit, however, holds true only below 500° . As this temperature is exceeded, the elastic limit of steel decreases very rapidly. For this reason no experiments were made at a temperature greater than 500° .

The pressure generated by heating water in a closed space to even 500° is very great and approaches the limit of safety calculated for the bomb. At its critical temperature the density of water is only 0.43. A volume of 60 cc. of water, therefore, expands at its critical temperature and pressure to 138 cc. In order to avoid any hydrostatic pressure in the bomb it was not considered advisable when working at this temperature to use a larger volume of water than 60 cc.

The pressure P , which this volume of water will generate in a space of 150 cc. at a temperature of 500° , may be calculated by means of the well-known van der Waals equation:

$$\left(P + \frac{3\pi\phi^2}{V^2}\right)\left(V - \frac{\phi}{3}\right) = RT$$

$$\text{or } P = \frac{RT}{V - \frac{\phi}{3}} - \frac{3\pi\phi^2}{V^2}$$

If P is expressed in atmospheres and V in liters, then the gas constant R will have the value 0.08207. The value of π , the critical pressure of water in atmospheres, and of ϕ , its critical volume, are 200 and 0.0038, respectively (Landolt-Börnstein Tables). Since 60 grams is the weight of water taken, then the value of V , the volume in liters occupied by 1 gram-molecule of water vapor, under the conditions of the experiment is

$$\frac{18 \times 150}{60 \times 1000} = 0.045 \text{ liter.}$$

Substituting these values in the equation given above it is seen that the pressure generated in the bomb by 60 cc. of water at 500° is equal to 1,448 atmospheres, or 21,285 lbs. per sq. in. The actual pressure generated in the bomb under the conditions of the experiment would be slightly greater than this, since there was necessarily inclosed in the bomb a volume of air equal to the difference between the internal capacity of the bomb and the volume of water added. On raising this to a temperature of 500° , an additional pressure of about 2 atmospheres would result giving a total pressure of about 1,450 atmospheres.

Considerable difficulty was at first experienced in making a joint which would prevent the escape of steam at such high pressure. This was finally accomplished by the use of a washer of annealed copper $\frac{1}{16}$ in. thick (Fig. 1). As the cap was screwed down the washer was pressed down to fit the dovetailed corrugations on the bomb and washer cap and thus made a joint which held perfectly for pressures up to 100 atmospheres. At higher pressures a leak of steam occurred, but so slowly that the bomb could be heated

at 475° for 15 hours or more before all the water added had escaped.

The desired temperature was obtained by placing the bomb in a simply constructed home-made electric furnace built especially for this purpose.

The feldspar used in these experiments was ground to pass a 100-mesh sieve and contained 13.72 per cent of potash (K_2O) and 2.18 per cent of soda (Na_2O). For the treatment under pressure 5 grams were placed in the bomb together with 60 cc. of water. To enable it to be opened more readily the thread of the bomb was lubricated with oil and graphite before adjusting the cap, which was screwed down firmly by means of a large wrench. The bomb was then placed in the furnace and maintained at a temperature of 500° for 10 hours. On removing the material from the bomb it was found to have gone over partly into a colloidal state, and a clear solution was obtained only after prolonged centrifuging. The solution was then boiled to expel carbon dioxide and titrated with dilute sulfuric acid, using phenolphthalein as indicator.

The amount of alkali which was thus found to pass into solution by this treatment proved to be very slight and did not exceed what could be obtained in an equal time by digesting with the same quantity of water on the water bath. This result is in agreement with that obtained by Dr. Patten,¹ who studied the action of steam on such minerals as feldspar, muscovite, etc., under pressures given by temperatures ranging up to 800° .

DECOMPOSITION OF FELDSPAR BY DIGESTING WITH LIME UNDER PRESSURE

When the feldspar was mixed with one part or less of lime an entirely different result was obtained. Complete decomposition of the feldspar was then found to have taken place, yielding a mixture which could be readily filtered and washed. The alkalis of the feldspar were converted into the caustic form, and the residue of calcium-aluminum silicate was found to be readily soluble in hydrochloric acid.

It was soon ascertained that a much lower pressure than that given at a temperature of 500° was sufficient to bring about the decomposition of the feldspar. Consequently all subsequent experiments were carried out at a temperature of 300° and less.

Since 300° is below the critical temperature (365°) of water, the pressure generated will be the vapor tension of water at this temperature plus the tension of the air contained within the bomb, and, apart from the small effect due to the solubility of the air in water, will be independent of the volume of the water, providing the amount taken exceeds the minimum volume and is not great enough to give a hydrostatic pressure through expansion.

In Table I, which gives the vapor pressure of water at the temperatures used in these experiments, the vapor pressure at 300° is shown to be about 20 atmospheres.

¹ In view of the remarks of Dr. H. E. Brown (Ann. Assoc. Am. Chem. Soc., 1907, 29, 100) that the work of the Bureau of Chemistry, U. S. Dept. of Agr., Nov., 1901, the work commenced by him was concerned with the action and use of the steam of acid vapors were negative, pressure could not be used in the action of the method and apparatus used, and of the statement that results were negative, consequently such statement is here made.

pheres. The minimum volume of water which must be taken to give the maximum pressure at 300° may readily be calculated by substituting the proper values for P, R and T in the van der Waals equation already given, using the same constants as before. The volume V which would be occupied by one gram-molecule of steam under these conditions would be about one-half a liter, and the minimum weight of water required for a space of 150 cc. is therefore about 5 grams.

TABLE I—VAPOR PRESSURE OF WATER AT DIFFERENT TEMPERATURES
Temperature, 150 175 200 240 270 300° C.
Pressure (a) (Atmos) 4.7 8.7 15.3 33.1 57.0 89.0
(a) Battelli, *Mem. di Torino*, [2] 43 (1892), 63

In all experiments carried out at 300° or less the volume of water taken amounted to 75 cc. Since the capacity of the bomb was 150 cc., the volume of air inclosed in each experiment was likewise 75 cc. The total pressures generated in the bomb at different temperatures by the water vapor and inclosed air are given in Table II.

TABLE II—TOTAL PRESSURE GENERATED IN THE BOMB AT DIFFERENT TEMPERATURES

Temp. ° C.	PRESSURE Water vapor Atmos.	Due to Inclosed air Atmos.	Total Pressure Atmos.	Total Pressure Lbs. per sq. in.
150	4.7	1.4	6.1	150
175	8.7	1.3	10.2	150
200	15.3	1.6	16.9	248
240	33.1	1.8	34.9	513
270	57.0	1.9	58.9	866
300	89.0	2.0	91.0	1338

In Table III is given the amount of potash obtained in percentage of the feldspar when the latter was digested with water at 300°, under pressure of 91 atmospheres, with varying proportions of lime. The total potash in the feldspar amounted to 13.72 per cent.

TABLE III—POTASH OBTAINED WHEN 5 GRAMS OF FELDSPAR WERE DIGESTED AT 300° UNDER PRESSURE OF 91 ATMOSPHERES WITH VARYING PROPORTIONS OF LIME

Calcium Oxide Grams	POTASH OBTAINED EXPRESSED IN PERCENTAGES OF	
	Feldspar	Total K ₂ O in Feldspar
1	2.13	15.5
2	3.54	25.8
3	6.80	49.6
4	8.30	60.5
5	10.73	78.2
8.4	13.49	98.3
15	13.65	99.5

The results show that when a sufficient amount of lime is taken, almost complete decomposition of the feldspar takes place under the conditions of the experiment. The potash passes into solution by this treatment in the form of the hydroxide. As lime is the only other constituent which likewise goes into solution in appreciable quantity, the caustic potash can thus be recovered in tolerably pure condition by simple concentration of the solution, providing the feldspar contains no appreciable quantity of soda and contact with carbon dioxide is avoided.

No aluminum passes into solution by this treatment, for any solvent action which the liberated caustic potash would tend to have is prevented by the excess of lime present. The insoluble residue remaining after the digestion is readily soluble in hydrochloric acid.

When 8.4 parts of lime are digested with 5 parts of feldspar at the pressure specified the potash recovered amounts to 98 per cent of the total. The percentage of silica in the residue amounted to 3.2 times that of the alumina while the sum of both was equal to exactly one-half the percentage of lime present. This

residue is therefore of suitable composition to make Portland cement, and would simply require ignition for its manufacture.

TABLE IV—POTASH RECOVERED WHEN FELDSPAR AND LIME IN THE PROPER PROPORTIONS TO MAKE CEMENT WERE DIGESTED WITH STEAM AT DIFFERENT PRESSURES

Temp. ° C.	Pressure Atmos.	POTASH OBTAINED EXPRESSED IN PERCENTAGES OF Feldspar Total K ₂ O in Feldspar
150	6.1	6.70
175	10.2	11.65
200	16.9	12.80
240	34.9	13.56
270	58.9	13.44
300	91.0	13.49

Table IV shows that at a pressure of 10 atmospheres, the potash extracted amounts to 85 per cent of the total present and that about 95 per cent extraction is to be expected when the pressure is twice as great. It is thus seen that increasing the lime with which the feldspar is digested, between certain limits, is much more effective in bringing about decomposition of the feldspar than a corresponding increase in pressure, and when a proportion of lime is taken equal to that used in the manufacture of cement, the greater part of the potash in feldspar may be set free at pressures obtainable with safety in any steam boiler.

In the patent issued to Pohl¹ in 1910 on a process for preparing mineral fertilizer, specifications are given for decomposing feldspar and other silicates by adding 10 to 45 per cent of lime and digesting under a pressure of 6 to 10 atmospheres. From the results given in Tables III and IV it is apparent, however, that only a small percentage of the total potash would be rendered soluble under these conditions. Much more favorable results were obtained when treating feldspar according to the process outlined by Gibbs,² which consists in adding to a potash silicate a quantity of lime in the proportion of two molecules for each molecule of silica and one molecule for each molecule of alumina in the silicate, and then digesting under a steam pressure of 125-150 lbs. per sq. in. No reference is made in either of these patents to the recovery of any other product in addition to the potash.

DECOMPOSITION OF FELDSPAR BY DIGESTING WITH LIME AND A SALT OF CALCIUM UNDER PRESSURE

As shown in Table III, feldspar may be almost completely decomposed when digested at 90 atmos-

TABLE V—POTASH RECOVERED WHEN A SALT OF CALCIUM, OR SODIUM, WAS DIGESTED WITH A UNIFORM MIXTURE OF 5 GRAMS OF FELDSPAR AND 3 GRAMS OF LIME UNDER PRESSURE OF 91 ATMOSPHERES

Salt added	Amount taken Grams	POTASH OBTAINED EXPRESSED IN PERCENTAGES OF Feldspar Total K ₂ O in Feldspar	
		Feldspar	Total K ₂ O in Feldspar
CaSO ₄	1.25	9.16	66.0
	3.0	8.10	59.0
	5.0	7.80	56.9
CaCl ₂	1.0	9.00	65.6
Ca(NO ₃) ₂	1.5	9.00	65.6
	5.0	9.49	69.2
Ca ₃ (PO ₄) ₂	2.0	6.01	43.8
	1.0	6.72	49.0
NaCl.....	2.0	7.94	57.8
	3.0	7.94	57.8
None.....	...	6.80	49.6

pheres with 2 to 3 parts of lime, but only partial decomposition takes place when the proportion of lime is decreased much below this limit. It was found, however, that by adding to the mixture when a limited proportion of lime is taken a quantity of chloride, sulfate, or nitrate of calcium equivalent to, or greater

¹ U. S. Patent No. 952,278.

² U. S. Patent No. 910,662 (1909).

than, the alkalis in the feldspar, the amount of potash recovered is considerably increased.

The results under this procedure are given in Table V, from which it would appear that the chloride, sulfate and nitrate of calcium have all approximately the same effect in increasing the decomposition of the feldspar when digested with a small amount of lime. When any one of these salts is mixed with the feldspar the potash is no longer recovered as the hydroxide but in the form of a salt, depending on the salt of calcium taken. Thus when calcium sulfate is taken the potash is recovered as the sulfate in tolerably pure condition by concentration of the solution with which the mixture was digested under pressure. The best result was obtained when an amount of sulfate was taken approximately equivalent to the alkalis in the feldspar. Increasing the sulfate above this limit results in a decrease in the quantity of potash rendered soluble.

A different result was obtained with calcium phosphate, which seems to have a neutral effect on the amount of feldspar decomposed. No increase in potash obtained followed its use, and so long as an excess of lime is present no phosphate passes into solution.

The use of sodium chloride with lime in this treatment of feldspar does not appear to be so effective as any one of the soluble calcium salts. A further disadvantage attending its use lies in the fact that in common with calcium chloride any excess would be difficult to separate, on account of its solubility, from the liberated potassium salts.

In all these experiments the digestion under pressure was allowed to run over night for a period of 16 hours. The bomb was always placed in the furnace while cold, and about 10 hours were required for the bomb to reach the temperature desired for the experiment. The time that the digestion was continued at the maximum pressure was therefore only about 6 hours. More prolonged digestion at the maximum temperature set for the experiment did not produce much increase in the potash obtained. Thus when 5 parts of feldspar, 8.4 parts of lime and 1.25 parts of calcium sulfate were digested for 16 hours, during which time a maximum pressure of 17 atmospheres was maintained for 6 hours, the potash recovered amounted to 78.6 per cent of the total present. When the digestion at the maximum pressure of 17 atmospheres was continued three times as long, the potash rendered soluble amounted to 83.0 per cent of the total.

When lime is excluded little or no decomposition of feldspar takes place when digested under pressures up to 100 atmospheres with solutions of sodium chloride, calcium chloride, and calcium sulfate, either separately or in combination.

The action of a salt of calcium in increasing the potash rendered soluble when added to the mixture of 5 parts of feldspar and 3 parts of lime and digested under pressure of 91 atmospheres was likewise observed when the digestions were made at 17 and 35 atmospheres. As shown in Table III, increasing the proportion of lime without the addition of a salt of calcium produces a still more marked increase in the

potash recovered, and when the mixture approached the composition required of Portland cement the percentage of potash extracted, which varies but little with the pressure under which the digestion is made between limits of 17 and 91 atmospheres, amounts to about 95 per cent of the total present. The addition of a salt of calcium to this mixture of feldspar and lime does not seem to result in any increase in the potash extracted. This is shown by the results given in Table VI.

TABLE VI—PERCENTAGE OF POTASH RECOVERED WHEN 5 GRAMS OF FELDSPAR ARE DIGESTED UNDER PRESSURES OF 17 AND 35 ATMOSPHERES WITH DIFFERENT PROPORTIONS OF LIME, WITH AND WITHOUT A SALT OF CALCIUM

SALT	Amount taken Grams	Lime Grams	Pressure Atmos.	POTASH RECOVERED EXPRESSED IN PERCENTAGES OF	
				Feldspar	Total K ₂ O in Feldspar
None.....	8.4	17	12.80	93.3
None.....	8.4	35	13.56	98.8
CaSO ₄	1.25	8.4	17	11.39	83.0
CaSO ₄	1.25	8.4	35	13.21	96.3
None.....	3.0	17	5.36	39.1
None.....	3.0	35	7.33	53.4
CaSO ₄	1.25	3.0	17	6.72	49.0
CaSO ₄	1.25	3.0	35	8.30	60.5
CaCl ₂	1.0	8.4	17	12.55	91.5
CaCl ₂	1.0	3.0	17	7.10	51.9
Ca(NO ₃) ₂	5.0	3.0	35	8.55	62.3

From the results which were thus obtained in the decomposition of feldspar with lime under pressure it was thought that a method might be devised in this way whereby the alkalis in silicate rocks might be separated quantitatively. Digestions of feldspar were accordingly made under different pressures with varying amounts of lime, and with lime and various salts, as the sulfate of calcium and ammonium and the chloride of calcium, ammonium and barium. The results obtained, however, were in every case a little too low. The highest extraction of the alkalis amounting to about 99.5 per cent of the total present was obtained when the feldspar was digested at about 90 atmospheres with 3 parts of lime. The addition of 0.25 part of calcium sulfate gave the same result. The results obtained with the use of lime and barium sulfate were much too low. This is in agreement with the low results obtained when barium chloride is substituted for ammonium chloride in the J. Lawrence Smith method.

DISCUSSION OF RESULTS

The treatment necessary to bring into soluble form upwards of 90 per cent of the potash in feldspar is seen from these experiments to be a feasible and comparatively simple operation. The pressure required does not exceed that which a boiler is capable of withstanding with safety, and that the process would be at least as efficient when carried out on a large scale appears to be likely from the fact that when the quantity of material treated had been increased so that a little larger extraction of the potash was always obtained.

When the feldspar was digested under a pressure of 10 atmospheres with lime alone the potash rendered soluble amounted to 83 per cent of the total present, and to approximately 95 per cent when the pressure was twice as great. If the average potash content of commercial feldspar be taken as 10 per cent, a possible recovery by this process of, say, 90 per cent

is assumed, then 1 ton of feldspar would yield 214 lbs. of caustic potash. Assuming commercial caustic potash to have the normal market value of 5 cents per lb., the potash recovered in this way from a ton of feldspar would therefore be worth \$10.70.

In the process suggested for the recovery of potash from feldspar by its substitution for clay in the manufacture of cement, the potash recovered by volatilization in the cement dust would be combined, when the latter had become air-slaked, as the carbonate and sulfate, and would have a normal value when used directly as a fertilizer of about 75 cents per unit. Assuming as before, a 90 per cent recovery of the potash by this method, 1 ton of feldspar containing 10 per cent of potash would yield potash salts worth \$6.75.

If the caustic potash recovered from feldspar by digesting with lime under pressure would be of such a grade as to command a price of 5 cents per lb., then the value of the potash recovered by this method may be assumed to be greater than the value of the potash salts which can be recovered from the same quantity of feldspar by the process which brings about extraction of the potash by volatilization.

It may be assumed, however, that the operating expenses incident to the former process would be considerably greater than that required for the process just referred to. No decomposition takes place when feldspar is digested with calcium carbonate. The necessity of having to use the oxide of calcium requires that limestone must be previously burned as a separate operation which would add considerably to the cost of producing potash by this method. Assuming the average cost of burning 1 ton of lime to be in the neighborhood of \$1.00, the expenses involved in this operation alone when feldspar and lime are taken in the proper proportion to make cement would amount to \$1.70 per ton of feldspar. This operation alone would thus reduce the difference in value of the potash recovered by the two methods to \$2.25.

It happens, moreover, that the potash in feldspar is always accompanied by more or less soda and consequently the caustic potash recovered by the method of digesting under pressure would always be contaminated with caustic soda. It is possible that the quantity of soda present may be sufficient in many cases to reduce the price of the caustic potash recovered below the market value for a commercial grade of this material. The presence of the soda, however, would not depreciate the value of the potash for use as a fertilizer and potash in the form of the hydroxide would be especially suited for the manufacture of concentrated fertilizers. If made available for this purpose a slightly higher value might therefore be given to the potash of caustic potash even when used for fertilizer manufacture.

The potash in the freshly recovered flue dust obtained in cement plants where coal is used for burning is partly soluble in the form of sulfate and hydroxide, partly slowly soluble and partly insoluble. The slowly soluble combination is explained on the ground that during the burning of the cement part of the volatilized potash undergoes a recombination with

the silicates in the dust. It has been observed further that the potash in cement dust is less readily volatilized on ignition with lime than in the form in which it occurs in the original silicates. It thus happens that when the dust is reburned with a view to its use in the manufacture of cement, only a comparatively low percentage of the potash is recovered.¹ It is possible, therefore, that some process for separating and concentrating the potash in the dust before the latter is used for reburning into cement may prove advantageous and for the treatment of such material the procedure of digesting under pressure should be especially applicable. Since the dust always contains free lime, no further addition of lime would be necessary; most of the insoluble as well as the soluble potash would be recovered, and the residue would be available for cement manufacture. Experiments along this line are now in progress.

SUMMARY

1—When 1 part of feldspar and 1.7 parts of lime are digested with water at a steam pressure of 10–15 atmospheres, about 90 per cent of the potash in the feldspar passes into solution in the form of the hydroxide, and the residue has the composition required for Portland cement clinker. When the pressure is increased to 90 atmospheres almost complete decomposition of the feldspar then takes place, but if the proportion of lime taken is reduced much below the limit stated, only partial decomposition of the feldspar results even at the latter pressure. By adding to the mixture when a limited proportion of lime is used a quantity of a soluble calcium salt equivalent to the alkalis in the feldspar, the amount of potash recovered may then be considerably increased.

2—Since the dust which escapes from the kilns of cement plants already contains free lime it is suggested that the process of digesting with water alone under pressure may be applicable to the separation and concentration of the soluble and insoluble potash salts occurring in this material, leaving the residue available for cement manufacture.

3—With lime absent no decomposition of feldspar takes place when digested with water even at pressures up to 1,450 atmospheres.

4—A list of patents is given on processes for the extraction of potash from silicate rocks.

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

POTASH FROM INCINERATOR ASH OF THE NORTHWEST

By CURTIS W. THING
Received March 5, 1917

In the lumber industry of the Northwest, the larger part of the waste is burned in incinerators. The ash is disposed of in any possible way, generally being washed or dumped into the river or lake near the sawmill. The present potash shortage, due to the European war, drew some little attention to the incinerator ashes as a source of potash. The purpose of the following investigation was to determine the possibilities of such an industry.

¹ Anderson and Nestell, *This Journal*, 9 (1917), 253.

HISTORY OF THE POTASH INDUSTRY IN THE UNITED STATES

Sixty years ago the production of potash from wood ashes was an important industry. The principal woods used for this purpose were elm, birch, larch, and maple. Dating from the opening of the Stassfurt beds, the industry has diminished in importance until at the present time it is practically dead. The amount of potash now made in the United States is insignificant, being about 0.1 of the amount imported. The following table, taken from the 13th Census, Vol. X, page 541, shows well the decline of the potash industry of the United States, due to competition with the German supply:

TABLE I—THE U. S. POTASH INDUSTRY

Year	Establishments	Product (Lbs.)	Value	Av. Price per Lb.
1849	569	\$1,401,533
1859	212	338,550
1869	105	327,671
1879	68	5,571,671	232,643	5.09 cents
1889	75	5,106,939	197,507	3.86
1899	67	3,864,766	178,180	4.82
1909	31	1,866,570	88,940	4.76

The 12th Census, Vol. X, Part IV, pages 543-546, comments on the status of the industry in the following words: "Of the 67 establishments in the figures for 1899, 12 had an output of less than \$500 per annum. Although the average price of potash in 1899 was higher than in 1889 the industry was not remunerative, and consequently the total quantity and value of product decreased."

ASHES OF EASTERN AND WESTERN WOODS

Complete information as to the composition of the ash of eastern woods used in this industry, is lacking, but the following incomplete table is taken from Bradley:¹

Wood	Per cent Ash	Per cent K ₂ O	Per cent P ₂ O ₅
Elm.....	2.55	15.3
Larch.....	12.72(a)
Maple.....	0.49	12.61	4.44

(a) Contains both K and Na.

The following analyses of the ashes of Douglas fir and cedar are submitted by the author. The samples were obtained in the form of a wedge-shaped cut of the wood, extending from the bark to the center. The aim was to obtain representative samples.

TABLE II—ANALYSIS OF ASHES OF DOUGLAS FIR AND CEDAR

Wood	No. of Dets.	AVERAGE PERCENTAGES				
		Ash	K ₂ O	P ₂ O ₅	Ca	Na
Douglas Fir.....	6	0.23	7.7	8.7	19.8	1.35
Cedar.....	2	0.66	5.5	3.6	16.4	0.00

Other important western woods are hemlock and spruce but no analyses of them were to be had and none were made.

From these figures it can readily be seen that the ash used in the East has a higher potash content than the western woods. The average eastern ash contains more than 10 per cent, while fir, the most important northwest wood, contains 7.7 per cent and cedar 5.5 per cent.

POTASH IN WASTE WOOD OF WASHINGTON

In the manufacture of lumber, shingles, and other wood products, there is always a certain amount of

the timber lost, in the form of sawdust, slabs, butts, etc. The forestry department of the University of Washington states that 25 per cent by volume and 50 per cent by weight of the timber coming to the mills is wasted. The weight of finished green fir lumber is about 3 lbs. per board foot. Consequently, for every board foot of fir lumber there is a corresponding wastage of 3 lbs. As cedar weighs ¹/₅ less than fir, the estimated loss would be 2.4 lbs. per board foot for cedar.

The timber production¹ of the State of Washington for the year 1915 appears in Table II with an estimate of the total amount of ash and potash (as K₂CO₃) in the fir and cedar waste.

TABLE III—ESTIMATED POTASH VALUE OF FIR AND CEDAR WASTE

WOOD	PRODUCTION	ESTIMATE OF TOTAL WASTE	
	Board Feet	Lbs. Ash	Lbs. K ₂ CO ₃
Fir.....	2,920,000,000	20,148,000	2,275,000
Cedar.....	624,000,000	9,884,000	798,000
Hemlock.....	306,000,000
Spruce and others	100,000,000
	3,950,000,000	30,032,000	3,073,000

This potash at the prices prevailing in 1909 would have a value of \$146,175 and at present prices about ten times this amount. By reference to Table I it may be seen that this amount is nearly twice the total production of 1909. At that, no notice has been taken of woods other than cedar and fir.

Roughly speaking, all the waste wood is burned at the mills. A little is sold by the wagon load for fuel. About one-half is burned under the boilers for development of power. The remaining half is burned in large incinerators. No attempt is made to recover the potash or in any way to utilize this ash. When it is further recognized that the mills are not scattered over the whole state but are grouped around a few cities, it seems as though an arrangement for the treatment of this ash in central plants would be possible.

ESTIMATED AVAILABILITY OF INCINERATOR ASH AS A SOURCE OF POTASH OR AS A FERTILIZER

At the present time waste wood is burned in the incinerator which, instead of guarding against draughts and keeping the temperature as low as possible, provides expressly for strong draughts and the resultant high temperature. This is done that the rate of consumption of waste will equal the rate of production, since storage of the waste at the plant would be too expensive. Although a large amount of wood is burned the draught and temperature are such that most of the potash and lighter components are carried out. The following analyses of incinerator ash were made:

WOOD	No. of Determinations	As. Per cent		No. of Determinations	As. Per cent
		K ₂ O	P ₂ O ₅		P ₂ O ₅
Fir.....	8	1.1
Cedar.....	10	1.1

Qualitative tests of the dust found in the flues and chimneys of the power plant at the Seattle Cedar Lumber Company, showed the presence of every

¹ *Timberman*, 17, No. 1, 1916.

component of the ash. The following analyses of the same dust were made:

LOCATION:	Flue Chamber	Base of Chimney
Per cent K_2O	7.79	6.40

This shows the dust to have a higher potash content than the ash (cedar) itself, due to the fact that the potash is lighter and more volatile than the silica, ferric oxide, etc., which largely compose the residue left in the ash pits.

Interviews with the foremen or managers of the McDonnell and Phoenix mills at Ballard indicated that for mills of that size (60,000 to 70,000 log feet per day) the amount of ash remaining in the incinerator was under $\frac{1}{2}$ ton per week. The general superintendent of the Seattle Cedar Lumber Company of Ballard (190,000 log feet per day) stated that a large new incinerator had been in service for over a year and had not been cleaned out yet. From these statements it may be seen that an amount of ash sufficient for large potash production cannot be secured.

As has been shown, the eastern wood ashes which are used in the manufacture of potash, average over 10 per cent potassium oxide. From the above analyses of incinerator ash it has been shown that the average potassium oxide content is around 1.2 per cent. This means that a company attempting the manufacture of potash from incinerator ashes would be obliged to handle nearly ten times the amount of ash, to produce the same amount of potash. Its cost of production would be increased in nearly the same ratio. The war has increased the price of potash to about ten times its former value. Hence under present conditions it is possible that incinerator ashes might be used as a source of potash, for the increased cost of production would be counterbalanced by the increased value of product. However, if the end of the war should, as we quite reasonably expect, result in a rapid decrease in the price of potash, the production of potash from incinerator ash would not be a paying proposition. Further, in any case, the quantity of incinerator ash is not sufficient for commercial production.

CONCLUSIONS

I—Potash production from incinerator ash cannot be put on a paying commercial basis (barring war prices, which are of course inflated) because of

- 1—Low potash content;
- 2—Higher cost of production;
- 3—Insufficient supply of raw material.

II—Unless a new method for the disposal of waste is suggested, the prevailing method of disposal of incinerator ash is as economical as can be found. Analyses show it to be of little value for fertilizer.

III—If any plan were to be suggested for the successful production of potash from wood ashes, it must fulfil the following conditions:

- 1—Dispose of the waste as fast as it is produced.
- 2—Operate at low temperatures and with slight draughts.
- 3—Successfully meet foreign and domestic competition.

CHEMICAL LABORATORY
UNIVERSITY OF WASHINGTON, SEATTLE

AROMATIC HYDROCARBONS FROM THE THERMAL DECOMPOSITION OF NATURAL GAS CONDENSATE

By J. E. ZANETTI AND G. EGLOFF

Received March 23, 1917

In previous papers one of us¹ has shown that by the thermal decomposition of natural gas condensate aromatic hydrocarbons were produced together with hydrogen, methane and "unsaturated," which consisted chiefly of ethylene, when the condensate in the gaseous form was heated to a temperature above 750°. The amount of aromatic hydrocarbons obtained as "tar" was too small to permit any extended investigation and only three were positively identified, *viz.*, benzene, toluene and naphthalene.

By using the same method and apparatus, we were able to prepare about 250 cc. of "tar" from the fraction of natural gas condensate consisting chiefly of propane and butane. Even with this much larger amount, the composition of which is given in Table I, the fractionations did not allow us a sufficient amount of material to enter into a detailed investigation and

TABLE I—DISTILLATION ANALYSIS OF RECOVERED OIL
Specific Gravity 1.101 at 15.5° C.

Temperature	Per cent Volume	Sp. Gr.
To 170° C.	14.1	0.885
170 to 230° C.	13.6	...
230 to 270° C.	12.7	...
270 to 365° C.	16.3	...
Pitch.	43.3	...
To 95° C. (Benzene Fraction).....	4.8	0.885
95 to 120° C. (Toluene Fraction).....	2.0	0.870
120 to 150° C. (Xylene Fraction).....	3.9	0.871
150 to 170° C. (Trimethyl Benzene Fraction).....	0.7	0.876

isolation of the numerous hydrocarbons, which could be present, and although we had no difficulty in isolating anthracene, a much higher molecular weight hydrocarbon than we had hitherto obtained, there still remained a great number of possible ones whose presence we were unable to show definitely, owing to the scarcity of the material.

The yields of "tar" were essentially the same as obtained in the previous investigation, from 8.5 to 10 cc. per cu. ft. of the original gas, the procedure being in all respects identical, except as to the rate, which was slightly greater, *viz.*, about 0.6 cu. ft. per hr.

At the same time we prepared, by absorbing the unsaturated gaseous products in bromine water after the "tar" had been deposited, about 1 kg. of the bromides

TABLE II—COMPOUNDS ISOLATED: WITH PHYSICAL AND CHEMICAL PROPERTIES FOR IDENTIFICATION

HYDROCARBON	Boiling Point	Sp. Gr.	IDENTIFICATION AS
Benzene.....	79 to 83° C.	0.885	Nitrobenzene
Toluene.....	108 to 112° C.	0.870	Trinitrotoluene, M. P. 82° C.
Xylenes.....	135 to 145° C.	0.871	Naphthalene, M. P. 79.3° C.
Naphthalene.....	216 to 221° C.	...	Slight yellow crystals, M. P. 211° C.
Anthracene ...			Anthraquinone, M. P. 277°.

which were fractionated and analyzed as shown in Table III. The object here was to show more definitely than before that the unsaturated consisted chiefly of ethylene, a small amount of propylene and a considerable proportion of butane, as shown by the high percentage of tetrabrom butane, which was ob-

¹ Zanetti. THIS JOURNAL, 8 (1916), 674; Zanetti and Leslie, *Ibid.*, 8 (1916), 777.

tained quite pure, showed a constant melting point and gave the required percentage of bromine on analysis. In the "residue" there were doubtless bromides of higher hydrocarbons and possibly higher bromides of

TABLE III—DISTILLATION AND ANALYSIS OF BROM DERIVATIVES OF UNSATURATED HYDROCARBONS IN GAS RESULTING FROM THERMAL DECOMPOSITION OF PROPANE AND BUTANE
Specific Gravity 2.016 at 15° C.

Temperature	Per cent by Volume	Specific Gravity
To 100° C.	6.9	1.112
100° to 115°	2.7	...
115° to 129°	5.8	2.020
129° to 132°	38.0	2.118
132° to 135°	10.4	2.100
Residue	36.2	...
Tetrabrombutane	M. P. 116°	...

ANALYSIS OF BROMIDES ISOLATED FROM ABOVE FRACTIONS

Formula	Calculated Per cent Br	Found
C ₂ H ₂ Br ₂	85.1	85.1
C ₃ H ₂ Br ₂	79.2	79.9
C ₄ H ₂ Br ₂	85.5	85.4

the lower ones, but it was found impossible to separate them, as, above 140°, decomposition would set in,

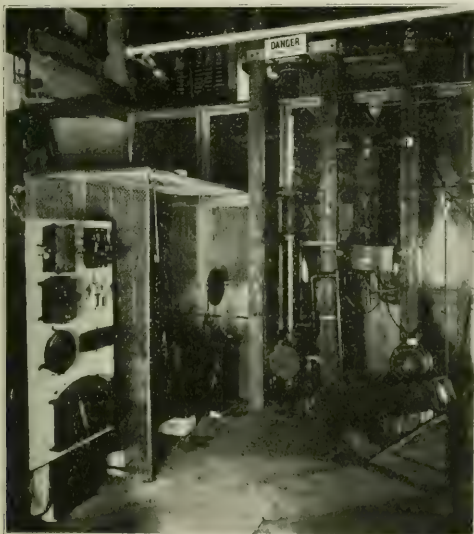


FIG. 1

and even on distillation *in vacuo* hydrobromic acid and bromine vapors would be given off so copiously that further investigation of this point was abandoned. No acetylene tetrabromide could be obtained but a small amount of dibrom benzol was obtained from the bromides showing that some benzene would remain in the gases after the deposition of the tar. This, of course, is to be expected since the gases were cooled only to 0°, at which temperature the vapor pressure of benzene is still quite appreciable. Had any appreciable amount of acetylene tetrabromide (B. P. 137°) been present, it would have appeared with the propylene bromide fraction (132–135°) from which propylene bromide was isolated, and raised considerably the specific gravity of this fraction [propylene dibromide 1.046 (17°), acetylene tetra-

bromide 2.97 (17.5°)] whereas this fraction showed only a specific gravity of 2.100 corresponding to a mixture of ethylene and propylene bromides. Further, it would have been practically impossible to separate it from propylene bromide, their boiling points being so close together (137° and 141°) and the analysis would have shown a very high per cent of bromide for the propylene fraction, whereas it corresponded exactly with the calculated [acetylene tetrabromide, 92.7 per cent bromine; propylene bromide, 79.2 per cent; found 79.9 per cent].

The method of procedure followed in the above thermal decomposition was quite satisfactory except as to speed. In order to obtain larger amounts of "tar" without undue waste of time, a larger apparatus was necessary, especially since the supply of the propane-butane fraction became exhausted, and it was found almost impossible to replenish owing to financial difficulties of the company which originally supplied it. The only available supply of natural gas condensate available in quantity gave a much smaller yield owing to the presence of large amounts of ethane. For the apparatus two things were essential, a heating device, and an electrical tar precipitator. We were fortunate in finding already set up the electrically heated furnace previously used by Whitaker and Alexander,¹ and Whitaker and Leslie;² this was loaned to us by the Department of Industrial Chemistry of this University. A Cottrell tar precipitator was set up for us by the Research Corporation of this city.

MATERIAL—The material used was natural gas condensate from West Virginia in containers under 800 to 1200 lbs. pressure. The material being commercially used for lighting purposes came in cylinders built on the principle of a soda syphon, with a delivery tube reaching nearly to the bottom so as to insure a gas of constant composition. The higher boiling hydrocarbons would thus be expelled along with the lower boiling ones, whereas they would remain as liquids if only evaporation were resorted to. These higher boiling hydrocarbons consisted mostly of pentanes, and as we were not interested in their decomposition, the cylinders were turned upside down so as to secure only the fractions containing the butanes, propane, and ethane. When nearly empty, the cooling produced by the rapid evaporation would bring the pressure in these cylinders to almost 0, and the flow of gas would stop, but if allowed to stand till warmed to room temperature, the pressure would rise again to 30–40 lbs. showing that even in the residue, a considerable proportion of butane was left. The high initial pressure in the cylinders would indicate the presence of methane in the first fractions that came over. This, however, was of no importance as at the temperatures used methane would be so stable as to make the effect of its presence negligible.

APPARATUS AND PROCEDURE—The apparatus is shown in photograph (Fig. 1) and in diagram (Fig. 11). For reasons explained above the cylinder of gas was turned upside down and the gas after passing

¹ THIS JOURNAL, 7 (1915), 484.

² *Ibid.* 8 (1916), 593.

through a reducing valve, where the pressure was dropped to 10–15 lbs., was sent through a dry meter provided with a scale reading to $\frac{1}{4}$ cu. ft. The gas was led from there through the furnace by means of a $\frac{1}{4}$ -in. iron pipe.

The detailed description of the furnace has already been published¹ and will not be given here. It is essentially the same furnace as used by Whitaker and Alexander, the only alterations being the removal of the prevaporizer which those authors used, and the fitting of a larger condensing apparatus. Essentially it consisted of a carbon tube, 1 in. inside diameter, 46 in. long, which was used as a resistor in circuit with a 25-volt, 50-kw. alternator. By varying the current sent through the resistor by means of a rheostat a wide range of temperature could be obtained. The resistor was surrounded by an air jacket and further insulated by a thick layer of petroleum coke so as to

running through the middle and carefully insulated from direct contact with it.¹

The body of the separator consisted of a 4-ft. section of heavy 6-in. pipe set vertically, flanged at both ends and provided with a piece of 2-in. iron pipe welded to the body of the pipe two inches above the lower flange. The inside of the welding was thoroughly smoothed so as to prevent any sharp edge of point. This is an important consideration in electrical precipitation since the object is to maintain as uniform a field as possible between the two poles and prevent any sparking, which of course would be facilitated by any sharp edge or rough surface. At either end of the pipe section was bolted a Standard 6-in. T, asbestos gaskets being used to make the connection gas-tight. In order to avoid the sharp edges of the pipe, a smooth bronze ring, 4 in. internal diameter, was placed between the flanges so that it projected over the edge of the

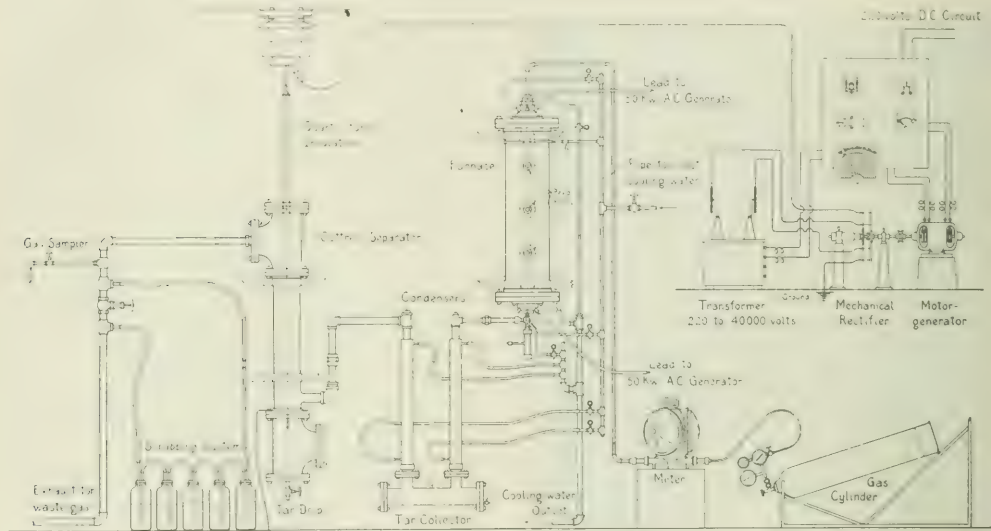


FIG. II.—DIAGRAM OF APPARATUS USED FOR THERMAL DECOMPOSITION OF NATURAL GAS CONDENSATES

diminish heat radiation. The outside jacket was a section of 10-in. wrought iron pipe cooled by a stream of water, the electrode holders being likewise cooled as shown in the diagram. The cooling apparatus consisted of two sections of $1\frac{1}{2}$ -in. pipe, each 4 feet in length, water jacketed and communicating through a piece of 3-in. heavy cast iron pipe which acted as a tar collector for that fraction of the tar which would deposit on mere cooling. The finely divided "fog" was then deposited in the Cottrell separator.

The principle of the separator is very simple. It consists in passing the gases containing the finely divided "fog" between two poles maintained at a great difference of potential. In this case one of the poles was the body of the separator, the other a wire

pipe. Through the top of the flange closing the upper T section passed a double-walled quartz tube $1\frac{1}{2}$ in. outside, $\frac{3}{4}$ in. inside diameter, projecting about 8 in. into the T and held in place by means of asbestos packing. The quartz tube was closed at both ends by sections of rubber stoppers held in place by washers, the whole being tightly screwed to a metal rod running the length of the quartz tube. The upper end of this rod was attached to a high voltage insulator and from the lower end hung an 8-lb. lead weight held by a No. 16 bare copper wire. The length of the wire was such as to bring the lead weight well below the lower end of the pipe section. The purpose of this was to prevent the current of gases which entered the separator from

¹ For details of this process see Cottrell, *This Journal*, 3 (1911), 542; also Rowley and Wirth, *Am. Gas Light J.*, 101 (1914), 177.

impinging on the weight and starting it to swing, thus causing a short circuit. The pipe section was grounded and the wire and lead weight connected to the negative side of a high voltage apparatus to be described shortly. The speed at which the gases were sent through the separator was approximately 3 cu. ft. per minute.

The gases passed out from this separator perfectly free from tar "fog" and either were led out as waste or passed through a scrubbing system consisting of five wide mouth gallon bottles containing each about $1\frac{1}{2}$ gal. lubricating oil. The purpose of the scrubbing system was to remove benzol, toluol, etc., which were carried along by the gas since the vapor pressure of these substances at ordinary temperatures is fairly great and the tar deposited in the separator was already saturated with those compounds.

The electrical apparatus consisted of a 2-h. p. motor generator operated on the 220-volt d. c. circuit of the building. The a. c. was stepped up by a 5-kw. oil insulated transformer, as high as 50,000 volts according to the coils used. For our purposes we found 35,000 volts quite sufficient. The current was then rectified by means of a mechanical rectifier run by the motor and therefore in cycle with the alternating current produced. The negative side was connected with the inside wire of the separator, the positive side grounded outside the building, to prevent interference with other electrical apparatus in the neighborhood. The high voltage side of the apparatus, including the transformer and rectifier, were completely enclosed in a wire cage to guard any one from accidentally coming in contact with the highly charged wires. In the photograph (Fig. 1) the front of the cage has been removed to show the arrangement inside. The cage was also connected to the ground in order to prevent any accumulation of static electricity in the neighborhood of the rectifier.

The regulation of temperature was at first carried out by inserting a pyrometer through one of the peep-holes till it touched the inner tube. After a while, however, we could easily determine it in terms of the energy consumed, with a given rate of gas, and also by the amount of "fog" in the gas as they issued from the heated tube. The temperature used was in the neighborhood of 900° C. The greater the rate the greater the amount of energy required as shown by the amperes consumed. A rate of 1 cu. ft. per min. and 350 amperes gave us the best result. The rate of gas was regulated by timing the gas going through the meter with a stop-watch.

COMPOSITION OF THE TAR

By the procedure above described we prepared about $1\frac{1}{2}$ kilos of tar which was distilled in separate portions and fractions collected as shown in Table IV. The fractions obtained as indicated in Table IV were re-distilled and fractions collected every ten degrees if the amount warranted. The low percentage of light oil led us to believe that much of it passed through uncondensed. The condensers were at best able to cool the gases to 25° at which temperature the vapor

pressure of these light oils was considerable. By scrubbing the gases after they issued from the tar separator and distilling the scrubber oil with steam we were able to obtain from 1 to $1\frac{1}{2}$ cc. of light oil per

TABLE IV—COMPOSITION OF RECOVERED OIL FROM THE THERMAL DECOMPOSITION OF NATURAL GAS CONDENSATE
Specific Gravity 1.109

Temp. C.	Per cent by wt.
To 170°	9.7
230°	18.7
270°	11.4
330°	15.4
Over 360°	50.1
Residue	50.1

cubic foot of gas used. Distillation of this light oil, after washing with concentrated sulfuric acid and sodium hydroxide, showed it to be composed of benzene, toluene and a little xylene. The specific gravity of the benzene thus recovered, after removal of the unsaturated, was low, however, indicating the presence of some saturated straight chain hydrocarbons.

Part of the tar deposited in the cooling pipes and was drawn off from the tar collector. Most of it, however, settled in the separator and dripped down into the lower T section from which it was drawn through a valve at the bottom.

TABLE V—AROMATIC COMPOUNDS FROM THERMAL DECOMPOSITION OF NATURAL GAS CONDENSATE

	M. P.		B. P.	Picrate	Identification
Benzene	4°	80-82°	Nitrobenzene
Toluene	107-110°	Trinitrotoluol M. P. 82°
Xylene	120-130°	
Naphthalene	80°	..	149°	..	Picrate yellow needles
Acenaphthene	98°	..	160°	..	Picrate orange needles
Anthracene	212°	..	138°	..	Picrate red needles
Phenanthrene	99-100°	..	145°	..	Picrate yellow needles
Pyrene(?)	145°	..	222°	..	Picrate red needles
Chrysene	249°	Small white plates

By allowing the various tar fractions to solidify, pressing out the oily matter and crystallizing from alcohol, the following hydrocarbons reported in Table V were obtained.

BENZENE—The benzene obtained after several distillations was water-white, boiled constantly at 80-82°, melted at 4° and showed a specific gravity of 0.879 at 15.5°. By treatment with HNO₃ and H₂SO₄ it gave nitrobenzene. Some benzene obtained from the scrubbing of the gas showed all these properties but had a much lower specific gravity, 0.873 at 15.5°.

TOLUENE—By fractional distillation toluene was obtained, boiling at 105-110°, water-white in color, specific gravity 0.864 at 15.5°. By treatment with HNO₃ and H₂SO₄ we obtained trinitrotoluene, M. P. 82°, crystallizing from alcohol in long, slightly yellow colored needles.

XYLENES—The xylene fraction being very small, individual xylenes could not be separated and it was no further identified than by its boiling point. It probably contained higher benzol homologues.

NAPHTHALENE—The naphthalene fraction, 149-222°, was considerable. The naphthalene itself was readily obtained pure by several crystallizations. It gave a constant M. P. of 80° and the characteristic yellow picrate melting at 145°. Attention is drawn to diphenyl (B. P. 222°) and the methyl naphthalenes which probably occur also in this fraction, have thus far proved fruitless.

ACENAPHTHENE—From the fractions 98-138° no

definite hydrocarbon was isolated in sufficiently pure condition to warrant its presence being reported. From the 280–300° fraction acenaphthene was readily obtained, crystallizing from alcohol in flat needles, sometimes $\frac{1}{4}$ in. long, which after two crystallizations gave the constant melting point of 95°. The picrate of this hydrocarbon crystallizes in orange needles melting at 160°.

ANTHRACENE—The 305–325° fraction consisted mainly of anthracene with phenanthrene and uncrystallizable oil. This latter was pressed out on a porous plate and to separate anthracene from phenanthrene advantage was taken of the much greater solubility of phenanthrene in alcohol. By several fractional crystallizations the two were obtained pure. The anthracene crystallized in transparent flakes with a greenish blue fluorescence, melting at 212°. The picrate was prepared by bringing together approximately equal amounts of anthracene and solid picric acid into a solution of picric and in alcohol saturated at room temperature and heating till the two had dissolved. On cooling red needles separated which melted at 138°.

PHENANTHRENE—The phenanthrene was obtained as described above, by crystallizing from alcohol, in small white flakes melting at 99°. The picrate was obtained in the form of yellow needles melting at 145°.

PYRENE—The fractions from 320–350° contained such a complex mixture of hydrocarbons that no individual one could be isolated owing to scarcity of material. From the 355–390° fraction by extracting with benzene, evaporating and crystallizing twice from alcohol, a mixture of crystals was obtained melting about 138°. These were dissolved in alcohol treated with picric acid and the resulting picrate after two crystallizations from alcohol decomposed by ammonium hydroxide. The free hydrocarbon thus obtained was crystallized four times when a melting point of 145° was finally obtained. By this time the material had dwindled to a very small amount and no further crystallizations were attempted. Under the microscope the crystals appeared as slightly yellow rhombic plates apparently free from any other crystals. The picrate of this compound is red in color and melts at 222°. This corresponds very closely to the properties of the pyrene picrate which is given in the literature as very characteristic. The pure hydrocarbon, however, melts at 149°, whereas ours melts at 145°. From the yellow color it would appear as if some phenyl anthracene, which crystallizes in the same system, melts at 152–153° and has the same solubility as pyrene, was present in sufficient amount to depress the melting point.

CHRYSENE—From the small fraction distilling over 400°, by treatment with carbon bisulfite, a yellow powdery residue was left. This residue was crystallized from toluol, then treated with alcohol and nitric acid to remove the color and crystallized twice from toluol when it was obtained in the form of white scales melting sharply at 249°.

No analyses were undertaken of the above hydrocarbons as little is to be gained from an analysis in the way of identification. Their melting points, the boiling points of the fractions where they occur, as well as the properties of the picrates were thought sufficient to identify them.

CONCLUSIONS

The isolation of the above highly complex aromatic hydrocarbons from the tar obtained by the thermal decomposition of simple, saturated hydrocarbons such as employed here leads to the conclusion that aromatic formation can take place by building up of the ring compounds from low molecular weight hydrocarbons which need not be higher than two or three or four-member chains. Indeed Meyer and his co-workers¹ have isolated from the tar obtained by the thermal decomposition of acetylene, a large number of aromatic hydrocarbons. Whether the mechanism of the reaction is such as to go through acetylenes or by first building up naphthenes then splitting hydrogen, will not be considered at present. In a recent paper by D. T. Jones² the writer favors the theory of the splitting of hydrogen from naphthenes or from side chains. The objections of the acetylene theory are that either it is impossible to isolate it or only minimal amounts are obtained. This seems to be borne out by our failure to obtain any acetylene tetrabromide from our gaseous products.³

The similarity between the tar we obtained and that obtained from coal is apparent. In this tar the only products which are not present are the phenols and nitrogen compounds which of course would not appear, since the original material contains neither nitrogen nor oxygen.

SUMMARY

I—The thermal decomposition of natural gas condensate is shown to give from simple to highly complex aromatic hydrocarbons. Among these the following have been isolated: benzene, toluene, naphthalene, acenaphthene, anthracene, phenanthrene, pyrene and chrysene.

II—An apparatus is described for readily obtaining these aromatic hydrocarbons from natural gas condensate and the precipitation of the tar "fog" by the Cottrell process.

The thanks of the writers are due to the Department of Industrial Chemistry of this University, and in particular to Prof. Samuel A. Tucker, for the loan of their electrical equipment and kind suggestions, and to the Research Corporation of this city for the setting up of the Cottrell precipitator.

Further work upon these topics is now in progress in this laboratory.

COLUMBIA UNIVERSITY
DEPARTMENT OF CHEMISTRY
NEW YORK CITY

¹ *Ber.*, **46** (1912), 1609; **46**, 3183; **47**, 2765

² *J. Soc. Chem. Ind.*, **36** (1917), 3.

³ For a review of the literature on pyrogenic reactions see Lomax, Dunstan and Thole, *Jr. Inst. Pet. Tech.*, **3**, No. 9.

THE DETECTION AND DETERMINATION OF SULFUR IN PETROLEUM¹

By C. K. FRANCIS AND C. W. CRAWFORD

Received October 23, 1916

The quantity of sulfur in different crude oils appears to vary within rather wide limits. Redwood² mentions the amount found by a number of chemists in petroleum from many fields. Specimens from Mexico, Texas and Algeria contained 2 per cent, a Canadian oil 0.98 per cent, some Ohio oils 0.5 per cent, California oils are reported to contain from 0.5 to 1.5 per cent and one authority is quoted as having examined a petroleum which contained no sulfur.

While working on oils from the Mid-Continent Field, especially samples from the Bartlesville sand in the Cushing pool, some difficulty was experienced in obtaining good tests for sulfur and many of the quantitative methods gave results which were thought to be too low. This work was started with the hope that a reliable test would be developed and that a satisfactory method would be found for accurate determinations which would not involve complicated and expensive apparatus.

Sulfur has been found in petroleum in various forms. Mabery and Smith³ have isolated several alkyl sulfides from Ohio oils. Richardson and Wallace⁴ report free sulfur in oil from Beaumont, Texas. Certain samples found near Newkirk, Oklahoma, contain hydrogen sulfide. The literature examined gives no record of mercaptans, sulfoxides or sulfones in the crude oil, but it is well known that petroleum products often contain sulfonates and sulfates, formed no doubt by the action of the sulfuric acid used in the refining process. In some instances free sulfur has been found in petroleum products obtained from an oil which did not appear to contain free sulfur. This fact may be explained as being due to the practice of using powdered sulfur in the agitator. Also, that some sulfur compounds are decomposed in the still causing the deposition of sulfur in the cool condenser tubes, and on the sight-boxes in the still-house; this sulfur is dissolved in the distillate.

QUALITATIVE TESTS

SILVER COIN TEST—A piece of bright sodium, about 3 mm. square, is placed in a hard glass test tube and covered with the oil to be examined. With gasolines or light burning oils a piece of glass tubing about 18 in. long should be fitted into the test tube to serve as a reflux condenser. The oil is heated over a free flame until it has been completely vaporized or charred. After cooling, water is added to the tube a drop at a time until the violent action has ceased, then 5 cc. more are added. The solution is filtered and a drop of the filtrate touched to a bright silver coin; a brown stain indicates the presence of sulfur in the oil. This test gives good results with crude oil but is not delicate

enough to detect the small amount, 0.035 per cent, sometimes present in the lighter petroleum products.

SODIUM NITROPRUSSIDE TEST—This test may be made on a part of the solution prepared under the silver coin test. The filtered solution obtained after heating the oil with sodium is treated with a few drops of a very dilute solution of sodium nitroprusside. The depth of the violet coloration produced is an index of the approximate amount of sulfur present.

METHYLENE BLUE TEST—It was thought that the methylene blue test, described by E. Fischer,⁵ for small amounts of hydrogen sulfide might be used for the detection of sulfur in petroleum. The method depends on the conversion of the sulfur in the oil to sodium sulfide by treatment with sodium as described under the silver coin test. The filtered solution is neutralized with a few drops of hydrochloric acid in the presence of a drop or two of phenolphthalein, then five or six drops of acid are added in excess. A small crystal of *p*-amidodimethylaniline sulfate is dissolved in the liquid and several drops of dilute ferric chloride are added. If the oil contains sulfur a blue color should be developed which becomes more intense on standing. The blue color is not formed in the presence of too little or too much acid. The amount of acid added after neutralizing should be about one-tenth of the volume. In the presence of cyanides, which may be formed if the oil contains compounds of nitrogen, the blue color may change to a violet on standing but it may be restored by adding more ferric chloride. This test showed a good reaction on a light distillate which gave negative results with the sodium nitroprusside test.

TESTS FOR SULFUR COMPOUNDS

Samples of oil from the same well, producing from the Bartlesville sand, were used for all tests. The crude oil was compared in the tests with portions of the fractions obtained when the oil was distilled. The temperatures at which the fractions were obtained are given in the table.

Fraction No.	FRACTIONAL DISTILLATION TEMPERATURES				
	1	2	3	4	5
Temperature (°C.)	Up to 125	125-150	150-225	225-300	300-350

The methylene blue test indicated the presence of sulfur in each fraction and in the residue. The quantity of sulfur as indicated by the depth of color in each fraction, increased in the following order: No. 2, No. 1, No. 3, No. 5, residue and No. 4. The color produced when the test was made on the crude oil was about the same as that obtained with Fraction 2.

HYDROGEN SULFIDE—About 50 cc. of the oil were shaken up with 10 cc. of water in a separatory funnel, then the water was drawn off and the methylene blue test made for hydrogen sulfide. Negative results were obtained with Fraction 1, 2, 3, and with the residue, but Fractions 4 and 5 produced a light blue color. Negative results were obtained when the test was applied to the crude oil. The hydrogen sulfide found in Fractions 4 and 5 must have been formed by the breaking down of the more complex compound at the temperature 225° and above.

From the thesis presented to the Department of Petroleum Technology, Oklahoma A. and M. College by C. W. Crawford in partial fulfillment of the requirements for the degree of Master of Science.

¹ A Treatise on Petroleum, 1, 539.

² *Proc. Amer. Acad.*, 26 (1891), 508.

³ *J. Soc. Chem. Ind.*, 31 (1902), 31.

⁵ *Ibid.*, 10, 234.

CARBON DISULFIDE—The five fractions were tested for carbon disulfide¹ by adding 3 drops of phenylhydrazine to 10 cc. of each. No precipitate was obtained, indicating the absence of carbon disulfide.

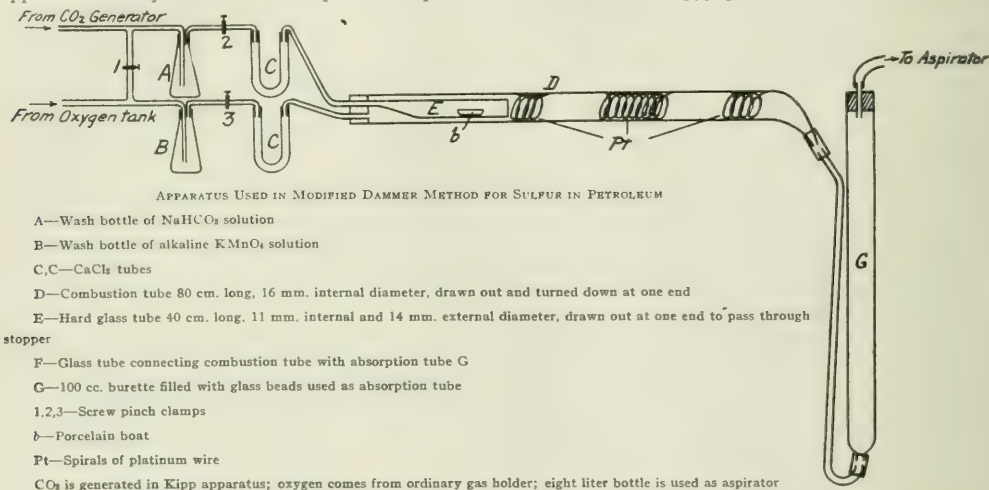
THIOPHENES—A crystal of isatin was dissolved in concentrated sulfuric acid and shaken with 10 cc. of the oil, then warmed (Indophenin reaction). Each fraction was tested and with each the acid was so darkened that no color could be detected. In Fractions 3, 4 and 5 a violet color developed in the oil: this is being investigated.

ALKYL SULFIDES—About 50 cc. of each fraction were shaken with 10 cc. of an alcoholic solution of mercuric chloride. The alcoholic layer was drawn off and diluted with water. On standing, a small amount of a white amorphous precipitate settled out in Fractions 2, 3 and 4, indicating the presence of alkyl sulfides.²

SUMMARY OF RESULTS BY QUALITATIVE TESTS—It appears that alkyl sulfides and thiophenes are present

a low flame for one hour, then the flame is increased and the heating continued over the full flame for at least three hours. After cooling, the fusion is dissolved in hot water, acidified with hydrochloric acid and heated to boiling. It is then filtered and the sulfur precipitated and weighed as barium sulfate. Thirteen determinations by this method gave a maximum of 0.19 per cent, a minimum of 0.13 and an average of 0.157 per cent total sulfur.

FUSION WITH SODIUM PEROXIDE—A mixture of 12 g. sodium peroxide and 0.5 g. potassium chlorate is placed in a Parr bomb and about 0.4 g. of the oil weighed into it, then all well mixed by stirring with a platinum rod. The bomb is closed and the charge ignited. After cooling, the bomb is opened and the fusion dissolved in hot water, acidified with hydrochloric acid and the sulfur precipitated as barium sulfate. Twelve determinations by this method gave a maximum of 0.373 per cent and a minimum of



in petroleum obtained from the Bartlesville sand in the Cushing pool. Other compounds of sulfur may be present in this oil, because the fraction distilling below 125° gave a positive reaction with the methylene blue test, but no reaction for alkyl sulfides, thiophenes, hydrogen sulfide or carbon disulfide. Moreover, the fraction distilling between 300 and 350°C. showed but a trace of hydrogen sulfide while the tests for total sulfur (methylene blue test) indicated a comparatively large amount.

QUANTITATIVE METHODS

MODIFIED ESCHKA METHOD—One-half of a mixture of 10 g. anhydrous sodium carbonate and 1 g. potassium chlorate is placed in a 25-cc. porcelain crucible. A weighed quantity, approximately 1 g. of the oil, is added and thoroughly incorporated with the aid of a platinum or glass rod. The remainder of the mixture is used to cover the mass and the crucible heated over

0.295 per cent. with an average of 0.328 per cent total sulfur.

MODIFIED DAMMER COMBUSTION METHOD¹—The parts of the apparatus and their arrangement are shown on the drawing. The first step in the determination is to start the combustion furnace and heat the part of the tube containing the platinum wire to the highest temperature the glass will stand. While this is being done 35 to 40 cc. of strong hydrogen peroxide are measured into the absorption tube G which is then connected to the combustion tube. About 0.75 g. of the oil is weighed into a porcelain boat filled with ignited asbestos and when the larger tube has become very hot, it is placed about 5 cm. from the larger end of the inner tube E. The aspirator is started and oxygen admitted into the annular space between tubes D and E. A very slow stream of carbon dioxide is then admitted through tube E. A low flame is started

¹ Lieberman Seyewetz, *Ber.*, **24**, 788.

² Beilstein, "Handbuch der Organischen Chemie," **1**, 357.

¹ Dammer, *Z. angew. Chem.*, **23**, 440, used platinized asbestos as a catalyst and absorbed oxides of sulfur in potassium hydroxide or lead peroxide.

under the boat and vapors from the oil soon ignite at the mouth of tube E. The heat is carefully increased under the boat until no more volatile matter can be driven off. Great care must be exercised to regulate the heat and the flow of carbon dioxide so that the oxides will not pass over too rapidly for complete absorption. The flow of water from the aspirator should be regulated so that neither undue pressure nor suction is developed in the hot tube. After all volatile matter has been driven over, the carbon dioxide is shut off at the generator and clamp 1 is opened so that oxygen will pass over the residue in the boat. Clamp 3 is shut down until a very small quantity of oxygen passes through. When the residue in the boat has been completely oxidized the absorption tube is disconnected and the flow of oxygen stopped. The liquid and beads are transferred from the absorption tube to a beaker and boiled with finely divided silica to decompose any excess hydrogen peroxide. After cooling, the sulfuric acid is titrated with standard sodium hydroxide after adding a drop or two of phenolphthalein indicator. It is convenient to use alkali so standardized that 1 cc. is equivalent to 1 mg. sulfur. Blank analyses should be made in order to correct for any sulfur which may be present in the reagents. The entire process may be completed in less than two hours, but the length of time required seems to depend upon the amount of oil weighed out. Four determinations by this method gave: Total sulfur 0.344, 0.379, 0.343 and 0.351 per cent, an average of 0.354.

Results agreeing very closely with each other were obtained by each method but those by the Eschka method were so much lower than the other results that it is evident this method permitted some loss of sulfur. The method of fusion with sodium peroxide in a Parr bomb and the modified combustion method appeared to give reliable results. The greater simplicity of the bomb method makes it more desirable than the combustion method, which requires the greatest care and vigilance on the part of the analyst.

An attempt was made to estimate sulfur in petroleum by burning in an ordinary combustion furnace and passing the evolved gas through standard iodine solution but concordant results were not obtained. Additional investigations were made of methods involving the treatment of the boiling oil under a reflux condenser with fuming nitric acid and the addition of potassium dichromate, potassium chlorate and bromine but low results were obtained in each experiment.

SUMMARY

1—The methylene blue test provides an extremely delicate test for the detection of any form of sulfur in petroleum. It may also be used for determining the presence of hydrogen sulfide.

2—The Eschka method for sulfur does not appear to be applicable to petroleum.

3—Fusion with sodium peroxide in a bomb and the modified Dammer combustion method seem to be accurate for determining sulfur in crude oil.

4—No sulfur as hydrogen sulfide or carbon disulfide

was found in the Cushing oil (Bartlesville sand). Hydrogen sulfide is formed from the oil when it is heated above 225°.

5—Most of the sulfur in the Cushing oil is probably in the form of alkyl sulfides.

PETROLEUM TECHNOLOGY LABORATORY
OKLAHOMA A. & M. COLLEGE
STILLWATER, OKLAHOMA

THE THEORY OF ORE FLOTATION

By H. P. CORLISS AND C. L. PERKINS

Received February 5, 1917

The physics and chemistry of ore flotation constitute the subject of extensive literature, but no one contribution presents an explanation of all the physico-chemical factors involved. These articles¹ include collectively considerable information of importance, but have failed to elucidate this very obscure problem.

In the present paper there will be presented an explanation of the actual factors involved in ideal flotation and also of other practical observations incident to the art. The theory presented herein has been worked out and substantiated by actual experiment. However, for the sake of brevity, only a brief résumé of the experimental results is included.

The greatest success in the art has been obtained in processes in which a gas, usually air, is introduced into the pulp, either by chemical means from carbonate and acid (Potter-Delprat process), by vacuum (Elmore process), by agitation (Minerals Separation process), or by blowing it in through a porous blanket (Callow process) and with or without the use of oil. The explanation offered in this paper is for this type of process especially, though the simple flotation principles involved in such processes as the Maquisten and Wood and the bulk oil process are included.

In all these processes the material floated must not be wholly wet by the water or solution in the presence of this gas or the material surrounding this gas, for example, an oil film on the bubble surface. If the material is completely wet by the water, it will not float, which is the case of the ideal gangue, while the material floated must go to the interface water-air bubble or entirely into the phase other than water, *e. g.*, the oil on the air bubble.

The relations of the forces acting to produce this result were first stated by Freundlich² and enlarged upon by Hoffman³ and Reinders.⁴ They were first stated for the behavior of a sol, which will be called disperse phase 3 in liquid 1, when shaken with an immiscible liquid 2. Let

If $T_{12} > T_{13}$ = Interfacial tension between phases 1 and liquid 1.

If $T_{12} = T_{13}$ = Interfacial tension between phases 1 and liquid 2.

If $T_{12} < T_{13}$ = Interfacial tension between gas 1 and liquid 2.

If $T_{12} > T_{13}$ = The oil will remain unbroken.

If $T_{12} = T_{13}$ = The disperse phase 3 will go entirely into liquid 2.

If $T_{12} < T_{13}$ = The disperse phase will collect at the liquid-liquid interface and will, if possible, separate the two liquids from each other.

¹ See especially the following: W. D. Bancroft, *J. Phys. Chem.*, **19** (1915) 59; *Flotation, Absorption and Adsorption*, 1915; Callow, *Am. Inst. Mining Eng. Bull.*, **1916**, 107; Anderson, *ibid.*, July, 1916, 1119; and Tougart and Beach, *ibid.*, Aug. 1916, 1311. For a very complete bibliography, see School of Mines & Metallurgy, Univ. of Missouri, *Bull.* **8**, No. 1, 1916, and *Am. Inst. Mining Eng. Bull.*, 1916, 1111.

² K. Freundlich, *1909*, 133, 134.

³ *J. Phys. Chem.*, **65**, 1903, 383.

⁴ *ibid.*, **13**, 1915, 135.

If, however, no one interfacial tension is greater than the sum of the other two, then the disperse phase will collect at the liquid-liquid interface, but the three phases will meet at a certain contact angle.

The application of these principles to flotation may now be stated, for while the greater part of the material floated is much less disperse than that which is considered colloidal, the interfacial tendencies are the same, it simply being a question if the forces holding the mineral to the interface are sufficient to overcome gravity, if the particle is to float.

WITHOUT THE USE OF OIL—This is known as the Potter-Delprat process, in which CO_2 is generated in the acid pulp, but may be carried out successfully on some ores in a Callow cell, using air. Here, if flotation is to result, the mineral must go to the interface water-gas and be carried at this interface to the top of the pulp. The word water will be used mostly to denote the aqueous phase, whether it is pure water or a solution, and the floatable material will be called sulfide, since this is the common case. On the basis of interfacial tensions, where if

$T_{s,a}$ = Interfacial tension sulfide-air (or CO_2),
 $T_{s,w}$ = Interfacial tension sulfide-water,
 $T_{w,a}$ = Surface tension water air (or CO_2),

either (1) $T_{s,w} > T_{s,a} + T_{w,a}$ or (2) no one interfacial tension is greater than the sum of the other two, must be true. It is obviously impossible to have $T_{w,a} > T_{s,a} + T_{s,w}$ as the latter two are very large in comparison with the first, according to theoretical reasoning and measurements.¹ Case 2 is the actual one, as can be seen if a drop of water is placed on a flat sulfide surface. Here the water does not spread over the entire surface, but comes to equilibrium with the three phases, sulfide, air and water in contact at a certain angle. Case 1 would require that the water should not wet the sulfide at all in presence of air. In flotation then the sulfide comes to the air-water interface and sticks through the bubble surface to a certain extent, or is held in such a way that the three phases are in contact. The gangue material is completely wet by water and does not float; i. e., $T_{g,w} > T_{g,a} + T_{w,a}$.

Some measurements were made to get an idea of these interfacial tendencies, by a method explained by the use of Fig. 1. Here a flat ground mineral surface was placed vertically in water or other solution as shown. By raising and lowering the mineral, a quite constant result was obtained for the rise of the meniscus against the mineral above the general level. Here the meniscus was always upward, showing a greater preference of the mineral for water than for air. In the case of the sulfides, when they were raised, the meniscus would soon draw back to a definite height, leaving the sulfide surface above quite dry. For gangue the water does not draw back quickly, but remains, wetting it for some time. The sulfides are proven interfacial in this way and the measurements of the height of the point of contact above the general level are interesting. The measurements were made with a cathetometer.

¹ Hulett, *Z. phys. Chem.*, **37** (1901), 385. Also the surface tensions of molten metals and fused salts are high.

MATERIAL	Water	0.1 Per cent H_2SO_4	0.1 Per cent NaOH
Chalcocite	1.55 mm.	2.10 mm.	3.07 mm.
Chalcopyrite	2.60	2.50	2.90
Gangue (silicate)	3.20	3.25	3.30

The figures for the gangue are not at the point of contact, for there is none, since it is thoroughly wet by water, but are at the point where the meniscus becomes parallel to the face of the mineral surface. The mineral giving the smallest rise should be the most interfacial and the best floating. This was found to be true, for, without oil, chalcocite is a better floating mineral than chalcopyrite, at least for the ores that were tested. The figures above also show that in alkaline solution a very poor float should be made, as the rise is almost as much as for the gangue. This was also found to be true. Differences even among sulfides are clearly shown, hence it is not surprising to find all gradations in floating properties among ores. These measurements, made on large pieces of mineral with ground and partially polished surfaces, may not correspond exactly to those for an ore surface, though in the cases mentioned above they were found to give results agreeing with practice.

Another point noticed in these measurements, which is an important one, is how quickly the water is displaced from a mineral surface when brought in contact with air. If an air bubble comes in contact with a sulfide particle immersed in water, it must partially displace the water from the sulfide rather quickly, if it is to be floated in a pneumatic cell. This was tested for the same minerals, by noting the time taken for the solution to come back to the final point of contact, when the mineral was raised, with the following general results:

- (1) Water and acid solutions are removed more quickly in air from chalcocite than from chalcopyrite.
- (2) Little difference is noted between acid and neutral solutions.
- (3) Alkaline solutions are removed very slowly from all surfaces.
- (4) All solutions adhere strongly to gangue.

These facts also agree with the practical results mentioned above. The success of the Potter-Delprat process may well be due to these facts, since the CO_2 is generated in contact with the sulfide and time is given for the solution to be partially displaced by the gas, or, in other words, for the sulfide to attain the interfacial condition and be floated.

When a soluble frothing agent is used, without oil, the same principles apply, the frothing agent simply modifying the water to a certain extent.

WITH OIL—The use of oil introduces several new factors which make the problem more complex, but the same principles apply. The sulfides can now be interfacial between water and air as discussed above, but in addition may be interfacial between water and oil or even go into the oil layer. This oil layer is on the bubble surface and the forces holding the sulfides to this surface, if it has an oil film, are much greater than when no oil is used. This point will be proven a little further on. The oil layer on the bubble surface need be only of minimum thickness to act, in contact

with water, the same as a layer of oil on water, as far as interfacial tendencies are concerned. Let

$$\begin{aligned} T_{s,w} &= \text{Interfacial tension sulfide-water,} \\ T_{s,o} &= \text{Interfacial tension sulfide-oil,} \\ T_{o,w} &= \text{Interfacial tension oil-water.} \end{aligned}$$

Then if (1) $T_{s,w} > T_{s,o} + T_{o,w}$, the sulfide will go into the oil layer completely.

(2) No one interfacial tension is greater than the sum of the other two, the sulfide will go to the oil-water interface and the three phases will be in contact at a certain contact angle. The gangue is thoroughly wetted by water, *i. e.*, $T_{g,o} > T_{g,w} + T_{o,w}$.

These inequalities have been stated and applied to the flotation process by Ralston.¹ The second condition given above, where the sulfides are interfacial seems to be by far the most general, though the first condition may be, and probably is, realized, especially when tarry oils are used which in grinding with the ore coat the sulfides more or less with this tarry material. It is doubtful if the lighter oils or the lighter constituents of a tarry oil mixture film the sulfide at all in grinding, but rather it is probable that this oil is emulsified in the operation. The condition where the mineral is completely filmed by oil would be the best floating condition, and this could be realized in the flotation cell, where this film would be continuous with the oil film on the bubble surface. All gradations of the interfacial conditions are possible, from those that show only a slight tendency to be wet by water

The following measurements were made after the meniscus had come to the true point of contact of the three phases, and this point was closely the same whether the mineral was wet with the oil or solution first. The averages of these two figures are given. Kerosene and a kerosene pine oil mixture were used mostly, as the interfaces are better defined, especially in acid and alkaline solution, than with many actual flotation oils. These other oils act in the same way, however.

DEPRESSION OF MENISCUS		KEROSENE AND CHALCOPYRITE	
Water	0.10 Per cent H ₂ SO ₄	1 Per cent H ₂ SO ₄	10 Per cent H ₂ SO ₄
2.99 mm.	2.02 mm.	1.32 mm.	0.75 mm.

Calcite in contact with neutral, acid, and alkaline solutions and kerosene showed interfacial tendencies in alkaline solution only.

Malachite exhibited a small interfacial tendency, except in alkaline solution in which it was thoroughly wet by the solution.

KEROSENE AND PINE OIL AND AQUEOUS SOLUTION
This was a flotation mixture of 90 per cent kerosene and 10 per cent pine oil

SOLUTION	DEPRESSION OF MENISCUS	
	Chalcopyrite	Chalcocite
Water	3.10 mm.	3.42 mm.
0.10 per cent NaOH	1.98	3.84
0.10 per cent H ₂ SO ₄	1.45	0.95

Gangue material in all cases is thoroughly wet by the solution, especially if it is wet by the solution before coming in contact with the oil, as is the case in actual flotation. The case of chalcocite in water given above is almost a condition of complete wetting by oil.

These experimental results in every way justify the theoretical discussion above and also show that alkali and acid lower the interfacial tension sulfide-water as the preference for oil is not as great in these solutions as in water, although the sulfide is still decidedly interfacial and hence can be easily floated from acid or alkaline pulps. These results were obtained by the use of a clean sulfide surface, but in actual flotation this may not be true for all the particles, and since the interfacial properties are a function of the surface only, we may expect many differences from these ideal measurements. In alkaline solution, for example, there may be some of the mineral which, like calcite, is more interfacial in this solution than in water, and hence would float although it would not do so in a neutral pulp. In tests it has been found with some ores and oil mixtures that in an alkaline pulp a better recovery was made in the usual length of time than by prolonged floating in neutral pulp. This might also be true in an acid pulp for some minerals.

NATURE OF THE SOLID SURFACE AND HYSTERESIS OF THE CONTACT ANGLE

It has been noticed that some surfaces have a strong tendency to hold fast to the liquid that wets them and not to allow it to be easily displaced by another liquid. In the work upon interfacial tensions, described above, such a surface would show a great difference in potential energy or weight of contact, depending upon whether it was wet with oil or water first. It has also been observed that in a process of

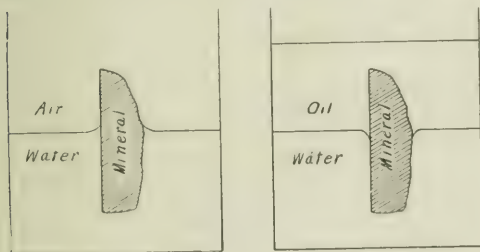


FIG. I

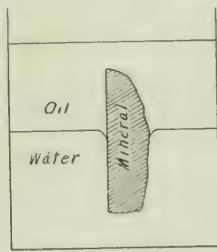


FIG. II

in the presence of oil, to those that are thoroughly wet, which is the case of the gangue material.

Experimental determinations of the interfacial tendencies of various minerals were carried out in the same way as described above, except that in this case the interface was oil-water, or aqueous solution. In Fig. II is represented the case of a sulfide surface at this interface. The floatable materials were all interfacial and the sulfides showed a decided preference for the oil. This is a very important point in showing that the same sulfides are much more strongly held to an oil-covered air bubble than to one not so covered. In Fig. I the sulfide, while interfacial, shows a preference for water over air and would easily be displaced in actual flotation from the interface and go back into the water. In Fig. II the meniscus is now pushed downward into the water, instead of upward and hence the sulfide is held much more strongly to oil than to air.

those substances having smooth or shiny surfaces which float, while those having dull or rough surfaces do not float.

These observations and others point to the following explanation of the mechanism of this action: there is first the inherent property of each substance to adhere to oil or to water to a certain degree. When the substance is brought to the interface between water and oil, these forces tend to come to equilibrium with the third force, the interfacial tension between oil and water at some definite contact angle. Here is where the physical nature of the solid surface comes into play. If the surface is smooth and shiny, such as that of a polished metal or a freshly fractured sulfide crystal, then the liquid first touching it is easily pushed back to the equilibrium position when brought to the interface with another liquid. If, however, the substance has a dull, *i. e.*, a capillary surface, so that the liquid first wetting it is strongly held in its pores, then, when it is brought to the interface it may exhibit no interfacial properties at all although, if it were smooth, it might even show a preference for the other liquid. This shows the reason for the difference, "or hysteresis," of the contact angle noted for some surfaces. It also explains why a particle having such a surface, if first wet with water, as is the case in flotation, will be very difficult to float, since it will not easily be brought into contact with oil.

FUNCTION OF THE BUBBLE—The function of the bubble is to give a large surface to which the sulfide may go and be floated. As already stated, the air bubble in oil flotation is covered wholly or in part by an oil film. For the action of oil on water, see Devaux¹ and Langmuir.² It is not necessary that the oil completely cover the bubble, and it probably does not in the greater proportion of the bubbles. The supply of oil for the bubbles will be discussed under the action of emulsions. If an oil droplet is placed on water or aqueous solution, it will spread out over the surface provided the surface tension of the water is greater than the sum of the surface tension of the oil plus the interfacial tension oil-water, *i. e.*, this inequality must be true:

$$T_{w,o} > T_{o,a} + T_{o,w}$$

For oil flotation this must be true for all solutions used, as the air in the bubble, surrounded by the pulp, presents this same condition. If to water is added some material which lowers its surface tension ($T_{w,a}$), without lowering $T_{w,a} + T_{o,a}$ to an equal amount, the inequality is reduced and finally a point is reached where the oil will not spread on the solution. This is easily realized in case of soap solutions, and with many other substances which lower the surface tension greatly. In this condition a poor float would result. In flotation, in order to produce a froth, material such as the soluble portion of pine oil is added which lowers the surface tension of water. Unless this helps in other ways than producing a froth, it should be used in as small a quantity as possible, and this agrees with many practical observations. The froth-

ing agent added also lowers the interfacial tension oil-water, but here it must be remembered that even if the interfacial tension is lowered in the same proportion as the surface tension, the inequality is less than before, since the interfacial tension is much smaller than the surface tension of water. The other factor, the surface tension of oil ($T_{o,a}$), is not changed much, for inorganic salts, etc., do not dissolve in it. If, however, some substance is added which will not lower the surface tension of water but will lower the interfacial tension oil-water, then this should produce better oiling of the bubble. This can be done with alkalies and in the case of some oils by acids.

An important point in connection with the use of the pneumatic cell is the time during which the bubble is in contact with the pulp as it passes through, as here it must be attached to the sulfide particles. Any reagent that will give a quicker filming of the bubble surface by oil, after it comes through the blanket, will be of benefit in the rapidity with which the mineral is attached and raised. Alkalies, as explained, produce a greater inequality between $T_{w,a}$ and $T_{w,a} + T_{o,a}$ and hence the oil will be spread out thicker over the surface than without their use.

A large number of surface and interfacial tension measurements were made, a few of which are as follows:

SURFACE TENSIONS		Dynes per cm.
Water 25° C.....		71.8
Kerosene.....		25.2
Coke-oven Oil.....		28.0
Pine Oil.....		30.0
0.01 per cent solution Terpeneol.....		68.6
0.10 per cent solution Terpeneol.....		49.2
INTERFACIAL TENSIONS		
Kerosene-Water.....		32.8
Kerosene and Pine Oil-Water.....		11.6
Kerosene and Pine Oil-0.05 per cent solution NaOH.....		7.3
Kerosene and Pine Oil-0.20 per cent solution NaOH.....		4.5
Kerosene and Pine Oil-0.20 per cent solution H ₂ SO ₄		13.2
Coke-oven Oil-Water.....		14.1
Coke-oven Oil-0.05 per cent solution NaOH.....		5.8
Coke-oven Oil-0.20 per cent solution NaOH.....		2.6
Coke-oven Oil-0.10 per cent solution Na ₂ CO ₃		6.6
Coke-oven Oil-0.20 per cent solution Na ₂ CO ₃		4.4
Coke-oven Oil-0.20 per cent solution Na ₂ BO ₃ 10 Aq.....		8.0
Coke-oven Oil-0.10 per cent solution Na ₂ PO ₃ 10 Aq.....		9.6
Coke-oven Oil-0.20 per cent solution Na ₂ PO ₃ 10 Aq.....		7.4
Coke-oven Oil-0.40 per cent solution H ₂ SO ₄		14.4
Coke-oven Oil-0.01 per cent solution Saponin.....		9.3
Coke-oven Oil-0.01 per cent solution Tannic acid.....		12.7
Coke-oven Oil-0.01 per cent solution Hemoglobin.....		8.9

Considerable data of this kind are given by Lewis³ and Shorter and Ellingsworth² on the action of dyes, salts and soap. The drop number apparatus used was the same as described by Shorter and Ellingsworth. Their work also shows that soap and alkali together are very active in lowering the interfacial tension oil-water. This would be the condition in an alkaline pulp, as there would then be free alkali and some saponified material with many of the oils used.

The results when colloidal material is present are subject to great variation, due to different speed of formation of drops. The figures given above for these materials approach the dynamic value, as the rate of dropping was fairly rapid. The static values are very much smaller and are interesting in connection with the emulsifying power of these substances. As an example of this the following result on coke-

¹ Ann. Report Smithsonian Inst., 1913, 261.

² Met. & Chem. Eng., 16 (1916), 469.

³ Z. phys. Chem., 74 (1910), 619.

² Proc. Roy. Soc., 92 (1916), 231.

oven oil against 0.005 per cent hemoglobin solution is given. The time is for the total number of drops formed.

TIME	DROP NO.	INTERFACIAL TENSION
2 min. 40 sec.	22.5	13.2 dynes per cm.
1 hr. 4 min.	84	3.5 dynes per cm.

It is seen from the table above, that besides NaOH itself, any salt that hydrolyzes to give an alkaline solution lowers the interfacial tension, and all these salts are beneficial to flotation.

EMULSIONS—The behavior of the oil at the bubble and sulfide surfaces has been given. In the pneumatic cell this oil is supplied by an emulsion or a coarser suspension of oil in water. In the agitator type machine, the oil may be beaten in at the cell, though it is also customary to grind the oil with the ore. In either case the problem of emulsions comes in. In the pneumatic process this emulsion is formed in the grinding and must be good enough to last throughout the float, yet not so good as to fail to break down with sufficient rapidity to give free oil for the bubble surface. The subdivision of the oil is such that no doubt almost all degrees of dispersion exist; the larger droplets may be of sufficient size for one to coat a fair area of a bubble surface, but the better emulsified portion is of such size that many particles have to unite to give oil enough for the minimum thickness of an oil film, to spread over even a square centimeter. This can be calculated from the minimum thickness of an oil film¹ and the size of the particles in an ordinary oil emulsion.²

Experimental evidence on these points is very conclusive. If a coarse suspension of oil is made simply by shaking the ore, oil and water together in a bottle by hand, and then put in a small Callow cell, only a partial float results and the operation must be repeated several times, adding more oil each time, in order to get a good recovery. If, however, too good an emulsion is had, a poor recovery also results. For this purpose a kerosene pine oil mixture was emulsified with water in a De Laval emulsor and allowed to stand over night and a middle portion of this emulsion was removed for the tests. This emulsion added at the cell gave a small float at first and then stopped. On adding a little acid no further float resulted, but by allowing the pulp to stand for a few minutes an additional amount of sulfide was raised and finally a good recovery was made, though considerable time had to be given for the emulsion to give up its oil. This was also found to be true for another oil which gave an excellent emulsion on simply adding it to water.

It is interesting to note that in these cases it was proven that it was not necessary to grind the oil with the ore, but by adding it as an emulsion prepared by itself as good a recovery results. This probably is not true for oils containing tarry matter as explained above. It was also noticed in using the second emulsion, named above, that flocculation of the slimes took place in neutral solution and that these then floated

to a large extent, giving a non-preferential float; when, on the other hand, the emulsion was broken by acid and alum, a good preferential float resulted. It was found that these slimes in neutral pulp had flocculated with the oil emulsion so that on standing all the oil was carried down, though the emulsion was not appreciably broken.

The value of acid and salts having a polyvalent cation has been demonstrated in some cases, usually in connection with the M. S. type process. In this process there is greater danger of getting too good an emulsion than in the Callow process, and the value of acids and salts of this type consists in their power of breaking down an emulsion, or preventing too good a one being formed. These salts should be used in acid solution, or otherwise, due to hydrolysis, the insoluble hydroxides formed, *e. g.*, $\text{Fe}(\text{OH})_3$, and $\text{Al}(\text{OH})_3$ have the opposite effect, *i. e.*, of preventing the breaking down of the emulsion or promoting its formation.¹ Oil emulsions in FeCl_3 solution on standing give a yellow flocculent precipitate, but the emulsion is not broken. The mechanism of this is discussed by Ellis.² In a neutral, pneumatic, Callow float, such salts have been found to be harmful. If salts of iron or aluminum are present in the feed water then acid may be necessary to prevent this action between them and the oil emulsions.

The value of alkalies has been discussed as giving a better oiling of the bubble surface. In connection with emulsions, however, a greater effect can be ascribed to the action of alkalies or salts which hydrolyze to give an alkaline reaction and to those which have a polyvalent anion. If a neutral ore pulp is shaken with a small quantity of an oil emulsion it is found that the slimes are coagulated with the emulsion and settle out, often leaving the liquid quite free from oil emulsion. The emulsion is not broken, but simply carried down with the flocculated slimes. If alkalies are used, or salts such as last mentioned, then the slimes are deflocculated in the great majority of cases. They then settle more slowly, and when they have settled the emulsion is left free and still standing. This is very important, for now the emulsion is free to function as it should, *i. e.*, to give oil to the bubble surface. The ore particles, both sulfide and gangue, are also free to show their own behavior toward the water and the oil. This deflocculation should, and does, result in a higher grade concentrate and a greater and quicker recovery, since now no sulfide particles are coagulated with, or surrounded by, gangue particles that prevent their flotation.

The use of lime has not been found to be as beneficial as that of NaOH. This is explained by the fact that this substance, due to the predominating effect of the calcium ion, coagulates instead of deflocculating the slimes, and hence part of the emulsion is consumed and the individual particles are not free to float as they should. This coagulating action may be more noticeable in a Callow cell than in a cell of the Muesel

¹ Devaux, *loc. cit.*

² Ellis, *Z. physik. Chem.*, **80** (1913), 597.

³ Briggs and Abbott, *Trans. Am. Inst. Min. Engrs.*, **19** (1907), 418.

⁴ *Z. physik. Chem.*, **80** (1913), 597.

separation type, as in the latter the coagulated slimes may be broken up considerably, but the tendency is the same in either case.

QUANTITY OF OIL The principles involved when varying quantities of oil are used, is a question on which there is a great difference of opinion. From the theory there should be no difference whether a large or small amount of oil is used, provided this oil is properly emulsified. If a large amount, 2 per cent or 3 per cent, is used and is not emulsified sufficiently, the excess may float and be of disadvantage in several ways. To test this point a float was made with an amount of oil equivalent to 2 per cent of the weight of the ore, emulsified in a De Laval emulser, and added at the cell (Callow) and a float made. It behaved in every way the same as when 0.2 per cent or less of oil was used and the recovery was better, with as high a grade of concentrate. Of course, economy would settle the minimum amount of oil to use. This was repeated with other oils and ores. The extra amount of oil used gave a greater oiling of the bubble surface, and in fact these floats were better than when alkali was used to make the smaller amount of oil more efficient.

COLLOIDS AND "POISONS"—In the light of the above work the question of flotation "poisons" was taken up with the idea that any substance which will prevent the breaking down of an emulsion or coalescence of oil droplets, or which gives adsorption of colloidal particles at the oil-water interface is harmful to flotation. In the first two cases the proper amount of oil will not be freed, and in the other case the oil surface, if formed, would be covered by an adsorbed layer, so that no oil surface would be presented for attachment of the mineral.

Experimental work, by actual flotation, had shown what substances, including many dyes, were harmful. Solutions of these substances of 0.01 per cent strength were shaken in test tubes, with about 2 cc. of oil, for a few minutes to the same extent and at the same time. The tubes were then placed upright and the amount of emulsification and rapidity of coalescence of the oil droplets rising to the top noted, with the following results:

(1) **SLIGHT OR NO EMULSIFICATION AND RAPID COALESCENCE OF DROPLETS**—Methylene blue, saffranine and Bismarck-brown. These dyes really act like salts and are not colloidal, nor are they harmful to flotation. In fact, these dyes assist slightly in breaking an emulsion.

(2) **EXTREMELY SLOW COALESCENCE OF DROPLETS**—The finely divided oil layer lasting for several hours to days: Congo-red, bengoazurin, azo-blue, saponin, tannic acid, waste sulfite liquor, hemoglobin and eosin. These substances are all very injurious to flotation. Most of these are negative colloids. Hemoglobin is highly colloidal and positive and its adsorption is probably enhanced because it is oppositely charged to the oil emulsion. Several of this last class of substances, especially saponin, gave marked emulsification, even with the small amount of shaking received. Some of these substances also form quite stable and viscous skins at oil surfaces.

Another experiment consisted in dividing an oil emulsion in two parts to one of which tannic acid was added, and then frothing over equal volumes of each in a small cell. The one to which tannic acid had been added contained 3.5 times as much oil in the residue or tail water as the other. This shows that the oil emulsion had been kept from breaking down, and the oil from being frothed over.

Besides the substances given above, the injurious effect of insoluble hydroxides of the heavy metals has been explained under emulsions. Other inorganic colloids have been found to be injurious, *e. g.*, when floating with $K_4Fe(CN)_6$, the $Cu_2Fe(CN)_6$ formed from the oxidized and soluble copper hurts the float very noticeably.

The experimental evidence proves that the action of these colloids is, without doubt, as stated, though they may also adsorb at the solid surfaces and in that way cause a poorer result to be obtained. It is easily seen how the water used in flotation and the slimes coming from certain ores have a great effect in flotation. This has caused some to say that it is the gangue that determines the success of the process, and if the water supply be included in this, they are to a certain extent correct.

FROTHS—The froths produced in flotation are useful as a mechanical means of removing the mineral brought up by the bubble. The formation of a froth and its stability are due principally to dissolved materials in the water which give to the solution a variable surface tension. The static surface of a solution has a lower tension than a fresh surface, whether the substance added lowers or raises the surface tension of the solvent. Since a large lowering may be caused by a small amount of solute and only a small rise may be obtained, the best frothing agents are those that lower the surface tension. Pine oil is used to a large extent for this purpose in practice, the soluble portion causing a considerable lowering of the surface tension of water. In many articles that have appeared on the theory of flotation, it has been stated that oils lower the surface tension of water. This is not very clearly stated, since, as ordinarily understood, oil is insoluble in water and only soluble material can affect the surface tension of water. Besides the soluble portion of pine oil, a part of many other flotation oil mixtures is soluble and gives a froth. Terpeneol, menthol and many such substances are very powerful frothing agents. The lasting qualities of a froth, as stated above, are due to its variable surface tension, for if a bubble starts to thin out or break at a certain point this fresh surface has a greater surface tension than before and hence is automatically strengthened at this point and resists rupture. In using alkalis it is observed that a more quickly breaking froth results in a pneumatic cell. This can be explained by the fact, as stated before, that a greater extent of bubble surface is covered with oil and hence there is less surface which contains only the adsorbed frothing agent, and since oils themselves do not produce good froths, the froth breaks more quickly than when alkalis are not used. Or, this observation may be used

to support the view that the bubbles are better oiled in an alkaline pulp. A froth is also stabilized by the slimes present in a pulp or by other colloidal matter. Colloidal material dissolved in the oils will make an oil froth more lasting. A mixture of oils, the same as an aqueous solution, gives a better froth than a pure oil.

ELECTRICAL EFFECTS—Considerable weight has been placed by many upon the electrostatic forces that might be present in the flotation process. Some have even considered the attraction that holds the sulfide to the bubble surface to be of this origin. Air bubbled through water has been found to carry ions,¹ and from this and the fact that most substances have a contact difference of potential when in contact with water or solutions, an electrical theory has been built up, though in many cases serious errors have been made regarding the action of these forces.

Measurements were made to determine these forces. The small metal Callow cell used was grounded, as this condition prevails in actual practice. The charge carried by the air issuing from the flotation pulp was discharged on a metal screen placed above the cell, and the effect measured by means of a Dolezalek electrometer. The readings in this case are measured in volts per minute. The charge upon the air from several pulps was measured and in no case did it exceed 0.011 volt per minute, and was usually only about half the value. The air was negative in neutral pulps, but slightly positive in one of the alkaline pulps.

The charge on the froth was also measured and this varied from zero to 0.011 volt as the maximum. This was sometimes positive and under other conditions negative. In two good floating pulps the froth was at almost zero potential, though 0.002 volt could easily be determined. It seems, then, that these electrostatic effects are far too small to have any important part in flotation, and cannot possibly be the force that holds the sulfide to the bubble. This, too, would require a dielectric film, *e. g.*, oil, between the two oppositely charged bodies, the sulfide and the gaseous ions in the bubble; but since flotation results without the use of oil in many cases, and without doubt the bubble surfaces are often not completely covered by oil even when oil is used, it seems that this theory cannot hold.

The contact difference of potential of various minerals has been used in some theories. These were also measured by an electro-endosmose method as described by Perrin.² To this apparatus a small calibrated tube was sealed at the top of the diaphragm side, so that when dilute electrolytes are used the gas generated can be forced over into this tube, after the experiment is over, and this correction applied to the amount of liquid apparently transferred through the powdered material. The distance between the electrodes was 12 cm. and the potential 110 volts.

The results obtained give the sign of the charge on the solid in contact with the water or solution, but

quantitative results as to the actual potential differences are very difficult to obtain in this way. However, some idea can be had by comparing the amount of liquid transferred for the minerals, to that transferred in the case of silica, whose potential difference against water has been found by cataphoresis measurements. This is found to be approximately —0.042 volt. For quartz and ferric hydroxide, see Whitney and Blake.¹ The results obtained are as follows:

MINERAL	LIQUID	Sign of Solid	Liquid Transferred Cu. mm. per min.
Silica	Water	Negative	30.7
Alumina	N/100 HCl	Positive	40.0
Chalcopyrite	Water	?	Approx. 0
Galena	Water	Negative	3.6
Sphalerite	Water	Negative	6.1
Molybdenite	Water	Negative	3.7
Malachite	Water	Positive	4.0
Malachite	N/500 HCl	Positive	17.8
Galena	F. W./500 FeCl ₃	Positive	44.3

Here the sulfides tested are seen to be slightly negative against water or practically zero in case of chalcopyrite. This agrees with our ideas concerning the contact difference of potential of these substances and with cataphoresis experiments on colloidal sulfides, etc. Malachite is positive, as would be expected from its basic character. The last result given in the table is probably due to the formation, by hydrolysis, of ferric hydroxide, and its adsorption on the surface of the mineral, so that the action is exactly the same as for ferric hydroxide itself.

In this case again, we see that no attraction can exist on the basis of electrical charges between sulfides and oil in emulsions, since they are of the same sign. The charges on oil in emulsions in dilute salt solutions, etc., are given by Ellis³ and Powis⁴ and others. This, however, would not determine the charges on a mineral and oil, if the two were in actual contact, as is necessary for flotation.

The charges carried by the oil in emulsions are important probably in connection with positively charged colloids which act as poisons, and, of course, the coagulation of slimes and the breaking of an emulsion by electrolytes is a function of the charge carried by them; but it is not possible to use these charges as an explanation of the primary principles involved in flotation.

CONCLUSIONS

The following is a summary of the conclusions arrived at as a result of the work reported in this communication:

I—For an ore particle to float, it must be interfacial between oil and water or it must go completely into the oil phase. If no oil is used, the particle must be interfacial between water and air. The force holding the particle to the bubble is much greater when oil is used.

II—In addition to its value as a lifting agent, the bubble serves to produce a large wet surface in contact with the pulp. This surface is covered to a greater or less extent by an oil film to which the mineral may go so that a small amount of oil is very efficient.

III—Fla oil should not be so well consolidated that it will not be given up to the bubble surface, and yet

¹ Lord Kelvin, McLean and Galt, *Proc. Roy. Soc.*, 1894, 57; Cochran and Moore, *Ann. Physik*, 43 (1914), 1048.

² *J. chem. phys.*, 2 (1904), 601.

³ *J. Am. Chem. Soc.*, 26 (1904), 1439.

⁴ *J. phys. Chem.*, 78 (1911), 475.

⁵ *Trans.*, 89 (1914), 93.

should be sufficiently emulsified, in a pneumatic process, to last during the time of floating.

IV—Colloids in general are harmful, owing either to their causing too stable an emulsion, or to their adsorption on the oil film at the bubble surface preventing mineral attachment. This is the action of the so-called "flotation poisons."

V—The froth formed is attributable either to the soluble portion of the flotation mixture, which produces a variable surface tension, or to finely divided or colloidal materials.

VI—Acids, alkalies and salts affect all these factors, as discussed under the several headings in the paper.

VII—The electrical effects, other than the colloidal charges, are not important in flotation.

VIII—The nature of the solid surface in relation to its wetting properties has been discussed and an explanation of the "hysteresis" of the contact angle advanced.

In the light of present knowledge, it is impossible to measure many of the forces operative in flotation, such as, for example, the interfacial tensions between solids and liquids, or to explain the mechanism of adhesion. Such problems are, however, nearer solution, due to the material advances made recently by Laue¹ and by Bragg and Bragg,² by which the actual arrangement of the atoms in a crystal may be determined, and also by Langmuir,³ whose work on the constitution of solids and liquids, the structure of solid surfaces, and the mechanism of adsorption leads toward the solution of this problem.

While the flotation of each ore still remains more or less of a problem in itself, yet a clear understanding and the proper application of the principles involved will lead to an earlier solution of the problem.

In conclusion, the authors wish to express their thanks to Dr. R. F. Bacon and to Mr. E. R. Weidlein, under whose direction this research has been carried out.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH
PITTSBURGH

NOTES ON THE ANALYSIS OF CAST NICHROME

By E. W. REID

Received March 6, 1917

It is no new experience for chemists to find that each alloy has its own personal equation in yielding itself to sharp analytical results, and the remarkable group of mixtures which are coming into such general use under the popular name "Nichrome" form no exception.

The following notes are submitted, not with the supposition that they are the best ideally possible, but with the hope that they may help to call the attention of those specially interested in related lines of research to the need of reliable methods for the analysis of this group of alloys.

¹ *Sitz. Akad. Wiss.*, Wien, June, 1912.

² *Proc. Camb. Phil. Soc.*, 17 (1912), 43, and treatise on "X-Rays and Crystal Structure."

³ *J. Am. Chem. Soc.*, 38 (1916), 2221.

Some difficulty will usually be experienced in getting the alloy into solution, and after several solubility determinations, the following method was adopted. There is always a slight residue left in the bottom of the casserole after treatment with hydrochloric and nitric acids, which appears to be small particles of metal enclosed by gelatinous silica; hence the usual necessity of first removing the silica, and then dissolving the residue in acid, with subsequent fusion of any undissolved chromium with sodium peroxide. Cast nichrome contains approximately 58 to 62 per cent of nickel, 23 to 26 per cent of iron, 8 to 14 per cent of chromium, 0.5 to 2.0 per cent of manganese, zinc and silica, 0.2 to 1.0 per cent of carbon and sometimes a bare trace of copper. The ingredients were determined in the order given.

SOLUTIONS

AMMONIUM CHLORIDE—Saturated solution.

HYDROCHLORIC ACID (SP. GR. 1.12)—8 cc. water to 12 cc. hydrochloric acid (sp. gr. 1.20).

SULFURIC ACID (SP. GR. 1.40)—43 cc. water to 40 cc. sulfuric acid (sp. gr. 1.83).

N/10 POTASSIUM PERMANGANATE—3.161 g. pure salt dissolved in water, diluted to 1 liter.

FERROUS AMMONIUM SULFATE—39.2 g. pure salt dissolved in 500 cc. water and 50 cc. concentrated sulfuric acid added; diluted to 1 liter.

POTASSIUM IODIDE—2 per cent solution.

POTASSIUM CYANIDE—13.5 g. pure salt and 15 g. of potassium hydroxide dissolved in water, diluted to 1 liter.

N/10 SILVER NITRATE—8.495 g. of the salt dissolved in water, diluted to 1 liter.

TARTARIC OR CITRIC ACID—25 per cent solution.

BROMINE WATER—Saturated solution.

POTASSIUM FERROCYANIDE—21.55 g. pure crystallized salt dissolved in water; diluted to 1 liter.

DMETHYLGLOXIME—1 per cent solution.

URANIUM ACETATE OR NITRATE—15 per cent solution.

"STOCK" SOLUTION—(Described under Silicon).

SILICON

Dissolve 2.5 g. of nichrome turnings in a 250 cc. casserole, with 20–30 cc. concentrated hydrochloric acid and 3–5 cc. concentrated nitric acid. Evaporate the solution to dryness, take up with the above amounts of acids, again evaporate¹ to dryness, and ignite to redness for a few minutes. Take up with hydrochloric acid (sp. gr. 1.12) and a few drops of nitric acid; bring to boiling; dilute with cold water and filter.

Wash the residue on the filter paper thoroughly with dilute hydrochloric acid (1 : 3), and finally with hot water. Carefully ignite the filter paper with its contents by means of a platinum wire over a platinum crucible, and after the ash and residue are allowed to fall into the crucible, ignite to a high temperature for 15 to 20 minutes, or until all the carbon of the paper is burned; cool in a desiccator and weigh. Then moisten the residue with a few drops of sulfuric acid

¹ The evaporations may be accomplished in a short time by manipulation of the casserole over a free flame, observing the usual precautions.

and 5 cc. of hydrofluoric acid, dry, ignite, and weigh; again moisten with sulfuric acid and 5 cc. hydrofluoric acid, dry, ignite, and weigh, repeating, if necessary, to constant weight. The loss in weight is silica. This weight multiplied by 0.4693, divided by 2.5 times 100 gives the per cent of silicon.

Dissolve the residue, left after the volatilization of the silica, in the platinum crucible with about 10 cc. of concentrated hydrochloric acid and a few drops of nitric acid, and heat. If any of the residue remains undissolved, dilute the acids carefully, decant through a filter, dry the residue thoroughly, mix with about 15-20 times its bulk of sodium peroxide, and fuse until the contents of the crucible are liquid, then cool, dissolve in dilute hydrochloric acid (1:3) and combine the solution with the former filtrates. Transfer the combined filtrates to a 500 cc. volumetric flask and make up to mark. This is the "stock" solution.

NICKEL¹

The cyanide method permits the determination of nickel with speed and accuracy even in the presence of iron, manganese, chromium, zinc, vanadium and tungsten; it was adopted in preference to the dimethylglyoxime method, after repeated comparisons with the two methods.

STANDARDIZATION OF POTASSIUM CYANIDE—Dilute about 30 cc. of the potassium cyanide solution to 200 cc., add 5 cc. potassium iodide solution, and titrate with *N*/10 silver nitrate until a faint opalescence is obtained, which may be cleared up with a small drop of potassium cyanide. The equivalent of silver nitrate, per cc. of potassium cyanide, is calculated.

THE DETERMINATION—Dilute 25 cc. of the "stock" solution to 200 cc.; add about 20 cc. of the tartaric or citric acid solution, 5 to 10 cc. ammonium chloride, and ammonium hydroxide until slightly alkaline; then add 5 cc. of potassium iodide and 0.5 cc. of *N*/10 silver nitrate, the latter being accurately measured from a burette. While stirring constantly with a glass rod, add the standard potassium cyanide solution until the precipitate of silver iodide dissolves completely. Then add the silver nitrate solution until a faint opalescence is obtained, which may be cleared up with a small drop of the potassium cyanide.

Assuming that the silver nitrate solution was exactly *N*/10, that 1 cc. of potassium cyanide = *N* cc. of the silver nitrate solution, that *T* cc. of the potassium cyanide and *t* cc. of the silver nitrate were used in titrating *A* g. of the substance, and that 0.002634 is the silver nitrate equivalent for nickel, then the per cent of nickel is found by the following equation:

$$\text{Per cent Nickel} = (TN - t) 0.2934/A$$

IRON AND CHROMIUM

Transfer 50 cc. of the stock solution to a 350-400 cc. beaker, dilute to 150-200 cc., add 20-25 cc. of the saturated solution of ammonium chloride, make the solution barely alkaline with ammonium hydroxide

and heat to boiling. Allow the precipitates of the iron and chromium hydroxides to settle, decant the supernatant liquid through a filter paper, wash the precipitates several times by decantation with ammonium chloride and water, allowing the precipitates to settle each time and decanting off the liquid through the filter, and finally transfer the precipitates to the filter paper and wash them thoroughly with hot water. Use the filtrate for the determination of *zinc*.

IRON—Dissolve the precipitates on the filter paper with hydrochloric acid (sp. gr. 1.12) allowing the solution to run into the beaker in which the former precipitation was made, and wash the paper free from acid. Treat the solution of the chlorides with sodium or potassium hydroxide until strongly alkaline, add bromine water until the solution has a distinct yellow tinge and the ferric hydroxide has assumed its characteristic reddish brown. Boil the solution for a few minutes, dilute with water and filter. Wash the precipitate twice; dissolve on the filter paper as before; treat in the same manner, and filter onto the same paper, allowing the filtrate to run into the beaker containing the filtrate from the former precipitation; then wash the precipitate thoroughly with hot water, dissolve on the filter with hydrochloric acid (sp. gr. 1.12), wash the filter thoroughly with hot water, precipitate the iron with ammonium hydroxide and redissolve in sulfuric acid; finally reduce the iron with 5 g. of zinc (20 mesh) or pass through a Jones reducer, and titrate with potassium permanganate. As the zinc contains a small amount of iron, a blank determination should be made with the same amount of zinc as that used to reduce the iron, and the correction made.

CHROMIUM¹—Acidify the filtrate from the iron with sulfuric acid (sp. gr. 1.40) and add a small excess of the acid. Add a solution of manganous sulfate (equivalent to 3 to 4 g. of the solid); or, if preferred, dissolve 3 or 4 g. of the solid in the solution, and cool the solution. Add from a burette sufficient standard ferrous ammonium sulfate solution completely to reduce the chromium present (indicated by the change in color). Titrate the excess of ferrous ammonium sulfate with potassium permanganate to a decided pink. If preferred, the Mohr salt may be added in the solid form; this is best accomplished by placing a sufficient quantity of the pure salt in a small weighing bottle, carefully weighing the whole, adding the desired amount of the salt to the chromium solution, and reweighing the bottle to determine the balance used. It is usually better to standardize the ferrous ammonium sulfate directly against the permanganate, and also to titrate a blank of the same. The ferrous solution should be cooled to 25° C., the permanganate added drop by drop, stirring the solution constantly, or an error may be introduced due to the evolution of chlorine.

167.5 parts of ferrous iron are equivalent to reducing 87.1 parts of Cr in chromic acid to CrO₂, or 1 part Fe = 0.410 part Cr. The ferrous ammonium sulfate contains 14.24 per cent of ferrous iron, therefore

¹ Adapted from Spiller and Breton, *Anal. Chem.*, **31**, 1886, 64.

¹ Campbell and Andrews, *J. Am. Chem. Soc.*, **17** (1895), 126; Moore, *Chem. News*, **72** (1895), 92; Gaudal, *Z. anorg. Chem.*, **177** (1898), Broadley and Jarvis, *Chem. News*, **78** (1898), 157; Johnson, *J. Am. Chem. Soc.*, **29** (1907), 1201; Campbell and Arthur, *Ibid.*, **30** (1908), 1116; Grossman, *Chem. Abstr.*, **33** (1909), 1223.

x part of the salt equals 0.04427 part Cr. If X equal the amount of ferrous ammonium sulfate used, x cc. of the permanganate equal T g. of ferrous ammonium sulfate used, and assume y cc. of permanganate were used in titrating A grams of the sample, then the per cent of chromium is found by the following equation:

$$\text{Per cent Chromium} = (X - Ty) 4.427/A$$

MANGANESE

Evaporate 100 cc. of the "stock" solution almost to dryness, take up with concentrated nitric acid, and evaporate to about half the bulk. Precipitate the manganese with 5 g. potassium chlorate, and evaporate to small volume, adding potassium chlorate a second time. Dilute the solution with water, filter through a thin layer of asbestos on a Gooch filter, and wash thoroughly with water. Transfer the precipitate and asbestos to a beaker, add ferrous ammonium sulfate from the burette until the precipitate is dissolved, dissolve with ferrous ammonium sulfate, the precipitate clinging to the sides of the crucible, and wash the crucible thoroughly with hot water. Titrate the excess of ferrous ammonium sulfate with permanganate. Metallic iron times $0.3918 = \text{Mn}$. The per cent of manganese may be found by the following equation, where X is the number of grams of ferrous ammonium sulfate used, y the iron equivalent per cc. of the permanganate solution, T the cc. of permanganate used, 14.25 the per cent of iron in ferrous ammonium sulfate, and A the grams of the substance used.

$$\text{Per cent Manganese} = (0.1425X - Ty) 49.18/A$$

ZINC¹

STANDARDIZATION OF THE POTASSIUM FERROCYANIDE—Weigh about 0.2 g. of pure zinc into a flask and dissolve in hydrochloric acid. When the zinc is dissolved, dilute with about 50 cc. of water, neutralize with ammonium hydroxide and after making slightly alkaline acidify with hydrochloric acid, adding a slight excess. Dilute to about 250 cc., heat to $70-80^\circ \text{C}$., and titrate with potassium ferrocyanide solution as follows: place about one-third of the zinc solution in a 400-500 cc. beaker and titrate with potassium ferrocyanide until a drop, when removed and tested on a porcelain color plate with the uranium solution, shows a brown tinge; add another third of the zinc solution and continue the titration until the end-point is passed; then add the last portion and finish the titration very carefully. The reaction is sharper if several drops are taken for the end-point. A correction should be made for the amount of ferrocyanide required to produce the color when no zinc is present. The equivalent per cc. of the ferrocyanide is thus obtained.

THE DETERMINATION—Evaporate the filtrate from the iron-chromium precipitation almost to dryness, take up with concentrated nitric acid, evaporate to about half bulk, add 2-3 g. of potassium chlorate, boil for a few minutes, dilute and filter through a Gooch filter. Neutralize the filtrate containing zinc and

nickel with ammonium hydroxide, heat to boiling, and add 20 to 30 cc. of a 1 per cent solution of dimethylglyoxime. Allow the precipitate to settle and filter through a Gooch. Neutralize the filtrate with hydrochloric acid, add a slight excess, and heat the solution to $70-80^\circ \text{C}$. Conduct the titration as described under the standardization of potassium ferrocyanide.

CARBON

The carbon may be determined by direct combustion in a current of oxygen, and by the apparatus described by Blair, "The Chemical Analysis of Iron and Steel," 7th Ed., 1912, p. 134.

The writer is indebted to Dr. C. S. Palmer for his kindly advice and helpful suggestions during the progress of this work.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH
UNIVERSITY OF PITTSBURGH

A SIMPLIFIED INVERSION PROCESS FOR THE DETERMINATION OF SUCROSE BY DOUBLE POLARIZATION¹

By HERBERT S. WALKER

Received November 4, 1916

Probably the greatest drawback to the use of "true sucrose" determinations in sugar factory control work has been the necessity for such extreme care in the regulation of time and temperature required by the Herzfeld-Clerget inversion process. So sensitive to faulty manipulation is the method ordinarily used that an inexperienced chemist may get even less accurate results by double polarization than by simply assuming the direct polarization to represent "true sucrose."

To avoid any decomposition of fructose during inversion, Tolman² suggested inverting at ordinary laboratory temperatures. This method has never been largely adopted in cane sugar factories, owing to the fact that at least 10 hrs. are required for the complete inversion of the half-normal weight of pure sucrose in 50 cc., and probably a considerably longer time would be needed where organic impurities are present, as in the case of waste molasses.

Steuerwald³ has also proposed inverting in the cold, and shortens the time required to 2 or 3 hrs. by using three times the usual quantity of acid (30 cc. of a mixture of equal parts concentrated HCl and water). The convenience of using a diluted acid will be appreciated by anyone who has had to measure many successive portions of concentrated HCl with the same pipette. Steuerwald's method, however, as pointed out by Pellet⁴ when dealing with impure cane or beet products, accentuates the error inherent in the Herzfeld-Clerget process in that optically active substances other than sucrose may, in a strongly acid medium, have quite different rotation from that indicated in a neutral or slightly acid solution used for direct polarization.

¹ Presented at the Annual Meeting of the Hawaiian Chemists' Association, October 12, 1916.

² U. S. Bur. Chem., *Bull.* **73**, 69.

³ *Archiv.* **1913**, 831.

⁴ I. S. J., **1916**, 83.

¹ Adapted from Fahlberg's method, E. Prost, *Z. anal. Chem.*, **460** (1896); *Chem. News*, **76**, 6.

The writer has for some time held the idea that for rapid work in a sugar factory a compromise between these methods might be advantageously employed, heating the sugar solution before adding acid to some definite temperature and letting it cool down slowly in air during a time sufficient for the inversion to become completed. The only attention required would be to control the temperature of solution at the moment of adding the acid. Since the preliminary heating would be in neutral solution the time required to raise to a definite temperature would be immaterial. Aside from its convenience of manipulation, such a method should, theoretically, possess the advantage over the Herzfeld procedure of being less subject to error due to destruction of fructose, since the maximum temperature of the solution would coincide with the minimum amount of invert sugar present and at the time of nearly complete inversion the temperature should have dropped to such a point that there would no longer be any danger from this source.

In working out this method, 15 min. was chosen as a convenient time for the duration of inversion. To avoid if possible any great change in the inversion constant, the same concentrations of sugar and acid were used as in the Herzfeld method.

EXPERIMENT 1—Approximately 130 g. "Crystal Domino" sugar were dissolved in 500 cc. solution, giving a direct polarization of 99.66. Fifty cc. portions of this solution were pipetted into 100-cc. flasks, 25 cc. water added, the flasks heated in a water bath to certain different temperatures, 10 cc. of a mixture of equal volumes concentrated HCl and water added, the whole allowed to stand 15 min. in air, then cooled down to room temperature in water, made up to 100 cc. and polarized. A parallel test was made at the same time, using the Herzfeld procedure. The results appear in Table I. The percentages of sucrose were calculated, using the same direct polarization and the constant, 144.66 — 0.5*t*, for all. All tests by the new method yielded lower results than by the Herzfeld.

EXPERIMENT 2—To determine whether this was due to incomplete inversion in 15 min. or to too high or too low initial temperatures, a similar experiment was carried out at lower temperatures, letting the solutions stand in air for 30 min. after adding acid. With initial temperatures between 72 and 64° the results obtained are fairly constant among themselves and agree well with those obtained by the Herzfeld method.

EXPERIMENT 3—With a lower initial temperature than 56° inversion is not complete in 30 min.

EXPERIMENT 4—Here the time of inversion was cut to 15 min.

The surprising fact brought out by these tests is the comparatively great latitude of the method. While the Herzfeld procedure requires a rigid adherence to 69° and a definite time of heating, this method, with initial temperatures anywhere between 50 and 70°, yields concordant results which agree with those obtained by the Herzfeld method as closely as the latter do with each other. It also appears that 15 min. is an ample time for inversion and that standing 15

TABLE I—SUCROSE DETERMINATIONS ON "CRYSTAL DOMINO" SUGAR
Results by Herzfeld and Author's Methods with Differences
from Herzfeld Method

Expt. No.	Polarization	Inversion (Min.)	HERZFELD METHOD	NEW METHOD— Acid added at			
				77°	75°	73°	71° C.
1	99.66	15	99.93	99.81	99.65	99.71	99.83
			Difference	-0.12	-0.28	-0.22	-0.10
2	99.61	30	99.91	99.86	72°	70°	68°
			Av. 99.89	99.85	99.81	99.80	99.80
			Difference	-0.03	-0.08	-0.01	0.00
3	99.50	30	99.89	99.80	64°	60°	56°
			Av. 99.85	99.92	99.91	99.83	99.22
			Difference	-0.07	-0.06	-0.02	-0.63
4	99.62	15	99.89	99.99	70°	67°	65°
			Av. 99.94	99.93	100.03	100.03	100.00
			Difference	-0.01	-0.09	-0.09	-0.01

min. longer has no effect on results. With a laboratory temperature of 26° the solutions were found to drop from 70 to 46° and from 60 to 41° on standing in air for 30 min., so it is extremely improbable that any further destruction of fructose would take place, even if the inverted solutions were allowed to stand several hours longer.

Having obtained such satisfactory results from pure sugar, several experiments were next made to see if the method would work equally well on molasses. A large sample of molasses was clarified according to the method of the Hawaiian Chemists' Association and inverted by the Herzfeld and by the new method. Results of the tests are given in Table II.

TABLE II—SUCROSE DETERMINATIONS ON MOLASSES
Results by Herzfeld and Author's Methods with Differences
from Herzfeld Method

Expt. No.	Polarization	Inversion (Min.)	HERZFELD METHOD	NEW METHOD— Acid Added at			
				77°	75°	73°	69° C.
5	27.90	15	34.69	34.17	33.28	32.82	33.05
			Difference	-0.52	-1.41	-1.87	-1.64
6	27.66	30	34.51	34.33	34.29	34.10	34.09
			Difference	-0.18	-0.22	-0.41	-0.42
7	27.60	30	34.51	34.45	34.32	34.30	34.30
			HCl HCl	69°	67°	69°	67° C.
8	27.44	30	34.33	34.34	34.34	34.34	34.37
			Difference	-0.02	-0.05	-0.00	-0.03
9	27.40	30	34.51	34.58	34.59	34.59	34.59
			Av. 34.54	34.59	34.59	34.61	34.61
			Difference	+0.05	+0.05	+0.07	-0.13
10	27.58	15	34.54	34.50	70°	67°	65°
			Av. 34.52	34.61	34.63	34.63	34.63
			Difference	+0.09	+0.09	+0.11	+0.09

EXPERIMENT 5—71.50 g. waste molasses were dissolved in water, clarified with 80 cc. basic lead acetate, made up to 500 cc. and filtered. For direct polarization 50 cc. filtrate were treated with 1 cc. saturated aluminum sulfate solution, made to 55 cc., filtered and polarized. Reading $\times 2$ = direct polarization: 75 cc. of the first filtrate were inverted, cooled, made to 100 cc., decolorized with a slight excess of zinc dust, filtered and polarized in a 400 mm. tube. Reading $\times 4 \div 8 \div 10 \div 11$ = invert polarization. Factor = 142.

EXPERIMENT 6—Since all these results were much lower than those obtained by the Herzfeld method, 30 min. standing and a lower initial temperature were next tried.

While an improvement over the preceding test, these results were still rather low and irregular.

EXPERIMENT 7—It was thought that the excess of basic lead acetate in solution might have had a destructive effect on the fructose already present in the molasses during the heating prior to adding acid. To determine if this were the case this experiment was performed to prove one of each sample being investigated

as before, the other treated with 1 cc. of 1 : 1 HCl (this being approximately the amount of acid necessary to neutralize the alkalinity due to basic lead acetate) before heating.

It is quite evident that a serious loss occurs if solutions of molasses clarified with excess of basic lead acetate are heated before adding acid, while if the alkalinity be neutralized prior to heating all irregularities seem to disappear.

Further tests were made to determine the permissible limit of initial temperature. In all the following experiments the solutions to be inverted were first neutralized with 1 cc. of 1 : 1 HCl.

EXPERIMENTS 8 AND 9 showed initial temperatures between 70 and 60° to yield satisfactory results on 30 min. standing.

EXPERIMENT 10—A final test was made to cover the above range with an inversion period of only 15 min. The safe limit of initial temperatures for waste molasses thus appears to lie between 70 and 63° for a 15-min. inversion period.

MODIFIED INVERSION METHOD

The modified inversion method proposed, based on the above experimental evidence, is as follows:

Place 50 cc. or 75 cc. of the solution used for direct polarization in a 100-cc. flask (in case 50 cc. are used add 25 cc. water) and heat in a water bath to 65° C. Remove from bath, add 10 cc. of a mixture of equal volumes HCl (sp. gr. 1.188) and water, allow to cool down spontaneously in air for 15 min. or as much longer as may be convenient, then cool in water to room temperature, make up to 100 cc. and polarize as usual. In the case of low-grade products which have been clarified with a large excess of basic lead acetate, it is imperative that the excess alkalinity be neutralized before heating, this being best accomplished by the addition of 1 cc. (or 2 cc. in exceptional cases where a large excess of dry lead acetate has been used) of the dilute acid used for inversion.

When a considerable number of determinations are to be made at the same time, the writer uses for a water bath a flat bottomed iron pan accommodating a dozen or more flasks and containing only enough water to be above the surface of the liquid in the flasks. The whole is heated to about 70°, the flame turned out and when a thermometer in one of the flasks indicates 67° the flasks are taken out one at a time, acid added and set aside for inversion.

From a scientific standpoint this inversion process may be criticized on account of the fact that, due to variations in laboratory temperature and in thickness of flasks, marked variations in the rate of cooling, and hence in the speed of inversion, may occur. Practically no difference outside the experimental error could be detected, even when the temperatures at which acid was added varied as much as 10°. It may be also that the constant required for this method will be found on careful investigation to vary slightly from that now used in the Herzfeld method, which is itself under suspicion. In the above work no attempt has been made at much greater accuracy than what

might be expected in a well equipped factory laboratory, and within these limits the method has been found fully as accurate as that of Herzfeld, and much more convenient.

DEPARTMENT OF SUGAR TECHNOLOGY
COLLEGE OF HAWAII, HONOLULU

THE CHEMICAL CHANGES WHICH ARE CAUSED BY DEFECATION OF SORGHUM JUICE FOR SYRUP MANUFACTURE

By ARTHUR K. ANDERSON
Received November 4, 1916

The manufacture of sorghum syrup consists of three distinct processes: (1) The extraction of the juice from the cane; (2) the purification of the crude juice, which is the process commonly called defecation; and (3) evaporation. The quality of syrup produced depends to a large extent on the purity of the juice which is evaporated, which in turn is dependent upon the efficiency of the method used in defecation. Since defecation is the most important process in sorghum syrup manufacture, it was found desirable, in connection with the work on sorghum which is being done at the Minnesota Experiment Station, to undertake the study reported in this paper.

In the past there have been many different methods used in defecation.¹ Those which have survived and which are found in use at the present time in Minnesota are of two types. At the larger factories what is known as the lime process is employed, while at the smaller mills heat alone is used.

The factory method may be briefly described as follows: The juice from the press is pumped to a "defecator," which is a square tank of about 500 gallons capacity. Near the bottom of the tank are steam coils which are used to heat the juice during defecation. When the defecator is full, if lime is to be added, it is added as milk of lime and stirred in well. The heat is then turned on and the juice heated to the "cracking point." The heat is then turned off and the juice allowed to subside for about 15 min. During the defecation the impurities either rise to the top, forming a scum, or settle to the bottom of the defecator. After subsiding, the clear juice is drawn off and evaporated.

In some of the smaller mills the processes of defecation and evaporation are carried on together. In these places open pan evaporators are employed and the green juice is run directly into the evaporator. The impurities are skimmed off as they rise. As a rule no lime is used at such mills.

A third method, known as the "phosphate" method, has been proposed, and while not yet in actual use in Minnesota mills, it seemed so promising that it was decided to include it among those to be investigated. In this method the filled defecator is heated for 30 min. with calcium acid phosphate and then treated with lime. The tri-calcium phosphate which precipitates out has a clearing effect on the juice. The purpose of the preliminary heating with the calcium

¹ Harvey W. Wiley, "Record of Experiments with Sorghum in 1892," U. S. Dept. Agr., Bur. of Chem., Bull. 37 (1893), 80-95.

acid phosphate is to produce an inversion of sucrose, thus preventing its crystallization during the process.

PURPOSE OF THE INVESTIGATION

The purpose of the investigations which were undertaken was to make a study of the defecation of sorghum juice for syrup in order: (1) to determine the changes in chemical composition which the juice undergoes during defecation and evaporation; (2) to study the composition of syrups made by different methods; (3) to study the quality (color, taste, clarity, etc.) of syrups made by the different methods; (4) to make a special study of the lime method, as practiced in the larger mills with particular reference to the proper amount of lime to use, and a simple means of factory control; and (5) to investigate the feasibility of the proposed phosphate method.

METHODS OF PROCEDURE

In studying the chemical changes which take place during defecation most of the work was done under actual factory conditions. Lots were run with no lime, with lime added to alkalinity, with lime to apparent neutrality, and with the calculated theoretical amount of lime required to neutralize the acidity of the juice. Samples for analysis were taken of original juices, of the juices after defecation, and of syrups made from these juices. When juices had to be kept for any length of time before being analyzed they were preserved with a 1 per cent solution of mercuric iodide, using 10 cc. to 250 cc. of juice. Where this was used corrections were made in the subsequent calculations.

In addition to these factory experiments a series of laboratory defecations was run in which juice taken from cane produced on University Farm was used. These experiments were carried on in Erlenmeyer flasks using 500 cc. of juice for each experiment.

In studying the lime method, with special reference to the amount of lime to use, the acidity of the juice was determined by titration. The theoretical amount of lime to neutralize this acidity was added. Also other amounts were added to serve as a comparison. Where this was carried out in the factory the opinion of the owner was obtained as to the desirability of the product. A careful study of this was made in the laboratory on a small scale where the conditions could be carefully controlled. The phosphate method was studied both in the laboratory and under factory conditions. Calcium acid phosphate was added at the rate of 5 lbs. per 1000 gallons and after boiling for 30 min. the juice was neutralized with milk of lime.

The study of the syrup was made on 40 samples collected from various parts of the State. They were made under various conditions and for study were classified according to the method of defecation. The quality of the syrups was considered from the standpoint of color, clarity and taste, market value being the criterion upon which the standards of judging were selected.

ANALYTICAL METHODS

The usual analytical methods were employed with the following modifications of procedure to make them applicable to the materials which were being studied.

Acidity was determined with standard $N/10$ potassium hydroxide, using phenolphthalein as an indicator. Some difficulty was experienced in determining the end-point but with sufficient dilution the method is accurate to within 0.5 of a cc. Results are expressed as the number of cc. of $N/10$ acid in 10 grams of dry matter.

Dry matter in the juices was determined by drying in a hot water oven for 8 hrs., the bulk of the water having first been removed on the steam bath. A new method¹ for determining *dry matter in the syrups* was used in which the amount of moisture present was found by measuring the acetylene generated when a weighed sample of the syrup was treated with calcium carbide in a special apparatus.

Ash was determined on the same sample in which the dry matter was determined in the case of juices. With syrups a separate sample was used and in this case the soluble and insoluble ash were determined, together with the alkalinity of the soluble ash. In all cases *calcium oxide* was determined on the ash. The calcium was precipitated as calcium oxalate and determined volumetrically with standard potassium permanganate solution. In a few cases *phosphorus pentoxide* was determined.

The *lead subacetate precipitate* was determined as follows: In the case of juices the Official Method² was carried out exactly, but with syrups, it was found that if 5 cc. were used the volume of the precipitate was too large to be measured in the tube and that the recommended amount of lead subacetate was insufficient for complete precipitation. It was found that by using $1\frac{1}{2}$ cc. of syrup the volume of the precipitate could be read and that there was sufficient excess of lead. The results were afterwards calculated to the 5 cc. basis.

Sugars were determined as "Sucrose" and "Reducing Sugars." The sucrose was determined by the polariscope, and the reducing sugars, which are reported as dextrose, by means of a modification of Low's volumetric method,³ the modification consisting of the determination of the unprecipitated copper in a standard Fehling's solution.

CHEMICAL CHANGES DURING DEFECTION

FACTORY EXPERIMENTS—Table I shows the analyses of 6 series of defecations showing the composition of the original juice, of the juice after defecation and of the syrup resulting from the juice. In the case of one phosphate defecation an analysis is given of the juice after adding the acid phosphate and boiling for 30 min. In the phosphate method calcium acid phosphate was added, 4½ to 50 lbs. per 1000 gallons of juice. This was equivalent to that used in the industrial amount of a commercial phosphate sold for this purpose. After boiling 30 min. lime was added until the juice was nearly alkaline.

In the experiments where the theoretical amount of

¹ E. M. Wiles, "The Determination of Moisture in Syrup by the Calcium Carbide Method," *Ind. Eng. Chem.*, **8**, 1116 (1916).

² H. W. Wiles, "Colloid and Electrical Methods in Chemistry," *Dept. Agr. Res. Station, Ind.*, **107**, 1916, p. 41.

³ *Ind.*, **1912**, 3, 11.

lime was added, 50 cc. of the juice were titrated with $N/10$ potassium hydroxide using phenolphthalein as an indicator. From the amount of potassium hydroxide used the amount of calcium oxide necessary to neutralize the acidity in the volume of juice in the defecator was obtained and this amount was added.

In the last cases, lime was added until the juice was considered by the factory operator to be neutral to litmus. It was still slightly acid, however.

In Series 2 and 3 the lime had been calculated as calcium oxide instead of calcium hydroxide due to a misunderstanding of the analysis which came with the lime. Hence, only 75 per cent of the theoretical amount was actually added. This accounts for the high acidity after defecation. In the other sample the true theoretical amount was added.

A closer study of the acidity as related to lime added will be made later. At this point it is of interest to note that the acidity of the syrup is in all cases higher than that of the defecated juice, but lower than in the original juice. Some of the possible explanations for these phenomena are as follows:

According to Maxwell¹ the material precipitated from sorghum juice by alcohol is composed largely of mucilaginous materials. We may consider that in ordinary defecation with heat and lime much of this material remains in solution. According to O'Sullivan,² the gums are complex compounds which on hydrolysis give rise to sugars and complex acids of high molecular weight. This being the case, the increase in acidity could be accounted for by the supposition that during the high temperature of evaporation the gums are hydrolyzed, liberating the free acid. This theory would also account for some of the increase in dextrose after evaporation.

Lamy³ gives the following figures for the amounts of calcium oxide dissolved by 1000 g. of a 10 per cent sugar solution at various temperatures:

At	0°	15°	30°	50°	70°	100° C.
Grams CaO in solution.....	25.0	21.5	12.0	5.3	2.3	1.55

If this calcium oxide is not simply in physical solution but partly in chemical combination in the form of saccharates it may be that with the high temperature of evaporation some of the calcium is split off from the sugar and deposits on the bottom of the evaporator. It is a known fact that at this stage of the process there is actually a deposition of lime. The decrease in lime content of the syrup as compared with the juice also confirms this theory, since as long as the lime is present in solution it will react alkaline to the indicator, and upon its removal the acidity of the syrup will rise.

The darkening of the syrup during evaporation indicates an oxidation. The oxidation of glucose produces acids. This would also contribute to the increase in acidity.

¹ H. W. Wiley and Walter Maxwell, "The Composition of Bodies Precipitated by Alcohol from Sorghum Syrups," U. S. Dept. Agr., Div. of Chem., Bull. 29 (1890), 14-23.

² Paul Haas and T. G. Hill, "The Chemistry of Plant Products," 1912, 120, London, New York.

³ John E. Mackenzie, "Sugars and Their Simple Derivatives," 1913, 31-42, London.

The volume of the lead subacetate precipitate was determined with the hope that it would serve as an indication as to the completeness of defecation. The results, however, are not as consistent as was expected. The high value in the case of syrups is undoubtedly due in part to the high acidity of the syrup.

The ash content increases after lime is added. This would indicate that some of the lime added remains in solution in the juice and syrup. The decrease in ash after defecation in Series I may be explained by the fact that insoluble phosphates were formed which removed some of the iron and calcium.

In all cases the calcium oxide content increases after defecation and decreases again in the syrup. The increase in the defecated juice would seem perfectly natural. The decrease in the syrup would be accounted for by the lower solubility of calcium salts in sugar solution at a high temperature.¹ Calcium citrate, which would be present, is more soluble in cold than hot water.

Another possible explanation is that in the juice the calcium is present as acid salts which are soluble and which at the high temperature of evaporation and the higher concentration change over to the normal salts and are precipitated.

In studying the sugar content, it will be noted that in all cases the percentage of sucrose increases after defecation. According to Maxwell² solutions clarified by lead contain levogyrous nitrogenous compounds. If this is the case the percentages of sucrose on original juices are too low. The increase in sucrose in defecated juices would be accounted for by the removal of these levogyrous bodies by the heat and lime during defecation. Maxwell's work shows the following results on a syrup clarified with lead, with phosphotungstic acid, and with alcohol. The following are the polariscope readings:

Solution Clarified by Lead.....	64.99°
After treatment with H_2PWO_6	67.37°
After treatment with H_2PWO_6 and alcohol.....	72.93°

He accounts for the increase in reading after adding alcohol as due to the reduction of the levorotatory power of levulose in alcoholic solution. He says, "the body, precipitated by alcohol, is in appearance dextrinoid, and the logical supposition would be that the dextrogyrous property of the solution would be diminished, which in fact is not the case."

From the uniform decrease in reducing sugar after defecation it appears that some reducing substance must be removed. Maxwell's alcohol precipitate may contain some of the simpler dextrans which reduce Fehling's solution.

The decrease in dextrose after defecation may be explained as due to the removal of dextrin-like bodies which reduce Fehling's solution.

The increase in dextrose after evaporation may be explained as being due to the hydrolysis of sucrose or of mucilaginous materials.

The increase in percentage of total sugar is of course

¹ John E. Mackenzie, "Sugars and Their Simple Derivatives," 1913, 31-42, London

² *Loc. cit.*

due to removal of impurities during defecation and evaporation.

In all cases the percentage of *nitrogen* decreases after defecation. This is especially noticeable in the phosphate method. This seems natural in that if the nitrogen is present as albuminous bodies it would be coagulated and thus removed during defecation. The marked decrease in the case of the phosphate method is due to the clearing effect of the phosphate precipitate. The increased percentage of nitrogen in the syrup, as compared with that in the juice, in some cases, is probably due to fermentative changes in the juice before it was evaporated which changed the nitrogenous compounds into non-coagulable forms. This phenomenon has been observed also in the case of juices from canes which have been stacked for some time after cutting and before pressing in the factory. It is obvious that only fresh canes can be used, if it is desired that the nitrogenous bodies shall be as completely removed as possible in defecation.

As would be expected, the per cent of *solids-not-sugar*

for factory practice. In this case, the theoretical amount of lime required to neutralize both the acid phosphate and the juice was added.

In the heat method, the juice was boiled for 30 min. to observe the results on the inversion of sucrose.

In the rest of the experiments different amounts of lime were added and at different times. Lime to one-half theory, to theory, and to neutrality was added. In these experiments the theoretical amount of lime was computed on the basis of an analysis made of the lime. This analysis was a determination of the alkalinity of the lime by dissolving in standard acid and titrating the excess with standard potassium hydroxide. In the case of adding lime to neutrality, lime was added until the juice gave a slight alkaline reaction. The amount of lime required to produce alkalinity was determined by making an aqueous suspension of a known amount of lime, and then adding small amounts of this to the juice until it was alkaline. The excess was then evaporated to dryness and weighed, the difference in weight indicating the amount used

TABLE I—SHOWING COMPOSITION OF JUICE BEFORE AND AFTER DEFECATION AND OF SYRUP

Series No.	TREATMENT	Lab. No.	DESCRIPTION	Acidity (a)	Lead Precipitate (b)	Dry Matter (Per cent)	PERCENTAGE COMPOSITION OF THE DRY MATTER					Nitrogen in Solids-not-Sugar
							Ash	Su-crose	Dextrose	Total Sugars	Solids-not-Sugar	
1	Phosphate Method	3085	Original juice	17.4	6.9	17.42	5.38	5.14	40.71	53.33	95.74	0.364 0.18
		3086	After adding phosphate	17.0	9.0	18.83	5.14	40.71	53.33	95.74	5.73	0.335 0.11 1.78
		3087	After neutralizing	17.0	10.3	18.84	4.87	41.72	52.55	94.27	5.73	0.525 0.06 1.79
		3352	Syrup	8.1	8.5	66.50	4.77	41.92	53.02	94.94	5.06	0.436 0.16 3.19
2	Phosphate Method	3174	Original juice	21.6	9.4	16.03	3.91	58.95	22.12	81.07	18.93	0.449 0.29 1.65
		3175	After phosphate def.	7.4	8.5	17.56	3.99	62.39	19.64	82.03	17.97	0.539 0.05 0.26
		3314	Syrup	21.0	14.4	72.70	4.33	65.81	24.73	90.54	9.46	0.281 0.20 2.06
3	Three-fourths Theoretical Lime	3174	Original juice	21.6	9.4	16.03	3.91	58.95	22.12	81.07	18.93	0.449 0.29 1.65
		3176	After defecation	11.7	11.8	16.17	3.97	64.23	19.35	83.58	16.42	0.449 0.20 1.25
		3315	Syrup	17.0	13.8	72.50	4.48	66.82	23.66	90.48	9.52	0.327 0.20 2.06
4	Theoretical Lime	3200	Original juice	17.4	11.4	18.80	3.24	57.38	34.57	91.95	8.05	0.280 0.28 3.65
		3201	Defecated juice	4.6	6.2	18.46	3.43	59.38	33.31	92.69	7.31	0.414 0.06 0.79
		3319	Syrup	13.8	12.6	75.60	3.56	57.57	34.55	92.12	7.88	0.403 0.23 2.88
5	Lime to Neutral (c)	3174	Original juice	21.6	9.4	16.03	3.91	58.95	22.12	81.07	18.93	0.449 0.29 1.65
		3177	After defecation	8.6	10.7	16.32	3.91	63.06	18.63	81.69	18.31	0.530 0.20 1.00
		3316	Syrup	15.9	13.9	77.20	4.47	66.40	24.35	90.75	9.25	0.332 0.16 1.75
6	Lime to Neutral (d)	3174	Original juice	21.6	9.4	16.03	3.91	58.95	22.12	81.07	18.93	0.449 0.29 1.65
		3178	After defecation	3.0	7.2	15.95	4.11	64.28	18.79	83.07	16.93	0.672 0.23 1.42
		3317	Syrup	9.1	17.8	64.70	4.90	68.50	24.68	93.18	6.82	0.592 0.23 3.36

(a) Expressed as cc. N/10 acid per 10 g. dry matter in sample.

(b) Expressed as cc. lead subacetate precipitate from 5 cc. sample, divided by the per cent of dry matter, to bring results to uniform dry matter basis.

(c) Neutral to litmus.

(d) Lime to neutral added after heating. Neutral to litmus.

was found to be much less in the syrups than in the juices.

In all cases the per cent of *nitrogen in the solids-not-sugar* increases in the syrup over that in the defecated juices. During defecation, the nitrogen which is in the form of protein coagulated by heat will be at once removed. At this point, there is not a very marked decrease of solids-not-sugar. During evaporation, the solids-not-sugar which disappear are mainly non-nitrogenous bodies, thus bringing the per cent of nitrogen relatively higher in the syrup. In all cases the per cent of *solids-not-sugar* and *not-ash* decreases after defecation and after evaporation. This shows that a decrease in organic matter-not-sugar takes place mainly during evaporation.

LABORATORY EXPERIMENTS—Table II shows the results of a series of laboratory defecations. Juice was obtained from cane which was cut and stored for a few weeks before pressing. Several methods of defecation were tried out as indicated in the table. In each experiment 500 cc. of juice were used.

In the phosphate method, calcium acid phosphate was added in proportion to the amount recommended

by the juice. The following typical results show the amount of lime required according to a theoretical calculation as compared with the amount actually required to produce a slight alkalinity to phenolphthalein: Sample 1—Calculated theoretical amount of lime to neutralize acidity, 0.73 g.; actual amount required, 1.60 g. Sample 2—Calculated theoretical amount of lime to neutralize acidity, 0.88 g.; actual amount required, 1.90 g. In both cases the actual amount is about 2.2 times the theoretical amount.

Notes were taken on the color of the juices after defecation. Where no lime was added the color was, of course, very light. Where lime was added to alkalinity the juice was a very dark brown color, in cases where lime was added to one-half theory the juice remained light colored. With lime added to theory the juice seemed to be just at the point where it had started to turn dark. Where lime was added after heating to boiling the same usually sank instead of rising. This shows the undesirability of adding lime after the separation of the cream has taken place.

A study of the acidity in Table II shows just what would be expected except that the juice should be

neutral after adding the theoretical amount of lime. The increase in acidity in No. 3206 is due to the acid phosphate. Nos. 3207 and 3212 correspond. No. 3209 is higher than No. 3212 because the lime was added after heating. The same thing is noticed in 3210 as compared with 3211. This would indicate a higher efficiency for the lime added before heat is

The nitrogen content shows what was pointed out in connection with Table I, namely, that where cane is kept for some time a change in the character of the nitrogen takes place putting it in a form which is not removed by the process of defecation.

DEFEATOR RESIDUE—In the factory study, it was noticed that there was a large amount of residue after

TABLE II—SHOWING RESULTS OF LABORATORY DEFECTION

Lab. No.	TREATMENT	Acidity (a)	Lead Precipitate (b)	PERCENTAGE COMPOSITION OF THE DRY MATTER						
				Dry Matter Per cent	Ash	Sucrose	Dextrose	Total Sugars	Lime (CaO)	N
3205	Original juice.	23.0	12.9	15.56	5.80	31.43	51.99	83.42	0.587	0.44
3206	Phosphate. After boiling 30 min. with phosphate	26.9	14.2	20.05	5.75	33.44	49.55	83.26	0.464	0.44
3207	Phosphate. After adding lime to theory	7.2	12.1	19.07	5.52	34.40	40.49	73.50	0.616	0.42
3208	Heat. Boiled for 30 min.	22.6	14.0	17.50	5.59	31.52	50.06	81.78	0.344	0.44
3209	Lime to theory. Heated first.	7.7	8.7	16.02	5.65	32.03	48.57	80.59	0.596	0.45
3210	Lime to half theory. Heated first.	15.7	10.8	15.73	5.78	32.20	51.05	80.11	0.607	0.44
3211	Lime to neutral.	14.5	11.4	14.81	5.74	33.02	52.81	83.83	0.585	0.44
3212	Lime to theory.	7.2	10.7	14.91	5.83	31.93	51.45	83.37	0.594	0.40
3213	Lime to neutral.	Neutral	8.8	15.34	6.52	32.21	48.83	81.03	1.068	0.41

(a) Expressed as cc. N/10 acid per 10 grams dry matter in sample.

(b) Expressed as cc. lead subacetate precipitate from 5 cc. sample divided by the per cent of dry matter, to bring results to uniform dry matter basis.

applied to a defecator. The neutralizing effect of the lime added is almost directly proportional to the amount of lime added up to the theoretical amount. The necessity for using nearly double the amount of

TABLE III—PERCENTAGE COMPOSITION OF DEFEATOR RESIDUES
Laboratory No. 54 Laboratory No. 3204
Theoretical Lime Used Factory Method

Dry Matter	28.74	25.02
Composition of Dry Matter:		
Ash	13.84	5.62
Sucrose	20.86	4.76
Dextrose	23.62	3.14
Total Sugars	2.46	0.61
Nitrogen	2.63	19.00
Lime (CaO)	0.81	14.33
CaO in Ash	0.81	14.33
P ₂ O ₅	0.81	14.33
P ₂ O ₅ in Ash	0.81	14.33

lime to neutralize about one-third the original acidity is difficult to understand. It is probable that at this concentration the lime is combining with the sugar or some other substance. A change of some kind is indicated in the darkening of the juice before alkalinity is reached.

The lead subacetate precipitate shows a decrease as the amount of lime used increases, the maximum being reached where lime has been added to theory.

The ash determinations show very little except in the case of 3213 where an increase of ash would be

the juice was removed from the defecator. An analysis of this residue from two defecators was made to serve as a basis for considering the advisability of using a filter press to recover the juice which is at present lost.

Table III shows the composition of defecator residues. This shows that there is at present a considerable loss of sugar, a great part of which could be saved by the use of a filter press. Whether the increase in yield of syrup would justify the added expense can be determined only by further experiments under factory conditions.

ANALYSES OF COMMERCIAL SYRUPS

Table IV shows the averages of analyses of syrups made by the indicated method of defecation. The first column gives the number of samples from which the averages are taken. Under the head of "Lime Used" are included all of the samples where lime was used in defecation excepting those where special amounts of lime were used. These are given under special heads. In one sample, bicarbonate of soda was used as a neutralizing agent in defecation. Under the head of "Crystallized" are included all samples which showed crystallization regardless of the method used in defeca-

TABLE IV—COMPOSITION OF SYRUPS FROM VARIOUS METHODS OF DEFECTION

DESCRIPTION	No. of Samples	Dry Matter	Acidity (a)	Lead Precipitate (b)	PERCENTAGE COMPOSITION OF THE DRY MATTER										COMPOSITION OF THE ASH					
					Ash	Soluble	Insoluble	Lime	Sugars	Dextrose	Total	Solids-not-sugar	Nitrogen	Alkalinity	Ratio of Alkalinity to Soluble Lime		Ratio of Insoluble Lime to Total	Ratio of Insoluble Lime to Total		
															(c)	(d)			(e)	(f)
No lime	17	76.2	18.8	13.3	3.90	3.02	0.881	0.202	51.01	40.69	91.70	8.30	0.161	1.94	8.91	2.290	2.98	22.44	5.35	
Lime used	11	76.7	13.6	12.4	4.25	3.38	0.998	0.265	55.50	35.98	91.48	8.52	0.173	2.05	9.65	2.190	2.84	22.98	6.35	
Lime to theory	2	74.0	15.4	13.2	4.02	3.01	1.008	0.365	62.20	29.10	91.30	8.70	0.214	2.46	8.92	2.193	2.98	24.96	10.70	
Lime to neutral	4	72.9	9.4	13.7	4.72	2.89	1.206	0.491	51.39	41.12	92.51	7.49	0.190	2.67	9.87	2.083	3.44	26.54	10.85	
Lime in excess	3	74.9	9.1	12.9	4.65	3.10	1.549	0.643	52.43	39.98	92.41	7.59	0.181	2.39	8.50	1.812	2.71	32.98	13.55	
Phosphate	3	68.6	12.7	13.0	4.58	3.39	1.193	0.395	49.60	43.87	93.47	6.53	0.095	1.45	8.87	1.932	2.61	26.09	9.35	
Bicarbonate of soda	1	70.0	17.6	15.7	2.90	1.97	0.932	0.097	50.48	44.09	94.57	5.43	0.201	3.70	5.82	2.020	2.95	32.12	3.35	
Crystallized	12	78.7	13.9	12.7	4.33	3.15	0.963	0.290	58.12	33.29	91.41	8.59	0.199	2.32	9.52	2.234	3.08	22.60	6.94	
Very badly crystallized	1	82.5	11.4	10.9	2.24	1.79	0.453	0.104	67.26	30.28	97.54	2.46	0.147	5.97	7.61	3.394	4.24	20.21	4.65	

(a) Expressed as cc. N/10 acid per 10 grams dry matter.

(b) Expressed as cc. lead subacetate precipitate from 5 cc. syrup.

(c) Expressed as cc. N/10 acid required to neutralize the ash from 5 grams of dry matter.

(a) Expressed as cc. N/10 acids per 10 grams dry matter.

(b) Expressed as cc. lead subacetate precipitate from 5 cc. syrup.

(c) Expressed as cc. N/10 acid required to neutralize the ash from 5 grams of dry matter.

expected. The calcium oxide content shows results similar to those reported in Table I.

With regard to the sugars there are the same general results as in Table I. The results here would indicate that there is no inversion of sucrose on boiling with acid phosphate. Sample 3208, where the juice is boiled for thirty minutes alone, shows the lowest percentage of sucrose of any defecated sample. This indicates some inversion.

The last sample is one made in 1912 and is very badly crystallized. It seems abnormal in many respects, probably from the fact that much of the uncrystallized portion of the original syrup has been used, leaving the remaining portion abnormal.

There is nothing exceptional with regard to the dry matter content of the different classes of syrup except that the crystallized samples contain a higher percentage than the others. This is especially true of

the badly crystallized sample. It is evident that crystallization is dependent to a large extent on the concentration.

The *lead subacetate precipitate* is smaller in the samples where lime was used than in those where it was not. The sample where sodium bicarbonate was used shows the largest precipitate. This is due to the presence of acids left in a soluble form by the sodium bicarbonate.

The *acidity* decreases with the amount of lime used. The high acidity of the "lime to theory" syrups is due in part to the fact that this series includes the sample mentioned above as having only three-fourths of the theoretical amount. A juice neutral to litmus gives an acidity equal to about one cc. *N/10* acid per gram of dry matter.

The *ash content* increases as lime is added. The sodium bicarbonate sample is very low in ash as is also the one which is badly crystallized. The increase in *soluble ash* where lime was used is due to the increase in *total ash*. The ratio of the soluble ash to total ash shows a definite relation to the amount of lime added. The ratio decreases with the addition of lime.

There is a direct relation between the percentage of *insoluble ash* and the *amount of lime added*, the former increasing as the latter is added. The same relationship holds in the case of the insoluble ash calculated on the basis of the total ash and with the calcium oxide calculated on the total ash basis and on the total dry matter basis. The percentage of calcium oxide is very low where sodium bicarbonate is used.

In a study of the *ash* it was thought that a relationship would be found between it and the crystallization. In speaking of molasses, Mackenzie states that formerly "the presence of invert sugar was supposed to prevent the formation of crystals, but, on the contrary, it is now known that it has no such effect. Gunning has shown that while concentrated alcohol does not dissolve sugar, an alcoholic solution of organic salts of potassium does dissolve sugar, forming a thick uncrystallizable syrup, which is very easily soluble in alcohol, methyl alcohol or water, but from which sugar is not again directly obtainable. This syrup consists of compounds of potassium saccharate with potassium salts of organic acids found in molasses." Applying this theory to the crystallization of sorghum syrup it would be expected that the percentage of soluble ash would be small. This, however, is not the case.

In studying the *sugar content* of the syrups it is at once seen that the sucrose content is less where no lime is used and the dextrose is higher. This, of course, is due to inversion with the stronger acidity. In most of the samples where no lime was used open pan evaporation and slow boiling were practiced, which would also favor inversion.

The syrup from the phosphate method shows the lowest amount of *sucrose*. This is due very likely to boiling with the acid phosphate. The high percentage of sucrose and low amount of dextrose in the

crystallized samples of course seems normal. This explains in part why these samples crystallized.

The lesser percentage of *solids-not-sugar* when no lime was added can be accounted for by the fact that in most of these cases slow open pan evaporation, with much skimming, was practiced. The long boiling would naturally remove more impurities than rapid evaporation. The phosphate method shows a higher purity than the samples where lime was used.

The percentage of *nitrogen* was less where no lime was used, which can be explained on the slow evaporation basis. In the other samples the nitrogen decreases with the amount of lime. In the phosphate method the nitrogen content is less than in any of the others.

QUALITY OF SYRUPS

In studying the *quality* of the syrups they were judged on the basis of color, clarity, and taste. Table V gives the number of each sample with a description of how it was defecated. In judging color the samples were arranged in order of their color by reflected light, the lightest being placed first. Two of the samples in which the phosphate was used are the darkest. The lightest samples were made without lime. A study of the acidity shows that those samples in which lime was used and which appear at the head of the list are still highly acid while those at the foot of the list are not as acid. The darkness of some

TABLE V—QUALITY OF SYRUPS

SYRUPS ARRANGED IN ORDER OF CLARITY							
No.	Description	Color	Light	Dark	Crystallization	Taste	
14	Phosphate	37	50(a)	26	20(a)	52(b)	Best
15	Lime to theory	24	49(a)	52(b)	44(a)	52(a,b)	
16	Lime to neutral	20(a)	34	47(a)	29	19(a)	
17	Lime to neutral	44(a)	37	52(b)	35(a)	34	
18	Lime	43(a)	36	23	19(a)	30	
19	Lime to theory	34	18(a)	48(a)	31	14(b)	
20	Lime	16(a)	38	53(a)	16(a)	53(a)	
21	No lime	51(a)	24	28	40(a)	47(a)	
22	No lime	22	54	46(a)	33(a)	50(a)	
23	No lime	38	32	21	43(a)	49(a)	
24	No lime	31	..	45(a)	41(a)	..	Good
25	No lime	29	..	39	22	26	
26	No lime	32	..	25	..	32	
27	No lime	40(a)	..	30	..	38	
28	No lime	33(a)	..	27	..	51(a)	
29	No lime	14(b)	..	14(b)	..	54	
30	No lime	15(a)	..	15(a)	..	18(a)	
31	No lime	49(a)	..	17(a)	..	50	
32	No lime	28	..	42	..	40(a)	
33	Lime	36	16(a)	
34	No lime	19(a)	43(a)	
35	Lime to neutral	54	33(a)	
36	No lime	21	
37	No lime	2	41(a)	
38	No lime	50(a)	44(a)	
39	No lime	18(a)	24	
40	Lime	35(a)	53	
41	Lime in excess	46(a)	48(a)	
42	Bicarbonate of soda	42	18(a)	Poor
43	Lime	30	21	
44	Lime	17(a)	48(a)	
45	Lime	25	28	
46	Lime	53(a)	
47	Lime in excess	39	40(a)	
48	Lime in excess	45(a)	48(a)	
49	Lime	4(a)	53	
50	Lime to neutral	48(a)	
51	Lime	26	
52	Phosphate	24	32(a)	
53	Phosphate	41(a)	52(a)	
54	Lime to nearly neutral	53(a)	50(a)	
54	No lime	52(b)	

(a) Lime used in defecation

(b) Phosphate method in defecation

samples, for example, No. 14 and No. 26, where lime was not used, is due to slow evaporation. The darkness of the phosphate samples is due to lime being

added to neutrality and to boiling one-half hour in the defecator before evaporation. Sample 14, made by the same method, excepting that lime was added to three-fourths the theoretical amount, is lighter in color. It can then be concluded that a dark syrup is due to much lime and to slow, long continued evaporation.

In determining the *clarity* of the syrup test tubes were filled with syrup and the transparency noted. There were two distinct types of syrups, the light and the dark. These two were not comparable so each group was arranged separately according to clarity. In the light syrups those in which lime was used are the clearest. The relationship is not the same in the case of the dark syrups as two of the phosphate samples are well toward the top of this list. Sample 14, the other phosphate sample, was not made neutral with lime but lime was added to three-fourths theory. It appears that clarity varies directly with the amount of lime.

Under the head of "Crystallized" are given all samples which show crystallization. Those which show the least amount are placed first. It is noticeable that most of them were made with lime defecation. From this it appears that lime defecation removes "gummy materials" which if present prevent crystallization. The presence of lime would also prevent inversion of sucrose. The relatively higher percentage of sucrose would favor crystallization. To prevent crystallization well defecated juices should not be evaporated to too great a concentration.

In judging *taste* two persons worked independently. They came to practically the same decisions as to which were the ten best samples.

In studying the taste, the syrups were tasted four times. Each time the poorest were eliminated. Those remaining at the end were considered the best. Among the best only 2 samples were made without lime. All of the phosphate samples remained in this group. No lime samples were found in the last group. From this it appears that the phosphate and lime methods produce the best tasting syrups.

THE PHOSPHATE METHOD

From the high rating which has been given the samples of syrup made by phosphate defecation it would appear that this is the most desirable method. If the quality alone were to be considered it undoubtedly would be. But one of the big factors is the extra cost of production, both in time and in extra materials and equipment.

Recently a method in which a phosphate is used has been recommended. This method advocates the addition of lime to alkalinity and allowing the juice to settle. After settling, the clear juice is run off into another defecator and made slightly acid with an acid phosphate. The juice is then heated and allowed to settle for a second time. The clear juice is then drawn off and evaporated. This method is said to give a very clear and bright product. The chief objection to this method is the time required to complete the process of defecation. It would take

2 or 3 hrs. while the method in use at present requires only 30 to 45 min. To use the phosphate method and handle the same volume of juice as is now handled would necessitate the installation of four to six times as many defecators. The added expense for lime and phosphate would be a minor objection to this method. As was pointed out, it requires 2.2 times the theoretical amount of lime to give the juice an alkaline reaction. The phosphate used can be obtained at five cents per pound. This would be used at the rate of 5 lbs. per 1000 gals. of juice. The added expense for lime and phosphate would not be serious, although on a large scale it would amount to considerable in a season's run.

LIME METHOD—FACTORY CONTROL

A syrup and molasses dealer,¹ who has handled large quantities of sorghum syrup, says that the best quality of syrup is light in color and mild in flavor.

With this in mind a special study of the lime method was made to determine the correct amount of lime to add to produce this result. Since one of the main objects in adding lime is to neutralize acidity it was thought that the theoretical amount was the proper amount to add. To confirm this, experiments were conducted at two factories where a 50-cc. sample of the juice from each defecator was titrated with *N*/10 potassium hydroxide and the amount of lime to correspond to this titration was added. Very satisfactory results were obtained. At one factory the system was put into actual operation and has now been used for two seasons. The manufacturers expect to use this method in the future.

Table VI shows the results of two samples defecated with the theoretical amount of lime. The uniformity of acidity of the defecated juice is striking. The last part of the table shows the lack of uniformity where the lime was added by the manufacturer in amounts

TABLE VI—RELATION OF LEAD SUBACETATE PRECIPITATE TO ACIDITY

Lab. No.	Description	Lead subacetate precipitate(a)	Acidity(b)
3200	Original juice.....	11.4	17.4
3201	Defecated juice.....	6.2	4.6
3202	Original juice.....	11.6	17.7
3203	Defecated juice.....	6.7	4.2
	Lime added according to factory method		
3103	Defecated juice.....	6.8	10.2
3198	Defecated juice.....	12.8	5.9
3199	Defecated juice.....	10.2	12.0
3177	Defecated juice.....	10.7	8.6
3178	Defecated juice.....	7.2	3.0

(a) Expressed as cc. precipitate from 5 cc. sample.

(b) Expressed as cc. *N*/10 acid per 10 grams dry matter.

determined by his judgment or by using litmus as an indicator. This shows the need for factory control.

Table VII shows the proper amount of quicklime to add to known quantities of juice where a 50 cc. sample requires the indicated number of cc. of *N*/10

TABLE VII—SHOWING THE AMOUNTS OF QUICKLIME (CaO) IN OUNCES REQUIRED FOR DIFFERENT VOLUMES OF JUICE HAVING THE GIVEN ACIDITY

Gals. Juice	Acidity in Cc. <i>N</i> /10 KOH Required to Neutralize 50 Cc. of Juice	(10)	(12)	(14)	(16)	(18)	(20)	(22)	(24)	(26)	(28)	(30)
1.00	7.5	9.0	10.5	12.0	13.5	15.0	16.5	18.0	19.5	21.0	22.5	24.0
2.00	15.0	18.0	20.5	24.0	27.0	30.0	33.0	36.0	39.0	42.0	45.0	48.0
3.00	22.5	27.0	31.0	36.0	40.5	45.0	49.5	54.0	58.5	63.0	67.5	72.0
4.00	30.0	36.0	41.0	48.0	54.0	60.0	66.0	72.0	78.0	84.0	90.0	96.0
5.00	37.5	45.0	51.5	60.0	66.5	75.0	82.5	90.0	97.5	105.0	112.5	120.0

potassium hydroxide to neutralize it, using phenolphthalein as an indicator. Where calcium hydroxide

¹ A. A. Denton, "The Manufacture of Sorghum Syrup," U. S. Dept. Agr., *Farmers' Bull.* 90 (1899), 31.

is used approximately one-third should be added to the indicated quantities. Or, to use the same table, the titration can be considered as one-third more and the figures read direct from the table. For example, if the defecator contained 400 gallons of juice and if the titration showed 18 cc. of $N/10$ potassium hydroxide solution used, instead of reading the lime as 42 oz., it would be very simple to run over to the column headed 24 cc. and read the lime required as 72 oz. The indicated amount of lime should be weighed out, slaked and added as milk of lime.

SUMMARY

1—The acidity of the juice of sorghum cane decreases during defecation and increases during evaporation, with the lime and phosphate methods. The acidity varies inversely with the amount of lime used.

2—The volume of the lead subacetate precipitate is not a good indication of the efficiency of defecation. With high acidity there is a large precipitate.

3—The ash content increases after lime has been added. In the phosphate method there is a decrease in the amount of ash.

4—Calcium oxide increases during defecation and decreases during evaporation.

5—During defecation there is an apparent increase in sucrose and decrease in reducing sugars.

6—The nitrogen content decreases during defecation. In cane which has stood after being cut the nitrogen is changed to a non-precipitable form which is not removed by defecation.

7—Solids-not-sugar decrease during defecation and evaporation, the larger decrease being during the latter process.

8—The color of the juice is not darkened materially until more than the theoretical amount of lime has been added. The amount of lime to produce alkalinity is 2.2 times the theoretical amount.

9—Acidity in syrups varies inversely with the amount of lime used.

10—In syrups the total ash, insoluble ash and calcium oxide increase with the amount of lime added.

11—Sucrose increases and dextrose decreases with the amount of lime used.

12—Crystallization is due to a high percentage of dry matter, a relatively high sucrose content and a juice relatively free from "gummy materials." It occurs most frequently in samples where lime was used in defecation.

13—The darkness of color of a syrup varies directly with the amount of lime used in defecation and with the time required for evaporation.

14—The phosphate and lime methods give the best tasting syrups. For economic reasons the lime method is considered the better to use.

15—The theoretical amount of lime gives proper defecation with the minimum darkening of the juice. The titration of the juice is an efficient method of factory control.

THE CORRECTION REQUIRED IN APPLYING THE BABCOCK FORMULA TO THE ESTIMATION OF TOTAL SOLIDS IN EVAPORATED MILK¹

By O. L. EVENSON

Received March 13, 1917

The Babcock formula,²

$$T = \frac{L}{4} + 1.2 \times \text{Per cent Fat},$$

where T = total solids and L = Quevenne Lactometer reading,³ or $1000 \times \text{sp. gr.}^3 - 1000$, might not be expected to yield as accurate results when applied to evaporated milk as when applied to whole, fresh milk because when milk is concentrated the specific gravity and total solids do not increase at the same rate. Babcock's² complete formula

$$\text{Solids-not-fat} = \frac{(1005 - sf)}{(100 - 1.0753 sf)} (100 - f) 2.5,$$

where s = specific gravity and f = per cent fat, gives still less satisfactory results than the short formula. While Richmond's⁴ formula,

$$T = 0.2625 \frac{G}{D} + 1.2 \times \text{Per cent Fat},$$

where T = total solids, G = $1000 \times \text{sp. gr.}^3 - 1000$ and D = specific gravity³, will give more accurate results than either, it is not as simple as the short formula of Babcock and is not directly applicable without a small correction. Bigelow and Fitzgerald⁵ showed that more accurate results could be obtained with the Babcock formula on the original evaporated milk than on the same milk diluted with an equal weight of water. No mention, however, is made of the temperature at which the specific gravity was determined or at which the evaporated milk had been kept preceding the determination of the specific gravity. That the specific gravity of freshly drawn milk,

when measured at a definite temperature, $\frac{15}{15}^{\circ}$ or

15.5° C., gradually increases on standing was, according to Fleischmann,⁶ first observed by Quevenne, but is generally known as Recknagel's⁷ phenomenon. It has been shown by Fleischmann⁸ to be due to a solidification or change in the physical state of the fat. When milk is cooled below the solidification point of butter-fat, the latter begins to solidify and in this way increases the specific gravity. Conversely when milk which has been cooled to its maximum specific gravity, is heated, its specific gravity decreases until the fat is again melted, when no further change takes place. The same phenomenon has been observed with an emulsion of butter-fat and water. This change in the specific gravity increases with the percentage of fat, skimmed milk showing little or no change.

¹ Read at the 34th Meeting of the American Chemical Society in New York City, September 8-10, 1916. Published by permission of the Secretary of Agriculture.

² Twelfth Ann. Report Wt. Agr. Expt. Sta. 1898, 120-126. Madison Wis.

³ At 15.56° C. (60° F.).

⁴ Richmond's Dairy Chemistry, 2nd Edition, p. 69, 1914.

⁵ Bull. 6, 1915. Research Laboratories, Nat'l. Acad. Agri.

⁶ J. Lande, 1913, 78.

⁷ Milchzeitung, 19, 1888, 119.

⁸ Ibid., also 1902, 33.

The purpose of this investigation was to determine the error of the Babcock short formula when applied to evaporated milk so that an average correction might be made and more accurate results obtained when the formula is applied to estimate total solids in milk at the temperatures of 5° and 37° to 40°.

For the work here recorded, 16-oz. samples of commercial evaporated milk were obtained as required, so that the samples were always in good condition.

The total solids were calculated from the specific gravity and percentage of fat by the formula

$$T = \frac{L}{4} + 1.2 \times \text{Per cent Fat},$$

and the results obtained compared with those obtained gravimetrically. The specific gravity of the milk was determined at 15.56° C. by means of a pycnometer.

Almost invariably duplicate results did not differ from each other by more than 0.0001. The Röse-Gottlieb¹ Method was used for the determination of fat and the Official Method,² using sand, was employed in determining solids.

In Table I is shown the change in specific gravity

TABLE I—THE CHANGE IN SPECIFIC GRAVITY OF SEVERAL COMMERCIAL EVAPORATED MILKS KEPT AT DIFFERENT TEMPERATURES

No.	Per cent Fat	Specific gravity at 15.56°/15.56° C.		Difference in Sp. Gr. of milk held at 5° C. and at 37-40° C.
		Held 24 hours at 5° C.	Held 15 hrs. at 37-40° C.	
1.....	8.06	1.0672	1.0668	0.0014
2.....	8.28	1.0735	1.0724	0.0016
3.....	8.24	1.0677	1.0668	0.0018
4.....	7.50	1.0711	1.0705	0.0010
Average.....				0.0014

of several commercial evaporated milks kept for certain intervals at different temperatures. In each case the milk was brought to 15.56° C. immediately after the holding period and the specific gravity taken without delay. It will be observed that a considerable difference in specific gravity may be obtained by holding the milk at different temperatures. The average difference obtained in the specific gravity of the milk when held at 5° C. and when held at 37-40° C. is 0.0014. This would make a difference of 0.35 per cent in the calculated solids. This does not apply to skimmed evaporated milk from which the fat has been largely removed.

In Table II is shown the application of the Babcock formula to evaporated milk which has been kept at 5° C. for 24 hours; also, to the same milk diluted with an equal weight of cold, recently boiled distilled water. It is evident that the specific gravity does not vary directly as the percentage of total solids when the milk is concentrated but increases at a more rapid rate. As a consequence, the calculated results are high. In normal evaporated milk which has been cooled so that no further increase in specific gravity occurs, the figure +0.46 given in Table II is believed to represent the average difference between the calculated and gravimetrically determined total solids when using Babcock's short formula. Consequently, when cor-

TABLE II—APPLICATION OF THE BABCOCK FORMULA TO EVAPORATED MILK HELD AT 5° C. FOR ABOUT 24 HOURS

No.	Per cent Fat	UNDILUTED			DILUTED 1 : 1			
		Specific Gravity	Per cent Solids (Dry-Ing) (Calc.)	Diff.	Specific Gravity	Per cent Solids (Calc.)	Diff.	
1	7.87	1.0656	25.52	25.84	+0.32	1.0318	25.34	-0.18
2	7.99	1.0658	25.67	26.04	+0.37	1.0318	25.49	-0.18
3	8.10	1.0652	25.74	26.02	+0.28	1.0318	25.62	-0.12
4	7.84	1.0673	25.76	26.23	+0.47	1.0327	25.76	0.00
5	7.90	1.0675	25.97	26.36	+0.39	1.0328	25.88	-0.09
6	8.04	1.0673	26.07	26.47	+0.40	1.0327	26.00	-0.07
7	7.86	1.0685	26.10	26.56	+0.46	1.0334	26.13	+0.03
8	7.74	1.0692	26.13	26.59	+0.46	1.0337	26.14	+0.01
9	8.02	1.0674	26.14	26.47	+0.33	1.0327	25.97	-0.17
10	7.47	1.0708	26.17	26.66	+0.49	1.0343	26.11	-0.06
11	7.80	1.0711	26.22	26.77	+0.55	1.0344	26.20	-0.02
12	8.26	1.0672	26.30	26.71	+0.41	1.0328	26.31	+0.01
13	8.24	1.0677	26.31	26.81	+0.50	1.0329	26.34	+0.03
14	8.08	1.0681	26.46	26.72	+0.26	1.0331	26.25	-0.21
15	8.26	1.0684	26.60	27.04	+0.44	1.0351	26.59	-0.01
16	8.38	1.0688	26.70	27.26	+0.56	1.0333	26.71	+0.01
17	8.44	1.0692	26.95	27.43	+0.48	1.0336	26.93	-0.02
18	8.03	1.0722	27.04	27.68	+0.64	1.0350	27.13	+0.09
19	8.04	1.0721	27.10	27.67	+0.57	1.0351	27.20	+0.10
20	8.10	1.0730	27.35	27.97	+0.62	1.0354	27.42	+0.07
21	8.15	1.0727	27.42	27.95	+0.53	1.0353	27.43	+0.01
22	8.28	1.0735	27.65	28.31	+0.66	1.0358	27.84	+0.15
23	8.23	1.0768	28.60	29.08	+0.48	1.0378	28.53	-0.07
Average.....				+0.46				-0.03

rected for this difference the Babcock formula becomes

$$T = \frac{L - 1.8}{4} + 1.2 \times \text{Per cent Fat}^1$$

if applied to the cooled undiluted evaporated milk.

In Table III is shown the application of the Babcock formula to some milks kept at 37-40° C. for one and a half hours, and also to the same milks diluted with an equal weight of water at about the same temperature. As mentioned above, the milk must be brought to 15.56° C. and the specific gravity taken without delay.

TABLE III—SHOWING THE APPLICATION OF THE BABCOCK FORMULA TO EVAPORATED MILK HELD AT 37-40° C. FOR 1½ HOURS

		UNDILUTED			DILUTED 1:1			
		Per cent	Solids		Specific Solids			
No.	Gravity	Specific (Dry-Ing)	(Calc.)	Diff.	Gravity (Calc.)	Diff.		
1	8.06	1.0659	26.06	26.15	+0.09	1.0321	25.72	-0.34
2	7.86	1.0671	26.10	26.21	+0.11	1.0328	25.83	-0.27
3	7.84	1.0664	26.12	26.01	-0.11	1.0323	25.56	-0.56
4	7.47	1.0696	26.17	26.36	+0.19	1.0338	25.86	-0.31
5	7.50	1.0701	26.22	26.52	+0.30
6	8.24	1.0659	26.31	26.36	+0.05
7	8.08	1.0669	26.46	26.42	-0.04	1.0325	25.95	-0.51
8	8.28	1.0719	27.65	27.91	+0.26	1.0350	27.44	-0.21
9	8.23	1.0757	28.60	28.80	+0.20
Average.....				+0.12				-0.37

As may be seen from Table III, the average difference is +0.12 when the formula is applied to milk held at 37-40° C. Therefore, the correction for milk at 37-40° C. is 0.5 and the formula to be used for this milk then becomes

$$T = \frac{L - 0.5}{4} + 1.2 \times \text{Per cent Fat}.$$

Lower results were obtained when the milk was diluted.

SUMMARY

It is clear that when exact percentages of total solids are demanded the Babcock formula cannot be applied directly to the determination of total solids in evaporated milk held either at 5° C. or at 37-40° C. But results, the accuracy of which are comparable with those obtained with the Babcock formula on whole milk, may be obtained if the formula

$$T = \frac{L - 1.8}{4} + 1.2 \times \text{Per cent Fat}$$

is applied to the undiluted evaporated milk cooled to its maximum specific gravity and if the formula

¹ In the formula, a difference of 0.46 per cent in solids is equivalent to 1.84 in the lactometer reading or 0.00184 in specific gravity, (4 × 0.46 = 1.84).

¹ U. S. Dept. Agr., Bureau of Chemistry, *Cir.* 66 (1911).

² U. S. Dept. Agr., Bureau of Chemistry, *Bull.* (Revised), 107 (1908).

$$T = \frac{L - 0.5}{4} + 1.2 \times \text{Per cent Fat}$$

is applied to milk kept at 37–40° C. for one and a half hours or until no further change in specific gravity occurs.

DEPARTMENT OF AGRICULTURE
BUREAU OF CHEMISTRY
WASHINGTON, D. C.

IMPROVEMENTS IN THE COPPER METHOD FOR ESTIMATING AMINO ACIDS

By PHILIP ADOLPH KOBER

Received December 15, 1916

For sometime we have been trying to develop further, methods for the study and analysis of proteins. In connection with this work, which will involve the scheme of Van Slyke, we have first attempted to improve and standardize some parts of the copper method¹ for estimating amino acids.

Our improvements are: (I) A simpler method for making standard copper solutions; (II) a method for making a stock suspension of cupric hydroxide which keeps for months, and (III) a method for making and keeping iodometric reagents; *i. e.*, saturated potassium iodide solutions, containing starch and acetic acid.

I—THE METHOD FOR MAKING STANDARD COPPER SOLUTIONS

In the original paper² no specific directions were given for making an iodometric standard, the directions in any standard text-book having been considered sufficient. None of the methods given in these books, however, are very convenient nor are the solutions stable. Standardization of copper solutions by electrolysis, which is of course most accurate, is decidedly unsuitable for biological laboratories, nor is it a particularly short method unless special apparatus involving rotating cathodes is used.

The weighing-out of a suitable amount of a pure copper salt was thought to be the simplest procedure. Cupric sulfate is the purest and cheapest source of copper on the market and the only disadvantage encountered in using it for standard solutions is its uncertain water content and, therefore, unknown copper content. This disadvantage may be practically overcome by dehydrating the salt, as shown below, in a very simple and inexpensive apparatus.³

About 1 lb. of "parowax" is melted in a liter beaker or other suitable container and used in a hood as an oil bath at 245° to 260° C. A test tube (18 mm. inside diameter, length 155 mm.) is cleaned and dried at 105 to 110° C., and weighed with a paraffined cork stopper. Allowing the stopper to remain in the desiccator, 1.77 g. of monohydrate cupric sulfate⁴ are put into the test-tube and connected with the aerating tubes as shown in Fig. 1. Upon heating for 2 or 3 hrs. with

¹ Kober and Sugiura, *J. Am. Chem. Soc.* **38** (1916), 1–16, applied to soils by Porter and Snyder, *Ibid.* **37** (1915), 2119. This journal, **7** (1916), 1049; applied to study of Lecithin, by MacArthur, *J. Am. Chem. Soc.*, **36** (1914), 1297.

² *J. Am. Chem. Soc.* **38** (1916), 1816.

³ For working out this method and for all the analytical work I am indebted to Mr. Weather, Librarian of this laboratory.

⁴ CuSO₄ · H₂O heated to 105 to 110° C. for several hours is converted to monohydrate CuSO₄ · H₂O, having only a light blue tint.

shaking every 15 min. the cupric sulfate is practically dehydrated and is obtained perfectly white; the apparatus is then removed from the oil bath without interrupting the aeration and the oil, while the tube is still hot, carefully and completely wiped off with a towel. Then, when cool, the paraffined stopper is quickly inserted and the tube placed in the desiccator until it is ready for weighing. By using apparatus with ground glass joints, which was not available to us for this investigation, more accurate results can undoubtedly be obtained. If care is taken the tube may be heated without an oil bath, by putting it over a Bunsen burner, so as to maintain it just below visible red heat at about 400° C.

The following results were obtained:

G. CuSO ₄ Taken	G. Cu (Electrolysis)	G. Cu Expected	Ratio Cu Found to Theory (%)
1.1846	0.4706	0.4720	99.7
1.0515	0.4173	0.4190	99.6
1.1044	0.4374	0.4390	99.6
1.0695	0.4247	0.4250	99.7

This method of dehydrating cupric sulfate, as the work of T. W. Richards¹ indicates, may not give suffi-

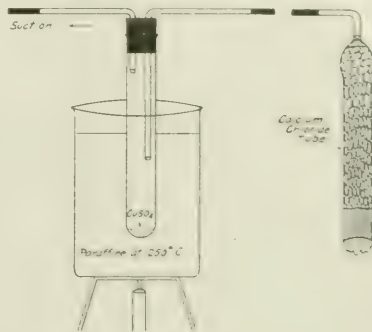


FIG. 1

ciently accurate results for the purpose of calculating atomic weights, but the shaking from time to time in an atmosphere of dry air, may make the results slightly higher than the lowest given by Richards at 99.9 per cent. However, with the apparatus and equipment at our disposal, we were not able to test this out.

DIRECTIONS—After weighing, the contents of the tube are dissolved, avoiding loss due to spattering by keeping the tube covered or in a horizontal position: 1.77 grams of the monohydrate cupric sulfate will give sufficient copper when dissolved in 250 cc. of water to make a 1/25 molar solution, which if carefully stoppered can be used for standardizing stock solutions almost indefinitely.

To guard against the formation of basic salts by hydrolysis and any acidity of the glass, it is well to add 1 or 2 drops of concentrated sulfuric acid.

II—A METHOD FOR MAKING A PERMANENT STOCK SOLUTION OF CUPRIC OXIDE

In the original method, cupric hydroxide was made from a stock solution. Its preparation, however, is required to be neutralized, alkaline, and

washing, consumed considerable time and attention. Furthermore, its use as a jelly made the amount taken for an analysis variable and at times uncertain.

Cupric hydroxide, as ordinarily made by neutralization of any cupric salt, is not stable, but slowly, and in most cases within 24 hrs., changes over into the black cupric oxide. This, owing partly to its agglutination, is not so reactive with amino acids, particularly the conjugated (the peptides). By avoiding an excess of alkali; *i. e.*, not adding enough completely to precipitate the copper from its salt, a suspension of cupric hydroxide can be obtained which keeps for months, if not indefinitely, and can be pipetted easily. The following results, with glycine, show its reactivity when freshly made and after the lapse of time:

Time Days	Titration	Per cent CuO Found to be Theoretical
1		99.3
11		100.2
27		99.6
31		99.6
73	20.64	100.0
	20.60	
	20.61	
78	20.60	100.0
Average, 99.8		

DIRECTIONS:—22 cc. $M/2$ cupric sulfate solution are diluted with water and chopped ice to 6 liters, and at 0 to 1° C. precipitated with about 175 cc. N CO_2 -free sodium hydroxide, using 1 cc. phenolphthalein indicator to test for final acidity. After filtering through paper containing some ice and washing slightly with a spray, the precipitate of cupric hydroxide is suspended in two liters of distilled water, preferably ammonia-free, allowed to settle, and the supernatant liquid poured off. This is repeated three or four times in the course of a day or so, finally suspending the precipitate in 250 cc. of water. Any ammonia in the water, and alkali dissolved from the glass, may interfere with its keeping indefinitely.

According to Abegg,¹ who mentions a similar preparation of Tommasi,² the final product is $\text{Cu}(\text{OH})_2$ and in the absence of salts and alkali will keep indefinitely. Its use and apparent excellent adaptability for amino acid work, however, was not discovered, so far as we are able to learn.

III—A METHOD FOR KEEPING A SATURATED POTASSIUM IODIDE SOLUTION, CONTAINING STARCH AND ACETIC ACID

In the original directions potassium iodide solutions had to be made fresh every day and titrated from time to time, almost constantly, to keep it free from iodine. This production of iodine occurs apparently regardless of the source of the iodide. Undoubtedly some if not most of the iodine originated from iodates or other impurities present in the iodide but the second and subsequent yields seem not to be due to iodate, and not as the literature on the subject states, to oxygen and carbon dioxide, but to the presence of nitrites and nitrates, which with any oxygen from the solution constituents and the air continue to decompose the potassium iodide, catalytically.

By removing most if not all of these substances,

and by decreasing the amount of available oxygen in contact with the solution, *i. e.*, keeping it anaerobically, saturated solutions of potassium iodide, starch and acetic acid can be kept for a long time, if not indefinitely.

Although the simplest and most efficient method of accomplishing this result has not been definitely decided upon yet, owing to the long time desirable for such a stability test, the following scheme has proved practical:

Four hundred grams of potassium iodide were dissolved in 450 cc. of distilled water, and with 40 cc. of 1.0 per cent "soluble" starch¹ solution, and 10 cc. glacial acetic acid were placed in a 750 cc. flask or Erlenmeyer. After adding 2.5 cc. of $M/2$ cupric sulfate solution and an inch of paraffin and mineral oil mixture (1:3), the solution was allowed to stand for 30 min., when the iodine was titrated with $M/2$ sodium thiosulfate to just the neutral point; *i. e.*, when it becomes colorless, when the flask was fitted with an inlet tube containing strong alkali, as shown in Fig. 2, and boiled for 30 min. This inlet tube is for the pur-

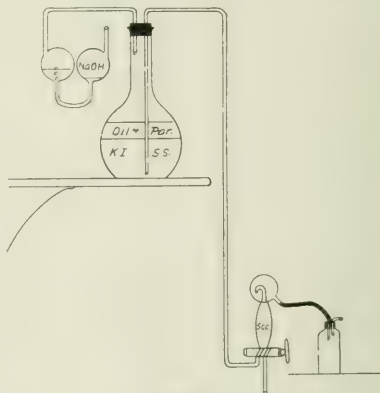


Fig. 2

pose of washing the air that enters the flask after boiling.

In this way we have had stock solutions keep three months or more and in certain experiments we have had a solution of potassium iodide, starch and acetic acid keep in contact with oxygen without oil for 42 days, which seems to us to indicate that when certain catalysts in the air are removed, oxygen has no effect upon potassium iodide or hydriodic acid, contrary to the statements in the literature.

This phenomenon we are studying further, with the hope of finding a reagent that will prevent the oxidation by means of nitrites and nitrates, or better, to remove these substances quantitatively from solution. We believe that this reaction may play a rôle in many obscure phenomena, such as the deterioration of toxins and antitoxins, and other biological changes, and any practical method that would prevent air from exerting an oxidizing effect, because of its nitrite and

¹ Stock solutions of 1.0 per cent starch may also be preserved separately, by adding tricresol to the extent of 0.2 per cent. An experiment with a large amount of cresol—20 to 40 times more than would be used ordinarily—showed that it had no effect on the iodometric titration.

¹ Abegg's "Handbuch der Anorg. Chem.," II, 356.

² J. Soc. Chem. Ind., 37 (1882), 197.

nitrate content, might find numerous and valuable applications.

CONCISE DESCRIPTION OF AMINO ACID ESTIMATION BY MEANS OF THE COPPER METHOD

SOLUTIONS AND APPARATUS REQUIRED—(1) A $1/25$ molar sodium thiosulfate solution, containing 0.993 g. $\text{Na}_2\text{S}_2\text{O}_3 + 5 \text{ H}_2\text{O}$ in a liter of CO_2 -free water, standardized against a $M/25$ cupric sulfate solution (2) made as just described under I. (3) A suspension of cupric hydroxide as described under II. (4) Iodimetric reagents as described under III. (5) Glacial acetic. (6) A "buffer" solution as described in previous paper is made as follows: Sodium hydroxide solution is made free from carbonate, according to the suggestion of Sørensen, as follows: 250 g. of sodium hydroxide are dissolved into 250 cc. of water and placed in a flask furnished with a soda-lime tube. After cooling and allowing the solution to settle, the clear, saturated supernatant solution which contains no carbonate—sodium carbonate being insoluble in saturated sodium hydroxide—is diluted with sufficient boiled distilled water¹ to make a normal solution: 0.2 gram-molecules of boric acid (12.404 g.) are dissolved with distilled water and 100 cc. of normal sodium hydroxide and made up to a liter. This solution is designated as "sodium borate" and, if kept free from carbon dioxide, can be preserved indefinitely. Three volumes of "sodium borate" mixed with one volume of 0.1 *N* hydrochloric acid, we have found thus far to be a suitable "buffer" solution. (7) 50 cc. graduated flasks. (8) Pipettes, burettes. (9) Glass funnels (2–2.5 in.). (10) Filter paper: 11 cm. No. 590, S. & S., or equivalent. (11) 150 cc. Erlenmeyers for filtering.

DIRECTIONS FOR MAKING ESTIMATIONS OF THE TOTAL AMINO ACID NITROGEN

(A) INCLUDING THE POLYPEPTIDE AMINO NITROGEN—All solutions to be tested for amino acids should be neutralized or made slightly alkaline to phenolphthalein. Insoluble substances may be dissolved with the aid of 0.1 *N* NaOH, using not more than 5–6 cc. For the factors given in this paper the solution should not contain more than 0.025 g. of amino acids in 25 cc. The volume after neutralization should be made to about 25 cc. and placed in a 50 cc. graduated flask, so that, when stoppered, carbon dioxide from the air can, to some extent, be avoided. Twenty cc. of "buffer" solution are now added and 2 to 3 cc. of cupric hydroxide suspension are introduced and the mixture vigorously shaken for about a minute. If the cupric hydroxide has not completely dissolved, and, therefore, is in excess, the solution, after bringing to room temperature, is made up to the mark² and shaken from two to three minutes longer. The mixture is now filtered through a good dry filter paper (S. & S. No. 590, 11 cm. in diameter is satisfactory). The filtrate contains all of the soluble complexes while the residue contains the insoluble complexes and the excess of $\text{Cu}(\text{OH})_2$.

¹ As a rule ordinary distilled water in all these solutions is suitable but boiled distilled water is preferable.

² The amount of cupric hydroxide, which should not be more than 0.060 g., will produce an error in the volume of solution of not more than 0.05 per cent, which is in most cases negligible.

An aliquot portion (25 cc.) of the filtrate is then taken and after acidification with 1 to 2 cc. of glacial acetic acid, 5 cc. of potassium iodide-starch solution are added and the solution titrated with 0.004 *N* thiosulfate solution. Every cc. of thiosulfate solution is an equivalent to 0.0003184 g. of cupric oxide or 0.0001120 g. of amino acid nitrogen, or, 1 cc. of 0.001 *N* thiosulfate solution is equivalent to 0.0000280 g. of amino acid nitrogen. When calculated in terms of peptide amino nitrogen, these values should be halved.

(B) EXCLUDING POLYPEPTIDE AMINO NITROGEN—If the free amino acids are to be determined alone, the procedure for making the copper complexes is almost identical with that described for the total amino nitrogen. The only change necessary is to add to 25 cc. of the filtrate, instead of directly titrating iodometrically, 5 cc. of 0.360 *N* $\text{Ba}(\text{OH})_2$, allow the mixture to stand for 15 minutes in a stoppered Erlenmeyer flask and then filter. This precipitates a definite fraction (87 per cent) of the copper from the amino acid complexes (see table of precipitabilities).¹ After washing the precipitate of cupric hydroxide, it is transferred with the filter paper to the Erlenmeyer flask and the hydroxide is dissolved in 10 cc. of 10 per cent acetic acid (warming if necessary). After adding the potassium iodide-starch solution, the copper is titrated with 0.004 *N* thiosulfate solution, every cubic centimeter being equivalent to 0.000112 g. amino acid nitrogen, divided by the proper precipitability.

On acidifying with acetic acid and concentrating to about 15 cc. the filtrate can then be titrated iodometrically. The amino acid nitrogen of the filtrate plus that of the precipitate will give, if the polypeptides have five or less conjugated amino acids, the total amino acid nitrogen. If polypeptides or peptones of six or more conjugated amino acids are present they will prevent the precipitation of the free amino acid copper. Therefore, the increase in the amount of copper dissolved after total hydrolysis, alone, will give the information as to the amount of polypeptide present. No particular method of hydrolysis has been tried, but it is probable that the method used by Levene² and Van Slyke will serve the purpose.

FOR SUBSTANCES WITH QUITE INSOLUBLE COPPER SALTS—For substances with slightly soluble copper complexes, the technic just described is suitable. Where the copper complexes crystallize out, as is the case when leucine, normal-amino-caproic acid, phenyl glycine, or citriline is present and are filtered off with the excess of cupric hydroxide, it is necessary to separate the two precipitates. Very satisfactory reagents for this purpose are the bicarbonates of sodium and potassium, which will dissolve the excess of cupric hydroxide without appreciably disturbing the complexes.³

The filter paper⁴ containing the insoluble complexes

¹ *J. Am. Chem. Soc.*, **39** (1917), 1881–7.

² *J. Biol. Chem.*, **12** (1913), 309.

³ See Kofler and Sanger, *J. Biol. Chem.*, **13** (1914), 14.

⁴ S. & S. No. 590 paper, 11 cm. in diameter is preferable, when it is necessary to determine the insoluble complex as it is easier to handle than the 11 cm. paper.

and the cupric hydroxide is transferred to a 100 cc. Erlenmeyer flask, and by means of a stirring rod the paper in the flask is unfolded so that the residue is on top, and so that it can be rubbed with a rod. Five cc. of 0.1 *N* HCl are then put into the graduated flask in which the complexes were originally made, so that the residue clinging to the sides of the flask is dissolved. This solution is then added to the filter paper in the flask and boiled gently. Another portion (5 cc.) of 0.1 *N* HCl is used in exactly the same way. Finally the graduated flask is washed with 6 to 10 cc. of water and this added to the complexes in the Erlenmeyer flask.

After the residue is dissolved the volume of the solution in the flask is made up to about 20 cc. and 2 g. of powdered potassium bicarbonate are then added as follows: a little (0.2–0.3 g.) of the bicarbonate is first added with a spatula and the solution shaken. This precipitates the insoluble complexes and the excess of cupric hydroxide or carbonate again. After standing one to two minutes the remainder of the bicarbonate is added. On shaking two to three minutes the excess of cupric hydroxide or carbonate is completely dissolved and insoluble complexes are then filtered through paper (S. & S. No. 590, 7 cm. in diameter) and washed with a little water. On returning the filter paper to the Erlenmeyer (also washed), adding 10 cc. 10 per cent acetic acid¹ and heating until the copper of the complexes is dissolved, the solution can be titrated iodometrically. As a table of precipitabilities in the original paper shows, a correction for solubility in KHCO_3 is necessary. This technic gives good results with most of the insoluble complexes, but with leucine the technic described in a former paper² is preferable; this technic required the washing of the first residue with small amounts of 10 per cent KHCO_3 until the filtrates gave no appreciable tests for copper: then the insoluble complexes were dissolved in 10 per cent acetic acid and titrated. It may be possible, by using an amino acid like glycine which gives a soluble complex, to replace this bicarbonate solution and reduce the solubility corrections appreciably. As may be seen from the table, 1 to 2 mg. of leucine and cystine may be determined as soluble complexes.

SUMMARY

The following improvements in the copper method for estimating amino acids are described:

I—A simple method for dehydrating and weighing cupric sulfate suitable for making standard copper solutions.

II—A stock suspension of cupric hydroxide, which is very sensitive in its reaction with amino acids, and keeps for months.

III—A method for making and keeping saturated solutions of potassium iodide, containing starch and acetic acid.

DIVISION OF LABORATORIES AND RESEARCH
NEW YORK STATE DEPARTMENT OF HEALTH
ALBANY

¹ The cystine complex dissolves only slowly in acetic acid. To expedite matters a few cc. of *N*, 10 HCl may be added.

² *J. Biol. Chem.*, **13** (1912), 4.

A STUDY OF THE DETERMINATION OF POTASH CHIEFLY CONCERNED WITH THE LINDO- GLADDING METHOD

By E. L. HUBBARD

Received December 1, 1946

This study was undertaken for the purpose of obtaining a more thorough and exact knowledge of the principles involved in the determination of potash according to the Lindo¹-Gladding² Method as practiced by the Association of Official Agricultural Chemists.^{29,30*}

Although no part of the original plan for the study of potash determination, some work was done on the Perchlorate Method and is here reported for the sake of completeness. As opportunity offered, the work has from time to time extended over many months. The writer feels that results obtained are of sufficient value to warrant this presentation.

THE LINDO-GLADDING METHOD IN BRIEF

Ten grams of the material are boiled in a 500 cc. flask with 300 cc. water for 30 min. To the hot solution ammonia and ammonium oxalate are added in excess to remove Fe, Ca, PO_4 , etc. The solution is cooled, volume made to 500 cc., filtered, and an aliquot of 50 cc. evaporated in a platinum dish. During evaporation, excess of H_2SO_4 is added, then the residue is slowly heated, finally to full red, so that the residue is white. The salts are dissolved in water, a little HCl added, and an excess of H_2PtCl_6 solution; the mixture is evaporated to paste. The residue is washed free of soluble platinum with 80 per cent alcohol, then sodium and magnesium salts, etc., are removed by washing with 20 per cent NH_4Cl solution and this is removed by the 80 per cent alcohol. The precipitate is dried and weighed as K_2PtCl_6 .

MAKING SOLUTION OF MATERIAL TO BE TESTED

The volume of water used in making solution is not important with many substances, provided it remains within 50 per cent of the official requirement. Ten grams of an ordinary fertilizer boiled with 150, 300 and 450 cc. gave 4.78 to 4.83 per cent K_2O as an average of four determinations on each solution, the variation on each being as great as those between the different solutions.

When the substance contains much soluble phosphoric acid or other material which gives a heavy precipitate with ammonia, the greater the dilution the more accurate the result in general, because of the occlusion of potash by gelatinous precipitates. If the volume in which precipitation takes place is larger there is a smaller proportion of the potash in the precipitate. By making the dilution 1 in 1000 instead of the usual 10 in 500, correct results were obtained as shown under "Soluble Phosphates" below.

Vigor of boiling causes no perceptible variation in result. Portions heated on a steam bath, boiled gently over a low flame, or boiled vigorously, gave results within the usual limits of error.

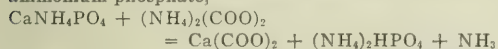
Time of boiling: Five, ten, thirty or sixty min. boiling gave nearly identical results.

* Numbers refer to corresponding numbers in "Bibliography," pp. 496 and 7.

Ammonia used to make the solution alkaline after boiling: One, five and twenty-five cc. gave results within the usual limits of error; sufficient to make alkaline is enough.

In order to remove P_2O_5 as much as possible, *ammonia must be added before ammonium oxalate*. If the oxalate is added first it removes the calcium, which is needed to form an insoluble precipitate with the P_2O_5 , thus leaving the latter in the filtrate as ammonium phosphate, which is, during ignition, converted into insoluble metaphosphate tending to cause errors which may be large.³

The quantity of ammonium oxalate used should be the least that will suffice. In many cases excess will do no harm, but when soluble P_2O_5 is present, any oxalate over the amount necessary to combine with the calcium tends to make more P_2O_5 go into the solution as ammonium phosphate,



A mixture of acid phosphate and kainit treated by the Official Method, but varying the amounts of ammonium oxalate, gave the results shown in Table I. This is not intended to indicate which result is nearest correct, but only to illustrate the effect of ammonium oxalate. In general, the higher results seem due to soluble P_2O_5 .

When the substance contains much acid phosphate there is no calcium remaining in solution after making alkaline with ammonia, hence it is not necessary to add ammonium oxalate, which should be avoided as indicated above.

VARIOUS IMPURITIES—*Sodium salts* have very little effect in moderate amounts except during the final ignition when they cause the residue to be more readily fusible.

Magnesium and calcium aid somewhat in burning by keeping the residue more porous and less likely to fuse. The chief effect of all these is seen in the purification of K_2PtCl_6 (q. v.). Calcium is removed by ammonium oxalate without loss of potash. In case there is considerable organic matter in the solution some calcium and iron may remain after treatment with ammonia and ammonium oxalate.

Sodium and magnesium together in moderate amounts have little effect, except in later processes.

Iron is chiefly removed by ammonia. In the presence of soluble carbohydrates and proteids and some other forms of organic matter, some iron is held in solution in presence of ammonia and remains to be separated from the K_2PtCl_6 . The precipitate with ammonia occludes some potassium. To secure accurate results it must be treated like the phosphate precipitate.

EFFECT OF SOLUBLE PHOSPHATES

Materials in which potash is to be determined frequently contain *water-soluble phosphates*. In the Lindo-Gladding Method these are supposed to be removed by ammonia. Ammonium oxalate is then added to remove calcium. In such cases P_2O_5 is usually present in the filtrate in proportion to the amount of ammonium oxalate used. This fact was

published by De Roode⁷ in 1895. But if calcium or barium is added in excess before ammonia, no P_2O_5 is found in the filtrate. Sufficient CaO alone completely precipitates P_2O_5 during boiling, without any ammonia. Attempts to remove P_2O_5 completely by boiling with excess of $CaCO_3$ or $BaCO_3$ failed. Excess of $CaCl_2$ or $MgCl_2$ added before the ammonia completely remove P_2O_5 ; $CaCl_2$ is preferable, as it is easily removed by ammonium oxalate. But since excess of oxalate causes P_2O_5 to go into solution as ammonium phosphate, the phosphate precipitate must be removed before adding ammonium oxalate to precipitate calcium. Ten grams of a mixture of equal parts of acid phosphate and kainit were treated as usual for a potash determination and varying amounts of ammonium oxalate added. In the filtrates P_2O_5 and K_2O were determined with the following results:

TABLE I—EFFECT OF AMMONIUM OXALATE

Grams Oxalate Added.....	0.0	0.5	2.0	5.0
Grams P_2O_5 Found.....	0.0004	0.0032	0.0117	0.0208
Per cent K_2O Found.....	4.54	4.53	4.62	4.70

The higher results for K_2O are partly due to P_2O_5 , not removed from the K_2PtCl_6 , as will be shown later; hence it should be removed before adding ammonium oxalate. But as the presence of P_2O_5 in the filtrate after adding ammonium oxalate is due to insufficient calcium to form $Ca_3P_2O_8$, it seems unnecessary to add ammonium oxalate to remove calcium which has already been completely removed by excess of P_2O_5 when made alkaline with ammonia. Hence in proceeding by the Lindo-Gladding Method, if the material contains much acid phosphate, omit adding ammonium oxalate. Even then the filtrate will usually contain some P_2O_5 , to prevent which excess of calcium is added before adding ammonia. This increases the volume of the precipitate.

Occlusion of potassium by this heavy gelatinous precipitate¹⁸ is¹⁹ the largest source of error, chemically, in the Lindo-Gladding Method. It may amount to from 1 to 10 per cent of the amount of potassium present. A mixture of 10 g. acid phosphate and 1 g. K_2SO_4 gave 5.40 per cent K_2O by the regular method instead of 5.72 per cent, the amount actually present, a deficiency of nearly 6 per cent.

The error due to occlusion is partly offset by the opposite error of diminished volume on account of the bulky precipitate. These errors are commonly known, and published, but no one seems to have devised a satisfactory plan for overcoming them. The alternate official modification of the Lindo-Gladding Method, which consists in washing the material on a filter to extract the potash, instead of boiling it with water, is helpful, but only partly overcomes the difficulty. The higher results obtained by this method may be attributed to the smaller volume of the phosphate and to the increased dilution.

In order to overcome the loss due to occlusion, the only feasible methods seem to be re-solution and re-precipitation, or greatly increased dilution.¹⁶

RE-PRECIPITATION METHOD

Boil 10 g. of the material with 100 cc. of water, adding 1 to 2 g. $CaCl_2$ to supply enough Ca to form

$\text{Ca}_3\text{P}_2\text{O}_8$ with all the P_2O_5 present. After boiling a few minutes, make alkaline with ammonia and filter at once. A 9 cm. filter in a 10-cm. Buchner funnel with suction is most convenient. Suck as nearly dry as possible, wash a little, then wash the precipitate off the filter, back into the beaker, to a volume of 100 to 150 cc., add a little HCl to dissolve the gelatinous precipitate, but not enough to act on the insoluble matter. Heat to boiling and again make alkaline with ammonia. If enough CaCl_2 was added in the first precipitation no more is needed here. Filter as at first. In most cases this is enough, but to secure all the potash one or two more re-precipitations will be necessary. The filtrates are combined, if desirable, concentrated to about 400 cc., in a 500 cc. flask, and while hot, sufficient (1 to 3 g.) ammonium oxalate is added to precipitate all the calcium in solution. Some excess of ammonium oxalate here does no harm. Cool, make up to 500 cc., filter and take a 50 cc. aliquot for the potash determination as usual. The precipitate of calcium oxalate seems to cause very little error.

LARGE DILUTION METHOD

Place 1.111 g. material in a liter flask, add 800 to 900 cc. of water and sufficient CaCl_2 to combine with the P_2O_5 , boil 30 minutes, make alkaline with ammonia, cool, make volume to 1000 cc. and filter. To the filtrate add dry ammonium oxalate to precipitate all calcium. Shake a few times for an hour or so to complete the precipitation of the calcium. Filter on a dry filter. Take 900 cc. of the filtrate (= 1 g. substance) and proceed with the potash determination.

This method is less time-consuming for the actual manipulations, but requires much longer for the evaporation and affords no opportunity for a duplicate determination on the same solution. In most instances it is likely the re-precipitation method will be found preferable. In case the solution is difficult to filter, the dilution method may be preferable.

RÉSUMÉ AS TO SOLUBLE PHOSPHATES

In potash determination, soluble P_2O_5 is the cause of three errors: (1) *Occlusion of potash by the heavy precipitate*, tending to low results; (2) *volume decreased by the precipitate*, tending to high results; (3) *formation of an insoluble substance in the later part of the determination*, causing high results. Besides these the soluble phosphate has a bad effect on the platinum dishes during ignition. These errors may or may not balance exactly so as to give a correct result. If accuracy is desired, some method, such as above outlined, must replace the usual unmodified Lindo-Glad-stone method.

Soluble proteids and carbohydrates frequently occur in materials in which potassium is to be determined. Hence their effects were studied. Soluble proteids make the solution more difficult to filter and the residue more difficult to burn, but the result is not much affected. When a few milligrams of gelatin were added to pure KCl , the result obtained for potash was the same as for pure KCl .

Many organic substances tend to prevent complete precipitation of iron and calcium by ammonia and

ammonium oxalate. When such are present, more or less iron and calcium will be found in the mixture of salts after the ignition. An infusion of alfalfa hay was mixed with iron and calcium solutions and treated with ammonia and ammonium oxalate. The filtrate still contained some iron and calcium. Infusions of ordinary tankage and bat guano fertilizer act in the same way. Extracts of bone meal, tankage, garbage tankage and bat guano were made and potash determined in them. Then to the same amount of the solutions was added a known amount of KCl and potash determined. The results tended to be low, but with proper care in burning were very good.

Soluble silica is often present in potash solutions. During the ignition it becomes insoluble and later must be filtered out before evaporating the solution with platinum. If carefully done this causes no loss. However it has been found better to add a few drops of hydrofluoric acid to the potash solution during evaporation. This entirely removes silica and is itself removed during the ignition so that it is not necessary to filter after taking up the salts in water. Presence of hydrofluoric acid in the solution in which K_2PtCl_6 is formed is not permissible, as it causes very erratic results. If desired to remove silica by hydrofluoric acid after the ignition it is necessary to replace hydrofluoric acid by several evaporations with hydrochloric acid before evaporating the solution with platinum.

Standing before filtration: It has been said by someone that in some cases, particularly in presence of soluble phosphates, more nearly correct results were obtained if the solution after boiling and addition of ammonia and ammonium oxalate is made up to volume and let stand several hours before filtration. The presumption is that diffusion of the potash occluded in the heavy precipitate occurs, thereby increasing the amount of potassium in solution. Several portions of a fertilizer containing considerable acid phosphate were treated by the Official Method and the solutions allowed to stand for periods of one-half hour, 18 hours and 7 days before filtering. Variations were too small to be conclusive, but tended to show lower results for the longer standing before filtration.

The alternate Official Method of *washing the potash out of the material* placed on a filter instead of extracting by boiling has been found preferable in many cases, if not all. The advantages of this method seem to be due chiefly to the less amount of foreign matter introduced into the solution. In the boiling method there is considerable humus matter brought into solution after addition of ammonia. This is avoided in the washing method. In the presence of acid phosphate the advantage of this method is probably due to the larger volume in which precipitation takes place.

The referees of the Association of Official Agricultural Chemists have found that the washing method tends to give higher and more nearly correct results. In connection with my study the figures given in Table II were obtained.

TABLE II—COMPARISON OF BOILING AND WASHING METHODS

CHARACTER OF SAMPLE	No.	PER CENT K ₂ O IN SOLUTION MADE BY	
		Boiling	Washing
Tankage and K ₂ SO ₄	4960	7.46	7.52
Bat Guano.....	5359	2.56	2.62
Garbage Tankage.....	5988	1.34	1.36
Mixed Complete Fertilizer.....	5361	4.78	4.91
Tankage and K ₂ SO ₄	5771	5.19	5.50
Tankage and K ₂ SO ₄	5666	4.83	4.78
Mixture containing Acid Phosphate.....	5544	5.37	5.34
Mixture of Acid Phosphate and Kainit.....	..	4.68	4.90

The washing method is perhaps more laborious than the boiling method in making the solution, but this is offset by greater ease of the subsequent operations.

The Official Method prescribes that 2.5 g. of the material placed on a 12.5 cm. filter shall be washed with successive small portions of boiling water till the filtrate amounts to about 200 cc.; 2 cc. concentrated HCl are added and the mixture is heated to boiling; ammonia and ammonium oxalate are then added, after which the procedure is as usual, using an aliquot of 50 cc. (= 0.5 g. original substance).

In many cases it is desirable to use an aliquot representing 1 g. of the substance. If the above instructions are followed this requires that 100 cc. be evaporated, which is not so convenient as a 50-cc. aliquot. If a more efficient method of washing is used the double dilution may be avoided. An ordinary carbon filter tube of 30 mm. diameter fitted with a plug of absorbent cotton is very satisfactory. Using this with suction, 10 g. of material may be completely extracted by 200 cc. of boiling water. Repeated tests have shown that potash remaining after this amount of washing is insignificant, *i. e.*, less than 1 mg.

Filter paper on a filter cone, used with suction, gave 5 mg. potash in the third 100 cc. of washing. Filter paper without suction is still less efficient. Ten grams of a material containing about 5 per cent potash were washed with 10 cc. portions of boiling water on a 11 cm. filter. In each successive 100 cc. of extract, potash was determined. In the first 100 cc. were found 4.88 per cent; in the second, 0.16 per cent; in the third, 0.05 per cent; in the fourth, 0.04 per cent; in the fifth, 0.01 per cent.

A folded or fluted filter is still less efficient than the smooth filter, but is more rapid. Because the whole volume of water used with the filter tube passes through the substance, instead of partly through the sides as with an ordinary filter, the tube is much to be preferred for this extraction.

FILTRATION OF THE POTASH SOLUTION

After the solution has been prepared and made up to proper volume it must be filtered to separate the insoluble matter. Three variable factors concerned in this operation may have some effect on the result: (1) evaporation, (2) turbidity of filtrate, (3) adsorption by the filter.

The time factor is most important. If the solution filters very slowly there may be an appreciable concentration unless evaporation is prevented. Two ordinary fertilizer solutions prepared for potash determination were filtered through 18.5 cm. folded filters, and the loss by evaporation was found to be $\frac{1}{2}$ to 1 cc. per hour. This is unimportant in most cases, but if filtration is prolonged for several hours,

evaporation should be avoided by the use of a suitable cover. It has been found expedient to use a linen filter for those solutions which filter very slowly. If the filtrate is returned to the filter for a few minutes at first, till a film is formed on the surface of the cloth, it will come through fairly clean and much more rapidly than through a paper filter.

The clarity of the filtrate seems to make little difference in the final result unless the liquid contains insoluble matter not removed by ignition. In direct experiments variations of the results due to cloudy or clear filtrates from the same solution were within the limits of ordinary experimental error.

Selective adsorption of potash by the filter paper from the solution passing through it was too small to be detected with certainty by the usual analytical methods, though there was some indication of such action. It may be assumed that if at least 100 cc. of the solution are filtered before an aliquot is taken out, any loss due to adsorption by the filter is negligible.

EVAPORATION OF THE SOLUTION

The Official Method directs that 50 cc. of the solution be placed in a platinum dish and evaporated nearly to dryness, when 1 cc. of 1 : 1 H₂SO₄ is added, and evaporation continued to dryness. Ordinarily this is the best procedure. But sometimes it is more convenient to add the acid at once, thus preventing escape of ammonia which might be undesirable. Numerous experiments in connection with this study show that there is no perceptible difference in the result due to time of adding the acid, whether first or last. All that is necessary is that the solution be acidified before becoming dry, in order to prevent loss of KCl on ignition.

To prevent loss it is important that water be driven off as much as possible before beginning the ignition. It is frequently desirable, especially when the solution contains salts having water of crystallization or which are liable to decrepitate, to heat the dish with residue in an oven somewhat above the boiling point of water, till quite dry, before beginning the ignition, thus avoiding loss by spattering.

IGNITION OF THE RESIDUE

It seems probable that in ordinary practice faulty ignition is responsible for more inaccurate results in potash determinations than any other single cause. Too rapid heating causes loss of material by spattering, and causes great difficulty in removing the last of the carbon, due to fusion of the salts on the surface whereby the interior is protected from oxidation so that the carbon does not burn. If in this condition heat is further increased the whole mass fuses and the sulfates are reduced to sulfides by the hot carbon. This is injurious to the platinum dish as well as to correctness of the determination. A great deal of work was done in the effort to find a method which would expedite the ignition as well as prevent loss.

(1) The essence of the whole matter consists in proper regulation of the temperature, and this is not the same for all cases. Heating must be so gradual that the H₂SO₄ is slowly volatilized without spattering

After the mass is dry it should *never be heated red hot till after the carbon has been all burned off*. After this it may be heated to fusion of the salts, momentarily.

Loss of potash occurs if the salts are kept near fusion for any length of time. It is commonly believed that K_2SO_4 is not lost in this way. But it is found that at about the fusion temperature, there is gradual loss of SO_3 , so that K_2O is formed and volatilized. However, there is absolutely no need for such loss as it is unnecessary to heat above redness, at which temperature $KHSO_4$ is changed to K_2SO_4 . Even if a little of the acid salt remains it will do no harm.

A good muffle is the most convenient device for making these ignitions in the most satisfactory manner. After removing the dish and residue from the steam bath it is placed in the cold muffle, which should be heated so slowly that there is no spattering and the temperature raised to very low red in about an hour, by which time the carbon should be all burned off without fusion of the salts.

If a muffle is not available the dish may be heated at first on a hot plate till the liquid is evaporated, then placed on a triangle 8 cm. above the flame of an evaporating burner. The flame should be as low as possible at first, and gradually increased to burn off the carbon below red heat. A piece of sheet metal, platinum, aluminum or iron held as a cover about 1 cm. above the dish simulates the action of a muffle and hastens the burning.

(2) Prevention of spattering when beginning the ignition is difficult if the solution contains no organic matter. The presence of 10 mg. of sugar helps materially to avoid spattering at this stage. On heating with the sulfuric acid the sugar puffs up into a porous mass in its well known manner, and encloses the salts so that they are less likely to be projected from the dish if the heating happens to be too rapid. When the mass becomes dry the carbon burns off easily without causing loss of potassium. For this purpose 10 mg. of sugar is a suitable amount. During this investigation sugar has been much used in this manner, greatly assisting to avoid loss. It is useful only when the solution contains very little other organic matter. As free H_2SO_4 and ammonium salts are the chief agents in causing this trouble, they should be kept as low as possible.

Free H_2SO_4 and ammonium oxalate cause considerable effervescence: if, instead of H_2SO_4 , an equivalent amount of $(NH_4)_2SO_4$ is used, the residue becomes dry on the steam bath, so there is no effervescence on heating, but there is likely to be decrepitation, which may be avoided by first heating in an oven at $110^\circ C$. In general there seems to be little gain from the use of $(NH_4)_2SO_4$ in place of H_2SO_4 . Several other substances were tried to prevent spattering. Ammonium salicylate seemed most efficacious, but finally it was decided that the official treatment with H_2SO_4 was best, with addition of a little sugar when the solution contained but little organic matter.

Much effort was made to find a means of hastening the burning off of the residue from solutions containing proteids and sodium salts such as those prepared from tankages or bat guanos which are very slow

burning. Ammonium nitrate helps, but it must not be added till after free H_2SO_4 is gone, as in the last part of the evaporation there is loss due to lively effervescence, so that it affords little gain in time. Magnesium nitrate has a similar effect. Magnesium acetate may be added to the liquid before it is evaporated. During ignition MgO is formed; this tends to prevent fusion and gives a greater surface so that combustion is more rapid. But if enough magnesium is used to help much it is troublesome in subsequent operations.

Soluble phosphates cause difficulty in burning. $CaCl_2$, or $MgCl_2$, sufficient to form the corresponding phosphates helps some, but it is best to remove the phosphates during the preparation of the solution. Sometimes, when very difficult to burn white, it is better to take up the residue with water and dilute hydrochloric acid and remove the carbon by filtration. If the unburnt matter is small it may be neglected, if large it should be again ignited and extracted, the soluble part being added to the main solution. If the solution contains soluble silica it is removed in the same manner, without difficulty, but as above mentioned, but it is more neatly removed by adding hydrofluoric acid to the solution before evaporation.

REMOVAL OF AMMONIUM SALTS AND ORGANIC MATTER BY EVAPORATION WITH AQUA REGIA

Removal of ammonium salts in this way was long ago published in Crooke's "Select Methods," and has been advocated by Moore⁹ for the preparation of potash solutions for analysis. Instead of placing the solution in a platinum dish to be evaporated, it is placed in a 200 cc. Jena Erlenmeyer flask, 2 cc. HNO_3 and 1 cc. HCl added. The solution is boiled, finally to dryness on a hot plate; the ammonium salts are thus decomposed and volatilized. If the solution contained much organic matter or oxalic acid, more or less of them will remain. If the amount of these substances is small, they are completely removed by two evaporations with aqua regia, in this manner. The final temperature should reach $160^\circ C$. in order to volatilize oxalic acid. After this the residue may be freed of nitric acid, by again evaporating with a little HCl . The residue is now quite suitable for the determination of potash. This method is slower, but takes less care than the ignition method, and in some cases may be preferable, as no platinum dish is required.

SOLUTION OF RESIDUE AFTER IGNITION

The ignited residue is dissolved in water, with addition of a few drops of HCl . It is best to add only a few cc. of water at first, together with 0.5 cc. of HCl , placing the dish on the water bath and heating a few minutes to see if there is any insoluble matter. If but little water is used the acid works better to dissolve portions of the residue which are insoluble in water alone, such as iron oxide and $CaSO_4$. After a few minutes heating, any insoluble residue should be filtered out. Several cc. of HCl may be used, if advantageous. On evaporation of the solution the acid is removed without harmful effect. If the solution contained silica it is removed by filtration without influence on the result, although it is more simply

removed by the use of hydrofluoric acid during the first evaporation as already explained. It is not permissible to use hydrofluoric acid after the ignition, as it is not completely removed by evaporation and causes low results, probably by replacing some of the Cl in K_2PtCl_6 by F. Calcium sulfate is somewhat difficultly soluble but should cause little trouble if enough HCl is used, and later considerable water.

Some kinds of organic matter combine with iron so that it is not removed by ammonia in preparation of the solution. In such cases the iron is found as oxide in the ignited residue. Strong hydrochloric acid dissolves it, so that filtration is not usually necessary, but the iron makes trouble in the later operations of purifying K_2PtCl_6 .

SEPARATION OF K_2PtCl_6

In order to obtain pure K_2PtCl_6 it is necessary to observe certain conditions.⁵ The potash solution must be sufficiently dilute so that there is no precipitate formed on adding H_2PtCl_6 . If the precipitate forms at once it is impure and the crystals are too small to be filtered and washed easily. So long as the solution is acid the amount of hydrochloric acid present is not important. Free H_2SO_4 should not be present. But if some remains as $KHSO_4$ or $NaHSO_4$ it does no harm.

When there is much sodium present the amount of platinum used should not be much more than enough to combine with all the potash, because it is much easier to remove sodium as NaCl or Na_2SO_4 by means of NH_4Cl wash than to remove it from the precipitate as Na_2PtCl_6 by washing with 80 per cent alcohol. When much Na_2PtCl_6 is formed the result is very likely to be too high, due to its imperfect removal by alcohol. In this case it is better to begin the determination over again with a new aliquot of the original solution. If this is not convenient the impure precipitate may be purified as follows: Dissolve in hot water, add a few drops of formic acid and evaporate to dryness. Take up in water, filter out the reduced platinum and proceed with the filtrate as at first, adding less platinum this time. In absence of much sodium the amount of platinum used is not important, provided there is enough to combine with all the potash. Nitric acid or nitrates must be absent. Organic matter reduces platinum hence must not be present.

The solution should be evaporated with $PtCl_4$ till the residue is pasty, not dry. In most cases this is not important, but when iron is present it is quite essential. When the solution containing $FeCl_3$ is evaporated to dryness, some of the iron becomes, by loss of chlorine, insoluble in the NH_4Cl wash and hence remains with the precipitate, causing high results.

PURIFICATION OF K_2PtCl_6

The K_2PtCl_6 is purified by washing with 80 per cent alcohol and then with 20 per cent NH_4Cl , which is removed by again washing with 80 per cent alcohol. A correct result depends very much on the proper conduct of these purifications. If a Gooch crucible or other efficient filter is used 5 or 6 successive 10 cc.

portions of each wash will generally be adequate. The precipitate of K_2PtCl_6 is much more soluble in 80 per cent alcohol than in the NH_4Cl wash, hence it is better to depend on removal of most of the impurities with the latter than to try to remove them as double platinum salts by using an excess of platinum and washing them out with 80 per cent alcohol.¹⁷ A small amount of hydrochloric acid^{9,15} added to these washes sometimes increases their effectiveness in removing impurities, but at the same time it increases their solvent action on K_2PtCl_6 .

A quantity of 0.33 g. K_2PtCl_6 washed with various solutions on a Gooch crucible lost about as follows:

TABLE III—LOSS OF K_2PtCl_6 BY 6 CONSECUTIVE WASHINGS OF 10 CC. EACH

PER CENT STRENGTH	Gram K_2PtCl_6 Lost
Alcohol Solution 99.....	0.0002
Alcohol Solution 95.....	0.0004
Alcohol Solution 85.....	0.0010
Alcohol Solution 80.....	0.0015
Alcohol Solution 60.....	0.0025
Alcohol Solution 80 (denatured).....	0.0020
NH_4Cl Solution 20.....	0.0002
NH_4Cl Solution 20 + 5 per cent HCl.....	0.0005

To show how much washing is required to purify K_2PtCl_6 , several portions of a solution of KCl were evaporated with platinum as usual, and the precipitates filtered off on Gooches. Each of the several filter crucibles received a different amount of washing; those showing highest weights had least washing. In each case there was taken KCl equal to 0.3304 K_2PtCl_6 with 0.05 g. NaCl, and a slight excess of platinum. The precipitate was given the specified number of washings with alcohol; then the washing was completed with NH_4Cl and again with alcohol as usual. The weight of the precipitate when washed with one portion of 10 cc. of 95 per cent alcohol was 0.3383, with 2 washings 0.3352, 3 washings 0.3337, 4 washings 0.3304; this shows that all the soluble platinum had been removed before adding NH_4Cl by four 10 cc. washings with alcohol.

To show how many times the precipitate must be washed with alcohol to remove the NH_4Cl wash a similar experiment was performed. The weight of the precipitate after one wash with alcohol was 0.3350, after 2 washings 0.3314, 3 washings 0.3306; thus three washings of 10 cc. each of alcohol were sufficient to remove all the NH_4Cl wash.

When the precipitate of K_2PtCl_6 is mixed with various impurities such as $CaSO_4$, Na_2SO_4 and $MgSO_4$, a little more time and stirring in the dish are needed to remove the foreign material. Most impurities dissolve in the NH_4Cl wash in a few seconds, but $CaSO_4$ is much slower. Calcium sulfate, 0.06 g., is soluble in 10 cc. NH_4Cl in a few minutes. Na_2SO_4 is easily soluble in NH_4Cl and quickly removed so long as it remains as such. But if an excess of platinum has been used so that there is considerable Na_2PtCl_6 formed, the results are very likely to be high. This salt is but slowly soluble in alcohol, so that it is quite likely to remain after completion of the test washing with alcohol. When NH_4Cl is added, ammonium and sodium exchange acids so that insoluble $(NH_4)_2PtCl_6$ is formed and causes high results. A large amount of Na_2SO_4 mixed with a little potash usually causes low results.

due to much washing necessary to remove it, or the result may be high from lack of washing. Sodium chloride is much more easily soluble in NH_4Cl than is Na_2SO_4 . A 20 per cent solution of NaCl dissolves K_2PtCl_6 easily. Therefore if the determination contains much NaCl , this dissolves in the water of the NH_4Cl forming a solution of NaCl which dissolves the K_2PtCl_6 , leading to low results. But if the sodium is present as Na_2SO_4 , this action does not take place so much; hence it is best to convert sodium to sulfate before attempting to separate it from potassium. Potassium chloride (0.1 g.) + 5 g. NaCl treated with platinum and precipitate washed with 80 per cent alcohol and 20 per cent NH_4Cl gave 0.3173 and 0.3152 g. K_2PtCl_6 instead of 0.3285 g. required by theory. When the NaCl was replaced by 5 g. Na_2SO_4 the result was 0.3200 and 0.3130 g., when evaporated rapidly in the usual manner. In this way the crystals of K_2PtCl_6 are very small and hence were dissolved by the washing. But when the evaporation was so slow as to require 24 hrs. the crystals were much larger and 0.3245 and 0.3226 g. were obtained. A still slower evaporation gave 0.3300 g. K_2PtCl_6 . All of these contained traces of SO_4 , though the larger crystals formed by slow evaporation were purest. More correct results in separating a small amount of potassium from much sodium are obtained, by first precipitating the potassium as cobaltinitrite; this is dissolved in hot dilute HCl (1 : 1) and the potassium separated from the solution by platinum in the usual way. In this way the sodium remains in the watery solution with the excess of cobaltinitrite reagent, as it is not necessary to evaporate the solution to separate all the potash. The cobalt is easily removed from the K_2PtCl_6 , partly by the alcohol wash, partly by the NH_4Cl wash. Thus 0.1 g. KCl + 5 g. Na_2SO_4 separated by the cobaltinitrite method, as above outlined, gave 0.3304 and 0.3282 gram K_2PtCl_6 ; KCl alone gives 0.3285 g. It seems probable that the same method will prove superior to the platinum method for separating potassium from much magnesium or calcium.²⁶ Because of its solvent action⁶ on K_2PtCl_6 , NaCl cannot replace NH_4Cl in the wash solution. Potassium chloride acts in the same way and is further objectionable because of its low solubility in 80 per cent alcohol. Sodium phosphate in mixture with K_2PtCl_6 is likely to cause high results, as it is imperfectly removed by the wash solutions; however, it is dissolved by the acid alcohol before mentioned so that a good result is obtained. Phosphate of course should be removed by the primary purification with ammonia and ammonium oxalate. Magnesium (0.01 g.), present as sulfate, caused a lowering of K_2PtCl_6 from 0.3285 g. (theory) to 0.3263 g. (found). The precipitate is pasty and difficult to wash free of excess platinum. NH_4Cl removes the magnesium salts easily. When present as CaCl_2 , 0.14 g. calcium produced hardly any perceptible effect, but when the amount was 0.70 g., the K_2PtCl_6 found was 0.3255 g. instead of 0.3285 g. taken.

EFFECT OF SOLUBLE P_2O_5

A small amount of phosphoric acid seems to have no

appreciable effect in the solution from which potassium is precipitated by platinum. But if the phosphoric acid amounts to 10 mg. or more it causes high results for potash. This apparently is due to formation of substances not readily soluble in 80 per cent alcohol or the NH_4Cl wash, such as $\text{Ca}_3\text{P}_2\text{O}_8$. In some cases both calcium and phosphoric acid may remain in solution after adding ammonia and ammonium oxalate. Acid alcohol removes these substances from the K_2PtCl_6 and tends to give a correct result. However, it seems best to avoid presence of phosphoric acid in the solution from which potash is to be separated by platinum. If ammonium phosphate is present in the potash solution which is evaporated with H_2SO_4 and ignited, the phosphoric acid remains as an insoluble metaphosphate as shown in *Bull.* 49, p. 44, Division of Chemistry, U. S. D. A.³ This may cause either positive or negative errors and should be avoided by excluding phosphoric acid.

0.1 g. KCl + 0.05 g. Na_2HPO_4 gave 0.334 & 0.332 g. K_2PtCl_6 (impure)

0.1 g. KCl + 0.10 g. Na_2HPO_4 gave 0.337 & 0.339 g. K_2PtCl_6 (impure)

Washed with acid alcohol this became 0.330 & 0.331 g. K_2PtCl_6 (impure)

0.1 g. KCl without Na_2HPO_4 gave 0.331 g. K_2PtCl_6

FILTER FOR K_2PtCl_6

A variety of filters for washing and collecting the precipitate have been tried. Of these the ordinary Gooch crucible with a good mat (at least $\frac{1}{8}$ in. thick) of well prepared asbestos is most reliable. A glass tube about 16 mm. in diameter, 60 mm. long, the top widened to 23 mm., the bottom drawn out and narrowed to a 4 mm. tube 50 mm. long, is very convenient. A wad of glass wool is packed into the bottom and covered with an asbestos mat. This filter is used with moderate suction. Such filters are most convenient and time-saving and have been in use here more than 10 years. They have the defect that the glass wool gradually breaks up and is lost into the filtrate with consequent loss of weight of the filter and inaccuracy of results. In general and for ordinary purposes this defect is negligible. A similar tube fitted with a finely perforated platinum disc for supporting the asbestos mat is free of this defect and is even better than a Gooch crucible.

Such a filter is described by Schollenberger²² except that he uses a linen disc on top of the platinum disc to hold the asbestos. This filter is quite effective and convenient, but is not suitable for weighing the precipitate on account of changes in weight of the linen disc due to action of chemicals and of heat of drying. He recommends that the K_2PtCl_6 be washed out into a platinum dish in which it is dried and weighed. When the filter contains no organic matter, such as cloth, it is suitable for weighing the precipitate without first washing into a dish. A filter tube fitted with a cotton plug supporting a filtering layer of paper pulp is very efficient but as above indicated cannot be used for direct weighing of the precipitate.

Filter paper is much less convenient than any of the above mentioned filters; besides, if used for accurate work, the filter paper requires a special preparation by washing in order that soluble matter be not carried into the solution with hot water when washing out the

purified K_2PtCl_6 . When very small quantities of potash are to be weighed, most of the above mentioned filters are not sufficiently accurate. Filter paper washed successively with dilute HCl , $NaOH$, HCl , H_2O , and 80 per cent alcohol serves pretty well, but cannot be safely used more than once as it gives up soluble matter to hot water after heating to remove alcohol. A felt of well washed paper pulp in a Gooch crucible is more convenient but otherwise no better. In use, after the precipitate is properly purified, either of these paper filters is dried to remove the alcohol, then the K_2PtCl_6 is washed out with hot water into a weighed platinum dish, dried and weighed. Working with 5 to 10 mg. of K_2PtCl_6 , duplicates agree to within about 0.2 or 0.3 mg.

A Gooch crucible with a felt of specially prepared asbestos, $\frac{1}{4}$ in. thick, has given as good or better results in the hands of G. R. Stewart of this laboratory. In this case the precipitate is weighed on the filter without washing into a dish. The alundum crucible is a very satisfactory filter, when means are at hand for giving it thorough washing. But it soon becomes blocked up by precipitated platinum so that washing is inefficient and filtration slow.

The Munro Gooch with platinum felt is also good at first, but rapidly gains weight due to addition of reduced platinum. This difficulty is found with all forms of the asbestos filter. After considerable use the asbestos becomes coated with platinum black, which, by catalytic action, perhaps, precipitates more and more platinum each time it is used. Eventually a new filter must be prepared. To show this, $\frac{1}{2}$ g. K_2PtCl_6 was placed on a Gooch with asbestos felt, washed with alcohol, dried, weighed; the precipitate was washed out with hot water, evaporated dry and again filtered on the same filter. This was repeated six times after which the K_2PtCl_6 recovered had lost 0.0076 g., while the crucible had gained in weight 0.0055 g. Apparently most of the decomposition of K_2PtCl_6 occurs during the drying due to action of alcohol. In general more reliable results are obtained if the weight of the precipitate is found by subtracting the weight of the filter before use from the weight of the filter and precipitate, instead of using the weight of the filter after washing out the precipitate.

DRYING THE K_2PtCl_6

After final washing it is usually directed to dry the precipitate at 100 to 105° C. There is very little change in weight of the precipitate by heating below 140°. One gram K_2PtCl_6 heated in the oven lost as follows:

1 hr. at 112° C., loss 0.03 per cent. 1 hr. at 155° C., loss 0.06 per cent.

The time required for proper drying depends on the temperature and nature of the filter. A Gooch with ordinary asbestos felt is very nearly dry after $\frac{1}{2}$ hr. at 110 to 120° C., and one hour is sufficient. But if the felt is very thick or the liquid not well sucked out, more time is needed.

TIME NEEDED FOR COOLING FILTER BEFORE WEIGHING

An ordinary Gooch weighing about 15 g. does not reach constant weight in much less than $\frac{1}{2}$ hr. after

removal from the oven. After standing about 10 min. it is apparently cool, but the weight indicated is about 1 mg. less than after it has stood half an hour. After this the weight is practically constant if it is kept in a desiccator. Standing in open air there is some variation in weight, usually a gain after 24 hrs.

PERCHLORATE METHOD FOR POTASH¹¹

In any case where the original solution contains SO_4 which must be removed in order to apply the perchlorate method this method is to that extent more tedious than the platinum method. When the bases are present as chlorides, there is not much difference in the amount of work required for each, except that one wash solution less is used in the perchlorate method. The solubility of $KClO_4$ in alcohol forms the chief difficulty in obtaining accurate results.

In order to use the perchlorate method the same procedure is followed as for the platinum method to the point where the solution is ready to be evaporated with platinum solution. If the solution contains SO_4 , it is removed by $BaCl_2$. Then the chloride solution is evaporated with $HClO_4$ which expels HCl and leaves all bases present as perchlorates; all of these are soluble in alcohol except $KClO_4$, which is practically insoluble in strong alcohol that has been saturated with the same salt. Absolute alcohol is the best wash as the $KClO_4$ is almost insoluble in it, but it is not so good a solvent for the other perchlorates which are to be washed out of the $KClO_4$. The chief difficulty with the use of 95 per cent alcohol saturated with $KClO_4$ as a wash is due to variation in solubility of $KClO_4$ with variation in temperature. When the temperature rises during use, the solubility increases and some of the precipitate is dissolved, causing a low result. If the wash is used at a temperature much below that at which it was saturated with $KClO_4$, the latter tends to go out of solution and become a part of the precipitate, thus producing a high result. So the same precipitate may gain or lose weight by repeated washing with the same wash solution of alcohol saturated with $KClO_4$ according as the temperature at time of use is above or below that at which it was saturated. Speed of washing also affects the result. The same wash percolating slowly through the filter is quite likely to add to the weight of the precipitate, while if drawn through rapidly by suction the precipitate may lose weight.

Various other washes were tried besides 95 per cent alcohol saturated with $KClO_4$. Alcohol nearly absolute (99 per cent) containing 0.2 per cent perchloric acid is the most satisfactory. It seems to have very little effect on $KClO_4$, but dissolves the other salts quite well. Alcohol 95 per cent saturated with $KClO_4$ is somewhat improved by addition of 0.2 per cent $HClO_4$. More than 0.2 per cent $HClO_4$ increases the $KClO_4$ solubility too much. Alcohol of 97 per cent strength similarly treated is somewhat better than 95 per cent, but has the same general effect.

Potassium acetate added to alcohol decreases the solubility of $KClO_4$ in it. But as it is necessary to use as much as one per cent, the wash must be re-

moved by one containing less matter in solution, such as 97 per cent alcohol + KClO_4 ; thus the method becomes cumbersome.

During this study nearly 100 determinations were made on a solution of pure KCl . But few results were close to theory; more were high than low. Portions of 0.1 g. KCl gave 0.1850 to 0.1950 g. KClO_4 at various times; theory requires 0.1882 g. KClO_4 . Presence of NaCl or of BaCl_2 , as when used to remove SO_4 , tends to give high results, but if entirely converted to perchlorates by repeated evaporation with excess of HClO_4 and the precipitate well washed, they do not seriously interfere.

Cost of perchloric acid is a considerable item in this method. It is expensive and not easily recoverable. If the acid costs \$4.00 per lb. and 10 cc. are used for one determination, the cost is about \$0.10. In using the platinum method there is some loss of platinum, but most of it is easily recovered so that the loss should not exceed \$0.03 per determination. In general it is likely that any analyst having equal experience with both methods will obtain more accurate results with less time, labor and expense by the platinum method.

SUMMARY

I—In making the solution of a material for the determination of potash, considerable variation in the following factors has but little effect on the result: volume of water used, vigor of boiling, time boiled, excess of ammonia, and time of standing after boiling but before filtering.

Ammonium oxalate must not be added till after the solution has been made alkaline by ammonia (which should not be added in excess), and if there is more than enough P_2O_5 present to form insoluble compounds with the bases present, ammonium oxalate should not be used, because it increases the amount of P_2O_5 remaining in solution. In order to obtain a correct result when the solution contains much soluble P_2O_5 , a special procedure is necessary—either addition of excess of calcium and reprecipitation, or larger dilution, as described in the text. This is because potash is occluded by the gelatinous precipitate of the phosphates.

The method of making the solution by extraction with hot water on a filter is preferable as it gives higher results and less impurities in the solution. For this extraction a tube filter is much more efficient than the ordinary paper filter in a funnel.

II—The effects of time, clarity of filtrate and absorption of potash by the filter are negligible with most materials under ordinary conditions.

III—In evaporation of the solution H_2SO_4 may be added at any time before dryness, preferably at first.

IV—Ignition of the residue is probably the chief source of low results in potash determinations. To secure correct results the heating must be so gradual that spattering, which is common, does not occur. About 10 mg. of sugar added during the evaporation sometimes aids materially. Various other substances added to assist burning or to hinder spattering were not found very useful. In order to secure good burn-

ing the heat must be kept below the fusing point of the salts till after the carbon is burned off. The final temperature need not be above a moderate red heat for a few minutes. Long heating near the fusion point of the salts causes loss of potash. A little SO_4 remaining as bisulfate does no harm. In case the residue is not easily burnt white, it is best to dissolve in water and a little HCl and filter out insoluble matter. In many cases organic matter and ammonium salts may be conveniently removed by evaporation of the solution with aqua regia.

V—Solution of the residual salts after ignition is best accomplished by adding a few cc. of dilute HCl and heating, before adding much water. Iron compounds thus dissolve readily and CaSO_4 dissolves on adding more water. Insoluble SiO_2 may be filtered out without loss of potash.

VI—Separation of K_2PtCl_6 requires certain conditions for an accurate result. Concentration of potassium at time of adding platinum must be low enough so that no K_2PtCl_6 is precipitated at once. Free H_2SO_4 , HNO_3 , or organic matter must not be present. The amount of platinum used should be only slightly in excess of that necessary to combine with all the potassium. Excess of HCl is unimportant. Evaporation should cease while some free HCl still remains; if evaporation is carried too far dilute HCl should be added and the evaporation repeated.

VII—Purification of K_2PtCl_6 is usually completed by 5 or 6 successive washings, with 10 cc. of the wash fluids. Effects of various strengths of alcohol, and of other wash fluids, and of many impurities in the precipitate are discussed in the text. Potassium is better separated from large amounts of sodium as cobaltinitrite than as platinichloride.

VIII—As a filter for collecting and purifying K_2PtCl_6 an ordinary Gooch crucible with asbestos felt is most suitable and reliable for accurate work. A filter tube is somewhat more convenient but less accurate.

IX—Drying of the K_2PtCl_6 precipitate may be done at any temperature between 100 and 140°C ., and is usually complete in an hour at 120°C .

X—Weighing the crucible and precipitate should not be done in less than half an hour after removal from the oven. During this time it should remain in a desiccator.

XI—The Perchlorate Method for the determination of potash was found less desirable than the platinum method. It is longer, more difficult and more expensive as to reagents.

BIBLIOGRAPHY

- (1) Lindo (1881), "Original Method for Potash Determination," *Chem. News*, **44**, 77, 86, 92, 129.
- (2) Gladding (1885), "Improvement on Lindo Method," U. S. Dept. of Agriculture, Division of Chemistry, *Bull.* **7**, 38.
- (3) Association of Official Agricultural Chemists (1886 to 1914), *Bulletins of Bur. of Chem.*, U. S. Dept. Agr., particularly the earlier work in *Bull.* **12**, **16**, **19**, **24**, **28**, **31**, **35**, **43**, **47**, **49**, **57**, **61**, **90**, **99**, **105**, **116**, **122**, **133**, etc.
- (4) N. Robinson (1894), "Study of Lindo-Gladding Method," *J. Am. Chem. Soc.*, **16**, 364.
- (5) A. L. Winton (1895), "Proper Conditions for Determination of Potash, Suitable Concentration at Time of Adding Platinum," *J. Am. Chem. Soc.*, **17**, 453.

- (6) W. E. Garrigues (1895), "Claims that 90 Per Cent Alcohol Precipitates NH_4Cl from Gladding Wash," *J. Am. Chem. Soc.*, **17**, 50.
- (7) R. De Roode (1895), "Recommends Aqua Regia Method for Purifying Potash Solution and Removal of NH_4 Salts without Ignition or H_2SO_4 ," *J. Am. Chem. Soc.*, **17**, 46, 86.
- (8) H. W. Wiley (1897), "Method for Determination of K_2O and P_2O_5 in Fodders, etc.," *J. Am. Chem. Soc.*, **19**, 320.
- (9) C. C. Moore (1898), "Use of Acid Alcohol for Purifying K_2PtCl_6 ," *J. Am. Chem. Soc.*, **20**, 340. Also see Crookes "Select Methods," p. 32.
- (10) Winton and Wheeler (1898), "Study of Effect of NH_4Cl ," *J. Am. Chem. Soc.*, **20**, 597.
- (11) F. S. Shiver (1899), "Determination of Potassium as Perchlorate, etc., and Preparation of Perchloric Acid," *J. Am. Chem. Soc.*, **21**, 33.
- (12) C. L. Hare (1903), "Use of $\text{Ca}(\text{OH})_2$ instead of Ammonia and Oxalate," *J. Am. Chem. Soc.*, **25**, 417.
- (13) C. B. Williams (1903), "Use of HF to Decompose Soil for Determining K," *J. Am. Chem. Soc.*, **25**, 495.
- (14) E. M. East (1904), "Use of Na_2SO_4 to Remove Ba, Thus Avoiding Use of NH_4 ," *J. Am. Chem. Soc.*, **26**, 297.
- (15) F. P. Veitch (1905), "Use of Acid Alcohol, etc.," *J. Am. Chem. Soc.*, **27**, 56.
- (16) Karl Regel (1906), "Difficulties Due to Sulfates. Estimates Pt after Reduction by Mg," *Chem.-Ztg.*, **30**, 684.
- (17) Wilcox, Buckley and Archibald (1908), "Solubility of K_2PtCl_6 in Alcohol of Various Strengths and in KCl and NaCl ," *J. Am. Chem. Soc.*, **30**, 749.
- (18) Breckenridge (1909), "Study of Causes of Low Results in Potash Determination by A. O. A. C. Method, Especially Effect of the Heavy Precipitate by Ammonia and Oxalate," *THIS JOURNAL*, **1** (1909), 409 and 804.
- (19) T. E. Keitt (1913), "Study of Effect of Phosphates, etc., in Potassium Determination," *Bull.* **173**, South Carolina Agricultural Experiment Station.
- (20) L. A. Hill (1903), "Colorimetric Determination of Potassium; Use of SnCl_4 ," *J. Am. Chem. Soc.*, **25**, 990.
- (21) Cameron and Failyer (1903), "Colorimetric Determination of Potassium; Use of KI on K_2PtCl_6 ," *J. Am. Chem. Soc.*, **25**, 1063.
- (22) C. J. Schollenberger (1911), "Effective Filter Tube," *THIS JOURNAL*, **4** (1912), 436.
- (23) W. A. Drushel (1909), "Volumetric Cobaltinitrite Method," *Z. anorg. Chem.*, **61**, No. 1, 137.
- (24) O. M. Shedd (1910), "Study of Cobaltinitrite Method," *THIS JOURNAL*, **2** (1910), 379.
- (25) L. T. Bowser (1911), "Qualitative Determination of Potassium as Cobaltinitrite," *J. Am. Chem. Soc.*, **33**, 1566. "Quantitative Determination of Potassium as Cobaltinitrite by Titration of the Precipitate with KMnO_4 ," *J. Am. Chem. Soc.*, **33**, 1752.
- (26) A. H. Bennett (1916), "Use of Sodium Cobaltinitrite to Separate Potassium from Much Sodium," *Analyst*, **41**, 165; *Chem. Abs.*, **10** (1916), 2334.
- (27) De Vries (1907), "Study of the Method and Various Sources of Error," *Chem. Weekblad*, **4**, 231.
- (28) W. B. Hicks (1913), "Reduces K_2PtCl_6 by Mg and Weight Pt Formed," *THIS JOURNAL*, **5** (1913), 650.
- (29) Official Method of Association of Official Agricultural Chemists, U. S. Dept. Agr., Bureau Chemistry, *Bull.* **107**, p. 11.
- (30) Same in *J. O. A. C.*, **1** (1916), 12.

¹ DIVISION OF AGRICULTURAL CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY

THE FERTILIZER VALUE OF CITY WASTES

II—GARBAGE TANKAGE. ITS COMPOSITION; THE AVAILABILITY OF ITS NITROGEN, AND ITS USE AS A FERTILIZER¹

By P. J. SCHROEDER

Among the various materials now obtained from city wastes, none has a greater importance as a fertilizer material than garbage tankage.² Its importance is far-reaching and is of concern to every urban resident, for it is necessary that some disposition be made of material produced in such large quantities in every city, and it is of undoubted benefit to every resident that this be done with as little cost as possible to the city. Rendering for the recovery of grease and preparation of a fertilizer material is the method of disposal which

possesses to a greater extent than any other the two most essential characteristics of any method of disposal, namely, economy and sanitation. The facts on which this statement is based will be presented in a subsequent communication. It is obviously desirable that the products obtained in this disposal be more generally understood, better appreciated and the fullest possible use made of them in order that they may bring as high a price as possible and that their production be made as lucrative as possible so as to bring the greatest return to the community.

In the first paper of this series, "The Composition of Garbage," the results of the analyses of 200 samples of raw city garbage were presented.¹ The average of 75 of the analyses, made of samples taken through a range of time covering a year, were as follows: Moisture, 73.78 per cent; ash, 3.60 per cent; oil (ether extract), 5.32 per cent; potash (K_2O), 0.27 per cent; phosphoric acid (P_2O_5), 0.43 per cent; nitrogen, 0.70 per cent; and combustible matter 22.63 per cent.

METHODS OF RENDERING

For the recovery of grease, garbage is treated in three different ways:

1—It is "tanked," i. e., cooked under pressure with steam, the water and liberated fats pressed out as completely as possible, and the oil separated from this by settling and skimming, the grease remaining in the solid residue after it has been dried being extracted with gasoline.

2—It is crushed to render the particles uniform in size, dried directly in rotary, hot air kilns, the grease extracted with gasoline, and the solids ground for tankage.

3—It is heated with gasoline to the boiling point of the latter, whereby the water contained is evaporated with the gasoline boiled off, while the grease is being extracted. The material is thus degreased and dehydrated in one operation and in one receptacle.

In some plants where the first-named process is in use, the dried tankage is not extracted with gasoline for the recovery of the grease still remaining therein, the operators contenting themselves with that recovered by cooking and pressing.

CHARACTER AND COMPOSITION

Garbage tankage, then, is the solid residue when the water, the grease, and, generally, the water-soluble portions of garbage have been removed. From the foregoing paragraph it is seen that by the first method mentioned the water-soluble ingredients are removed by cooking in steam and the subsequent pressing, while by the other two methods all the ingredients, except those volatilized by drying and dissolved out by the gasoline, are removed. In the first and the aqueous solution pressed from the material composed in the first named process is expressed by the recovery of its ingredients. The resulting concentrate is a sticky material, the substance known as "stilk" and may be added to the degreased tankage, which is

¹ Read before the Fertilizer Chemistry Section of the American Chemical Society at Kansas City, Mo., April 10-14, 1917.

² If considered on the tonnage basis it may be necessary to make an exception of stable manure.

W. T. O'Brien and John R. Lindbergh, *THIS JOURNAL*, **9**, 1915, 69-74.

then subsequently redried. The addition of the "stick" not only increases the proportion of the valuable constituents of the tankage, but materially improves its physical condition. The fibrous portion of the substances constituting the raw material after cooking, pressing and drying becomes light and fluffy and makes the tankage quite bulky. The application of "stick" corrects this and yields a granular product of increased specific gravity which can be handled more conveniently for fertilizer purposes.

In appearance garbage tankage is a coarse, brown powder, either granular or finely fibrous, depending on its method of preparation. In it generally can be detected small pieces of bone, crockery and glass, the proportion of these depending upon the thoroughness with which the various sorts of waste materials have been segregated in the households from which collected and the care with which sorting has been conducted in the rendering plants. In some cases glass and crockery are eliminated, while in other plants considerable quantities find their way into the products.

When the origin¹ of garbage tankage is recalled, it is seen that it is made up of the dried and degreased portions of various sorts of food materials, animals and vegetable, and of waste products resulting from the preparation of food and remaining after the more edible portions of food materials have been consumed. In addition it contains variable but generally small quantities of substances of an inorganic origin.

CHEMICAL COMPOSITION

Since, as will be seen subsequently, garbage tankage is of interest at the present only as a fertilizer material (and to some extent as a cattle food), only those constituents were studied which are of interest from the fertilizer point of view. These are nitrogen (from which protein may also be calculated), bone phosphate, potash, ash, organic matter (by difference), fat and moisture. The methods of analysis employed were those prescribed as official methods for agricultural analyses. The values recorded as fat represent ether extract.

Efforts have been made in recent months to utilize tankage as a hog feed. From the results reported from these experiments the conclusion may be drawn that as such it has not been an unqualified success. It is rich in protein and carbohydrate when prepared by modern methods; analyses of several samples show about 19 per cent protein and 45 per cent carbohydrate. These materials are digestible. As a fattener, it is not all that may be desired, but as a part of a properly balanced ration it gives promise of becoming useful.

Tankage prepared for hog or cattle feed is carefully freed from bone and other hard materials that might be injurious to the digestive tracts of the animals to be fed. Flotation methods for effecting this separation have been devised which are highly efficient and show promise of commercial applicability.

In Table I are given the results of analysis of 20 samples of tankage from various reduction plants. The analyses made, at the time of collection of the samples, represented all the larger garbage reduction plants in operation in this country. In these plants the various methods of rendering outlined above were employed; it is possible, therefore, to observe in a general way the effect of method of rendering on composition of the tankage.

Among the samples analyzed, Nos. 2, 15, 16 and 17 were dried without cooking as described under (2) and certain of these, it will be observed, were not degreased subsequently. Samples 14, 18 and 20 were tankage prepared by the method described under (3); *i. e.*, by drying and degreasing simultaneously with gasoline (the Cobwell process). The balance were tankages produced by the old tanking process, described under (1); No. 10 was not extracted with gasoline; No. 6 contained the concentrated "stick" water from the tanks. The effects of degreasing are shown by the samples referred to, which indicate an oil content of approximately 12 per cent. This oil is one of the most valuable products derived from garbage, especially at present prices, while its removal from the tankage is a benefit from the fertilizer view-point. Sample No. 6, containing the "stick," is of interest considering its high content of nitrogen and phosphoric acid and especially the high percentage of water-soluble nitrogen compared with the other samples as shown in Table IV.

It will be observed that the nitrogen content of these tankages is about 3 per cent. An occasional one exceeds this (cf. Nos. 6 and 19), a fact possibly explainable on the ground that in case dead animals and meat trimmings, if available only in small quantities, are rendered with garbage, or the tankage obtained from them is added to the garbage tankage, thus slightly raising its nitrogen content.

The high ash content is the product of the bone present and the various foreign substances, such as broken glass and crockery, which find their way into the raw material.

PRODUCTION OF GARBAGE TANKAGE

In 1914 there were 29 companies and municipalities engaged in the rendering of garbage on the large scale for the recovery of grease and the production of tankage. In the aggregate they were rendering 1,200,000 tons of garbage per year and were producing over 173,000 tons of tankage. This represents a yield of 15 per cent tankage. This tankage, not counting the value of the grease recovered, represents a value of \$1,157,000 on the basis of prices paid for this material before the beginning of the European War. At present prices this value amounts to over \$2,000,000. Only about one-half of the cities of over 30,000 population render garbage for the production of tankage. Installation of rendering plants in these cities where the garbage is not being conserved now would raise the annual production to over 345,000 tons and the value to over \$4,000,000 in addition to the value of the grease obtained from it.

¹ Cf. O'Brien and Lindemuth, *Loc. cit.*

GARBAGE TANKAGE AS A FERTILIZER

Garbage tankage is applied largely to the production of mixed fertilizer, being used as a base. For this purpose it is well suited. It is in the form of a powder and is non-caking, and since it has a drying effect on acidified phosphate rock, it imparts these properties to the mixed fertilizer of which it constitutes a part. While making an admirable base because of these characteristics, it contributes its quota of the fertilizer elements at the same time. It is a fertilizer diluent, so to speak, or base, but is not that in the same sense in which totally inert materials would be. In addition to these elements it supplies liberal proportions of organic matter which also plays an important rôle in a fertilizer way and is badly needed by many soils. When the farmer buys a fertilizer material containing garbage tankage as a base, he is not purchasing and paying freight on the large proportion of inert material that he would be in purchasing a fertilizer of the same grade containing inorganic matter as a base. He would even be justified in paying freight for short hauls on garbage tankage alone.

A certain quantity of garbage tankage has been used as a complete, low-grade fertilizer, without admixture with more concentrated materials. Its use in this manner has met with pronounced success in those cases investigated. Its cheapness makes possible its use in large amounts so that advantage is derived from its high content of organic matter, or the so-called humus-forming constituents. For this reason its use in this manner should be especially profitable in light, porous soils, constitutionally deplete in organic matter, since the application of such materials improves the physical condition of such soils, increases their water-holding capacity and accelerates bacterial activity.

AVAILABILITY OF THE NITROGEN

The principal value of garbage tankage, as suggested above, is in its utilization in the preparation of fertilizers. As such its value is based upon its analysis, and, among its constituents of fertilizer value, nitrogen is of chief importance. As a nitrogen carrier it gives promise of becoming one of the important sources of that element. The obstacle in the way of its extensive utilization in the past has been the question of the availability of the nitrogen. In certain quarters a prejudice seems to exist against its use; it is listed arbitrarily with carriers of non-soluble nitrogen. It is spoken of in connection with leather meal and the idea seems to prevail that it is similar to this. The farmer rightly has been instructed not to purchase unavailable nitrogen; as a result of this the value of garbage tankage has been rather discounted. The fertilizer laws of certain states require that the source of nitrogen in mixed fertilizer be stated on the label of the container. When such a label indicates the presence of garbage tankage the farmer is naturally restrained in the purchase of it because of his instructions. This militates seriously even against the use of garbage tankage as a base or filler, for which it is

admirably suited, and tends to encourage the use of totally inert and useless materials for that purpose. State fertilizer laws are designed primarily for the protection of the farmer against fraud and should of course be respected. They should, however, be considerate of all the facts. In excluding garbage tankage from mixed fertilizer, either directly or indirectly, no benefit is secured by any one and a positive injury is effected. It is not unavailable nitrogen in the same sense that leather meal is, and it cannot be used as a substitute for high-grade nitrogen carriers, as can leather meal, because it does not contain sufficient nitrogen. There does not appear to be any just reason then why its use should be discouraged. On the contrary, the benefits to be derived by its increased use justify its indorsement for the purpose to which it is now being applied.¹

The small price obtained for garbage tankage is due to the fact that such a low valuation is placed on its ammonia, that being only a fraction of the price assigned ammonia in other tankages. Thus while \$3.10 per unit was quoted for the ammonia of high-grade ground tankage,² \$3.44 for fish tankage and \$2.30 for cottonseed meal, only \$1.60 per unit was offered for that of garbage tankage.³ This is due to the fact that the ammonia of garbage tankage is rated as non-available.

Examination of the literature does not reveal experiments to determine the availability of the nitrogen of garbage tankage of sufficient number and definiteness to justify the conclusion that the ammonia is non-available. That decision seems to have been made largely arbitrarily. In the absence of definite proof there seems to be no reason for taking such a position as there are no *a priori* considerations supporting it. In fact, these considerations rather point to the conclusion that the nitrogen should be available. The animal nitrogen is contributed to meat scraps and bones, the vegetable nitrogen by such materials as the rinds of melons, the skins of fruits, the bruised and withered portions of leafy vegetables, etc. The treatment of these materials in the course of manufacture should contribute to their disintegration and aid in making the nitrogen more readily available.

The difference between present and old methods of collecting garbage should also be recalled.⁴ In

¹ In this connection it is interesting to quote a paragraph from the statement of the Committee on Fertilizer Legislation at the American Chemical Society at the New York Meeting Sept. 25-30 1916, which reads: "In previous reports we have referred to legislation which discriminates against ammoniacs which are known to have a definite value, even though this status be denied to them by the present empirical methods of testing for availability of organic nitrogen. Furthermore, the methods of stating the results of analyses in some states are very misleading, as to the quality of the nitrogen which has been used. Many of the sources of organic nitrogen, which were formerly used for fertilizers, are now reserved for other purposes and unless fertilizer manufacturers can procure all such sources as are known to be valuable, or can be made so by chemical processes, the prices of organic ammoniacs will go so high as to prohibit their use. There is a large demand for nitrogen from organic sources, and it is the desire of manufacturers to meet this demand, but such materials cannot be employed at a cost at which they cannot profitably be used by the consumer." See *This Journal*, 9 (1916), 1073.]

² Wholesale prices (January), 1914.

³ Current prices for ammonia in garbage tankage range from \$2 to \$2.50 per unit.

⁴ *Chemical and Engineering News*, 1916.

former times there was practically no selection of garbage, and all sorts of refuse were thrown into this material. Now, however, a selection is made at the point of origin, and at the city collecting stations the garbage is carefully sorted; such refuse as old shoes, tin cans, bottles, etc., is removed and sold as such at considerably higher prices than the weight

carrier is first thoroughly leached so as to remove all the water-soluble nitrogen and then the sample, which is so chosen as to contain 50 mg. water-insoluble nitrogen, is digested and distilled with 100 cc. of alkaline permanganate solution containing 25 grams potassium permanganate and 150 grams sodium hydroxide per liter. The nitrogen dissolved in this way,

TABLE I—ANALYSES OF GARBAGE TANKAGE FROM VARIOUS PLANTS. RESULTS IN PERCENTAGES

The analyses represented in this table were made by John R. Lindemuth formerly of this Bureau									
All results calculated on moisture-free basis NH ₃ calculated from N using 1.2 as factor			Bone phosphate calculated from P ₂ O ₅ using 2.2 as factor Oil extracted with Ether						
No.	SOURCE OF SAMPLE	N	NH ₃	P ₂ O ₅	Bone Phosphate	K ₂ O	Ash	Oil	Moisture
1	Penn Reduction Co., Philadelphia, Pa.	2.91	3.49	4.83	10.62	0.27	29.48	1.93	4.37
2	Allegheny Garbage Co., Pittsburgh, Pa.	2.40	2.90	2.35	5.17	0.95	...	2.80	3.95
3	Indiana Reduction Co., St. Louis, Mo.	2.69	3.23	3.83	8.43	0.79	...	1.74	...
4	Illinois Fertilizer Co., St. Louis, Mo.	2.95	3.54	3.05	6.71	1.66	27.58	3.83	3.72
5	Union Reduction Co., Cincinnati, Ohio	2.89	3.47	4.67	10.27	0.39	31.97	6.69	3.14
6	Municipal Reduction Plant, Columbus, Ohio	3.45	3.77	4.20	9.24	0.90	27.92	2.00	3.86
7	Municipal Reduction Plant, Cleveland, Ohio	2.36	2.87	5.32	11.70	0.39	48.92	1.86	2.51
8	New York Development Co., Barren Isle, N. Y. C.	3.06	3.34	5.46	12.01	0.48	32.84	3.12	5.44
9	New York Development Co., Barren Isle, N. Y. C. (Old tankage)	2.74	3.29	5.94	13.06	0.20	36.70	1.64	3.78
10	Genesee Reduction Co., Rochester, N. Y. (Not degreased)	2.74	3.29	4.52	9.94	0.19	29.12	11.25	2.36
11	Schenectady Municipal Plant, Schenectady, N. Y.	2.32	2.78	2.98	6.56	0.76	...	4.82	...
12	Boston Reduction & Sanitation Co., Boston, Mass.	2.63	3.16	3.99	8.77	0.65	36.47	2.08	2.92
13	Springfield Merg Reduction Co., Springfield, Mass.	3.20	3.84	2.69	5.91	1.09	20.74	7.10	3.48
14	New Bedford Extractor Co., New Bedford, Mass.	3.45	4.18	1.92	4.22	1.29	19.42	2.45	4.51
15	Municipal Reduction Plant, Chicago, Ill. (Not degreased)	2.08	2.50	1.37	3.01	0.91	28.03	12.09	3.99
16	The Mark Process Dryer Co., Chicago, Ill. (Not degreased)	1.74	2.09	0.49	1.08	0.79	...	13.92	6.67
17	Municipal Reduction Plant, Chicago, Ill. (from dryer, not degreased)	2.11	2.53	1.96	4.31	1.06	...	11.22	3.77
18	Bartlett & Snow Co., Exposition Grounds, San Francisco, Cal.	2.88	3.46	3.19	7.02	0.97	...	0.88	...
19	San Francisco Disposal Co., San Francisco, Cal.	4.98	5.98	6.73	14.81	0.81	25.27	3.49	...
20	Pacific Reduction Co., Los Angeles, Cal.	2.96	3.41	1.85	4.07	1.27	13.63	3.49	3.34
AVERAGE		2.78	3.34	3.56	7.84	0.80	29.15	4.92	3.67

value in garbage. The presence of this material in the old type of garbage tankage went a long way towards condemning its use, and the present carefully selected kitchen refuse, consisting mostly of vegetable matter, meat offal, and bones, is an entirely different product from the material formerly known as garbage tankage.

EXPERIMENTAL DATA ON THE AVAILABILITY OF THE NITROGEN

In view of these considerations it seemed desirable that further work be done. The question of the availability of the nitrogen of a fertilizer is by no means easy of definite solution. It has been the subject of a great deal of research for a number of years,¹ but has not resulted in much definite knowledge on the subject. The methods that are now most familiar and regarded as official are the alkaline permanganate

in addition to that soluble in water, is considered as available nitrogen.

The results obtained by the alkaline permanganate method with the principal types of garbage tankage are given in Table II. Cottonseed meal is taken as a standard. Its position as nitrogen-carrying fertilizer is well known, and of the various nitrogen fertilizers of recognized availability it seems most comparable to garbage tankage, the former being entirely and the latter largely a vegetable ammoniate.

When the relative availabilities as indicated in Table II are noted it is seen that only one of the tankages falls below 40, while the average is only 13 points below the availability of cottonseed meal. By referring to the first column of the table it will be noticed that the samples of garbage tankage necessary to furnish 50 mg. of water-soluble nitrogen ranges from about

TABLE II—AVAILABILITY OF THE NITROGEN IN VARIOUS GARBAGE TANKAGES AND COTTONSEED MEAL COMPARED BY THE ALKALINE PERMANGANATE METHOD

Fertilizer	Weight of Sample Containing 50 Mg. Water-Insoluble N for Alk. KMnO ₄ Det'n	WATER-INSOLUBLE NITROGEN RENDERED SOLUBLE BY ALKALINE KMnO ₄ SOLUTION				Sum of Water-Insoluble N rendered Soluble by alk. KMnO ₄ and Water-Soluble N (in terms of Total N)	
		In terms of—					
		Weight					
		Grams	Mg.	Per cent	Total N Per cent	Per cent	
Cottonseed meal	0.9560	26.2	52.50	47.82	56.82		
Garbage, Penn. Red. Co., Philadelphia, Pa.	1.9370	11.3	22.60	20.03	31.37		
Garbage, Mun. Red. Plant, Columbus, Ohio	2.1010	11.7	23.40	16.14	47.15		
Garbage, Mun. Red. Plant, Cleveland, Ohio	3.2900	13.6	27.20	17.53	53.02		
Garbage, Colwell System, New Bedford, Mass.	1.8570	16.5	33.00	26.02	47.17		
Garbage, Allegheny Garbage Co., Pittsburgh, Pa.	2.7170	15.5	30.98	23.77	47.09		
Garbage, Pacific Coast Reduction Co., Los Angeles, Cal.	2.1370	12.1	24.20	19.14	40.07		
Garbage, Barren Island, New York City	2.1190	11.7	23.40	18.05	40.92		
AVERAGE FOR TANKAGES	2.3056	13.2	26.39	20.09	43.82		

method proposed by Jones² and the neutral permanganate method, proposed by Street.³ These are described in *Bull.* 107, Revised, of the Bureau of Chemistry, United States Department of Agriculture. Of the two, the alkaline permanganate method is perhaps the more satisfactory. In this method the nitrogen

2 to 3 grams, while that in the case of cottonseed meal is only one gram. The size of the sample has an important effect on the results obtained by that method. Experiment shows that the larger the sample the smaller the availability indicated. It is of course necessary to gauge the size of the sample in some manner and the manner chosen is perhaps the best available; at the same time it must be admitted that a

¹ "Reports on Nitrogen during Last 10 Years," *Jour. of the A. O. A. C.*

² *Vt. Agr. Expt. Sta., Bull.* 173

³ *This Journal*, 4 (1912), 438.

fertilizer like the one in question with a low nitrogen content and a high non-nitrogenous organic matter content is at a disadvantage by this method.

A notable contribution to our knowledge of the availability of nitrogen in fertilizers has been made in recent years by the study of their nitrifiability under actual field conditions as well as in the laboratory. Many very interesting results have been obtained by this method and published by Dr. C. B. Lipman,¹ of the University of California. The method proposed by Lipman has not received the publicity and the recognition of the permanganate method, but it is more considerate of our present knowledge of soil processes and endeavors to approximate the natural processes that are actually operative in the soil and that control the assimilation of a fertilizer. In this method a small quantity of fertilizer is incubated at constant temperature and moisture content with a definite quantity, usually 100 grams, of fertile soil and the proportion of the nitrogen converted into nitrates is taken as an indication of availability. The results obtained by this method vary, of course, with the type of soil used. In Table III are given the results obtained with the various tankages when treated with the two soil types, sassafras silty loam and Norfolk sand. Results with other soil types are comparable with these.

TABLE III—AVAILABILITY OF THE NITROGEN IN VARIOUS GARBAGE TANKAGES COMPARED TO THAT IN COTTONSEED MEAL BY THE NITRIFICATION METHOD

FERTILIZER	SASSAFRAS SILTY LOAM					NORFOLK SAND				
	Total N	% Nitrate Produced	Per cent Nitrified	Availability Per cent		Total N	% Nitrate Produced	Per cent Nitrified	Availability Per cent	
Cottonseed Meal.....	192.3	6.1	2.41	56.82		97.3	24.0	9.45	56.82	
Garbage Tankage No. 1.....	164.1	1.2	0.93	21.94		69.1	5.0	3.75	23.30	
Garbage Tankage No. 2.....	169.5	2.3	1.48	34.90		74.5	11.1	7.25	43.61	
Garbage Tankage No. 3.....	158.6	2.6	2.47	38.23		63.6	15.1	14.45	87.00	
Garbage Tankage No. 4.....	164.1	2.7	1.77	41.75		74.3	18.9	12.35	74.37	
Garbage Tankage No. 5.....	159.0	1.9	1.76	41.52		64.0	9.0	8.45	50.42	
Garbage Tankage No. 6.....	164.6	2.4	1.83	43.70		69.6	17.0	12.96	78.02	
Garbage Tankage No. 7.....	165.6	2.8	1.82	42.93		70.6	15.7	11.62	69.98	
AVERAGE FOR TANKAGES.....	2.2	1.72	40.64			13.1	10.13	60.95		

(a) The quantities of nitrate indicated in the table are over and above that produced in the check.

For purposes of comparison the percentages of nitrogen nitrified are multiplied by factors which raise the per cent nitrified in the case of cottonseed meal to the figure representing the availability of cottonseed meal as determined by the alkaline permanganate method (cf. Table II). This factor is 2.36 in the case of sassafras silty loam and 6.0 in that of Norfolk sand. The results with the first soil show on the average an availability of about 16-18 per cent less than cottonseed meal. This is a heavy soil and nitrification should proceed relatively slowly. In the case of Norfolk sand the conditions are more favorable to nitrification and the statement in an earlier part of the paper in regard to the use of garbage tankage in light sandy soils is here in part substantiated. In the case of Norfolk sand only two of the samples show a materially lower percentage of nitrate formed than cottonseed meal. The total nitrogen content of the tankage is much less than that of cottonseed meal.

but the per cent nitrified is greater, the average of the tankages being 60.95 compared to 56.82 in cottonseed meal.

Especial attention is called to the relatively high percentage of water-soluble nitrogen carried by the tankages, shown in Table IV.

TABLE IV—WATER SOLUBILITY OF THE NITROGEN OF VARIOUS GARBAGE TANKAGES COMPARED TO THAT OF COTTONSEED MEAL

NOTE—Total nitrogen and water-insoluble nitrogen determinations in this and following tables were made by L. J. Jenkins of the Bureau of Chemistry, U. S. Department of Agriculture.

SOURCE OF GARBAGE	Per cent Total in Sample	Per cent Water-Soluble	Per cent Water-Soluble	Per cent Water-Soluble
Cottonseed Meal.....	5.73	5.22	0.51	8.90
Pa. Reduction Co., Philadelphia.....	2.91	2.58	0.33	11.34
Municipal Red. Co., Columbus, O.....	3.45	2.38	1.07	31.01
Municipal Red. Co., Cleveland, O.....	2.36	1.82	0.54	35.39
Cobwell System, New Bedford, Mass.....	3.45	2.72	0.73	21.15
Allegheny Garbage Co., Pittsburgh.....	3.39	2.84	0.55	33.33
Pacific Coast Red. Co., Los Angeles.....	3.06	3.34	0.28	20.93
Barren Island, New York City.....	3.06	2.36	0.70	22.87
AVERAGE FOR GARBAGE TANKAGES.....	2.94	2.25	0.69	23.74

It will be recalled that the water-insoluble nitrogen of the garbage tankages rendered soluble by alkaline permanganate, as shown in Table II, is relatively small in comparison to that of cottonseed meal. The fact that the total availability compares favorably with that of cottonseed meal is due, to a large extent, to the large percentage of the water-soluble portion. This in some cases is higher than the other portion. The percentage of water solubility is brought out in Table V, where the availability by the alkaline permanganate method, the nitrification method with sassafras silty loam and Norfolk sand, and the water-soluble nitrogen are all compared. For the purposes of this table the results are calculated to the basis on which the values for cottonseed meal, the standard, are the same for all methods.

TABLE V—COMPARISON OF AVAILABILITY OF NITROGEN BY WATER SOLUBILITY, ALKALINE PERMANGANATE AND NITRIFICATION METHODS COTTONSEED MEAL TAKEN AS STANDARD

NOTE—For purposes of comparison the percentages in the last three columns are multiplied by factors which raise the per cent in the case of cottonseed meal to the figure representing the availability of cottonseed meal as determined by the alkaline permanganate method (cf. Table II).

FERTILIZER	Per cent Total Nitrogen	Per cent Water-Soluble Nitrogen	Per cent Nitrified by KMnO_4 in Sassafras Silty Loam	Per cent Nitrified by KMnO_4 in Norfolk Sand
Cottonseed Meal.....	5.73	8.90	56.82	56.82
Garbage Tankage, No. 1.....	2.91	11.34	31.37	21.94
Garbage Tankage, No. 2.....	3.45	31.01	43.18	34.90
Garbage Tankage, No. 3.....	2.36	35.39	54.07	38.23
Garbage Tankage, No. 4.....	3.45	21.15	41.71	41.75
Garbage Tankage, No. 5.....	3.39	33.33	40.12	41.52
Garbage Tankage, No. 6.....	3.06	20.93	40.91	43.70
Garbage Tankage, No. 7.....	3.06	22.87	40.91	42.93
AVERAGES FOR TANKAGES.....	2.94	31.41	43.82	40.64

A series of experiments on the effect of treating garbage tankage with sulfuric acid show that the water solubility, and consequently the availability of the nitrogen, can be considerably increased. Unwashed samples of Philadelphia tankage were treated with the various quantities of sulfuric acid and the results indicated in Table VI, and applied for two hours in a ball grinding mill. The use of 100 cc. of acid, which would represent about one-third per cent increase in the water-soluble nitrogen from 2.36 per cent to 3.06 per cent. The percentage increase in availability of about 16 per cent. Whether such an acid treat-

TABLE VI. THE EFFECT OF SULFURIC ACID TREATMENT ON THE AVAILABILITY OF THE NITROGEN IN GARBAGE TANKAGE FROM PENN. REDUCTION COMPANY PHILADELPHIA, PA.

Volume of Sulfuric Acid Cc.	PER-CENT NITROGEN			WATER-SOLUBLE NITROGEN Per cent of Total	Weight of Sample Containing Nitrogen Water-Insoluble N for Alk. KMnO ₄ Det'n Grams	WATER-INSOLUBLE NITROGEN RENDERED SOLUBLE BY ALKALINE PERMANGANATE Percentages in terms of Water-Insol. N	SUM OF WATER-INSOLUBLE NITROGEN RENDERED SOLUBLE BY ALK. KMnO ₄ AND WATER-SOLUBLE NITROGEN Percentages in terms of Total N	
	Total as found	Water-Insoluble	Water-Soluble				Total N	Water-Insol. N
0	2.91	2.58	0.33	11.34	1.9370	22.60	20.03	31.37
10	2.82	2.58	0.39	13.83	2.0580	21.00	18.10	31.93
30	2.70	2.23	0.47	17.42	2.2420	21.20	17.52	34.94
40	2.48	1.90	0.58	23.39	2.6320	21.60	16.54	39.93
50	2.34	1.80	0.54	23.07	2.7780	20.60	18.74	41.61
60	2.30	1.64	0.66	28.70	3.0490	21.40	15.25	43.95
70	2.20	1.46	0.74	33.64	3.4250	20.80	13.80	47.44
80	2.30	1.48	0.82	35.65	3.3790	20.60	13.25	49.90
90	2.30	1.47	0.83	36.07	3.4010	20.60	13.15	49.12
100	2.10	1.34	0.76	36.18	3.7310	21.40	13.70	49.88

ment would be economically feasible would depend on various conditions. In the preparation of mixed fertilizer it might be possible to utilize the excess acid by mixing with rock phosphate and thus reduce the cost of the treatment.

CONCLUSION

The examination of the various garbage tankages has revealed no important fact that shows that they are unsuited for fertilizer material. The position is not taken that it is possible to determine the value of a fertilizer material definitely by present methods of chemical analysis, but from the examination the expectation would seem entirely justified that the proper use of garbage tankage should give the usual results obtainable from medium or low-grade fertilizers.

Garbage tankage offers a large supply of nitrogen. At the present time ever-increasing amounts of such ammoniates as cottonseed meal and high-grade tankage are being utilized for feeding purposes rather than for fertilizer and there is a growing scarcity of high-grade nitrogen carriers.¹ In view of these facts, the wider use of the low-grade materials becomes increasingly desirable. The intelligent use of garbage tankage will make available the not inconsiderable nitrogen which it is able to supply to the fertilizer trade and at the same time will tend to result in a larger conservation of the garbage of the cities with increased benefit to them.

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

THE IDENTIFICATION OF EMODIN-BEARING DRUGS

By W. S. HUBBARD
Received January 29, 1917

Emodin and emodin-like compounds are found in the various species of *Aloe*, family *Liliaceae*; various species of *Rheum*, family *Polygonaceae*; various species of *Cassia*, family *Leguminosae*, to which belongs senna; *Xanthoxylum tingoassuiba* St. Hil., family *Rutaceae*; various species of *Rhamnus*, family *Rhamnaceae*, to which belong cascara and frangula; *Rumex ecklonianus* Meissn; *Polygonum² cuspidatum* Sieb. et Zucc, family *Polygonaceae*; *Xanthoxylum tingoassuiba* St. Hil., a native of Brazil, is not very well known and apparently not used. *Rumex ecklonianus*³ is an herb indigenous to South Africa where it has been used in medicine

to some extent. It will be noted that it belongs to the same family as rhubarb, as does also *Polygonum cuspidatum*¹ Sieb. et Zucc., which is indigenous to China and Japan. The U. S. Pharmacopoeia, 8th Edition, recognized all species of *Aloe*, while the 9th Edition recognizes only *Perryi* Baker, *vera* Lanne and *ferox* Miller. The U. S. Pharmacopoeia recognizes the species *frangula* and *purshiana* of *Rhamnus* under the names of frangula and cascara sagrada; those species of *Rheum* which come from China and Thibet; the species of *acutifolia* and *angustifolia* of *Cassia* under the commercial names of Alexandria and India senna.

A great deal of work has been done on the constituents of the emodin-bearing drugs, notably by Tschirch and his co-workers in Switzerland and by Power and his co-workers in England. Reference to the more important work prior to 1911 may be found in "Die Pflanzenstoffe" (Wehmer). The principal constituents of Aloes as given by Wehmer are aloin, barbaloin, isobarbaloin, emodin, and aloes-resin.

The constituents of Cascara are best given by H. A. D. Jowett² and summarized as follows:

"1—In addition to emodin, the presence of which in the bark was fully confirmed, a small amount of a substance isomeric with emodin, melting at 183° C. was found. Glucose also occurs in the bark.

"2—No evidence whatever could be obtained of the existence of chrysophanic acid or chrysarobin in the bark, or of glucosides yielding on hydrolysis emodin, chrysophanic acid or rhamnetin.

"3—It was impossible to isolate a pure substance corresponding to either cascacin or purshianin.

"4—Attempts to obtain the bitter principle or derivatives of it in crystalline form were unsuccessful.

"5—No difference could be observed between the character of the fresh (1 year old) and of the so-called mature bark (3 years old).

"6—The examination of *Rhamnus purshiana* D. C., and *Rhamnus californicus* Esch. gave identical results.

"7—A hydrolytic enzyme was isolated which hydrolyzed amygdalin, but when administered in 1-g. doses had no gripping action.

"8—The physiological experiments made for the purpose of locating the active principle of the drug resulted in the following: Emodin is not the active principle, and exerts very little, if any, of the characteristic aperient action of cascara. The active

¹ Report on the Fertilizer Industry, Federal Trade Commission, Aug., 1916.

² Die Pflanzenstoffe, Wehmer, Jena, 1911.

³ Tutin and Cleeve, J. Chem. Soc., 97 (1910), 1.

¹ Perkin, J. Chem. Soc., 67 (1895), 1084.

² Report 47 (1904), of the Wellcome Research Laboratory.

principle or principles producing the aperient action of the drug are contained in the portion of the lead subacetate precipitate extracted by ethyl acetate, which is soluble in water and in alcohol."

The constituents of rhubarb are given by F. Tutin¹ and H. W. B. Clewer. In their paper a very good review of the literature is given and a number of points are elucidated. The main constituents isolated were: Cinnamic acid, 0.01 per cent; gallic acid, 2.2 per cent; rhein, 0.12 per cent; emodin, 0.78 per cent; aloë-emodin, 0.16 per cent; emodin monomethyl ether, 0.22 per cent; chrysophanic acid, 0.49 per cent; and rheinolic acid (an anthraquinone derivative); in addition a mixture of glucosides (2.0 per cent) of rhein, emodin, aloë-emodin, emodin monomethyl ether, and chrysophanic acid; an amorphous, non-glucosidic resin, 10.4 per cent. Of the anthraquinone derivatives only aloë emodin and chrysophanic acid have any purgative action, the mixture of glucosides being inert. The chief purgative principle is the non-glucosidic resin.

The constituents of senna leaves are given by F. Tutin.² A very good review of the literature is given and a number of points are elucidated. Tinnevely leaves were found to contain salicylic acid, rhein, kaempferol, aloë-emodin, kaempferin, and a mixture of the glucosides of rhein and aloë-emodin. Senna leaves from Lima and Peru were found to contain all these compounds and, in addition, isorhamnetin and a glucoside of isorhamnetin. Alexandria senna yielded rhein, aloë-emodin, kaempferol, and isorhamnetin, also the glucosides of these. The glucosides were found to be more abundant. Attention is called to the fact that "Cathartic acid" of Dragendorff has been for some time recognized as an indefinite mixture of substances. Quite contrary to what has been the usual belief, and contrary to the statement in most books dealing with the subject, no chrysophanic acid was found in senna.

While a great deal of work has been done on the constituents of aloë, cascara, rhubarb and senna, comparatively little has been done on the identification of them when in medicinal preparations or admixtures. E. M. Bailey,³ reporting some results obtained in an effort to find some color reaction which would serve to differentiate between these cathartics, states: "While experiments have thus far fallen short of success in this respect, they have, nevertheless, led to some interesting differences among the oxy-methylantraquinones themselves." A separation is made of the anthraquinone compounds by means of ammonium carbonate, sodium carbonate and sodium hydroxide, the method employed by Tschirch, the Wellcome Research Laboratories and others.

The greater part of the work along these lines has been on the chemical identification of aloë and differentiation of the species.

A majority of the nostrums on the market contain one or more of the emodin-bearing drugs. In order to

identify the drugs separately and in mixtures some recognized tests have been combined, and others developed as outlined below. It is necessary to try the tests on authentic samples in order to become familiar with the colors produced by the individual substances and by different combinations. The procedure indicated has been followed with success by various analysts in the Bureau of Chemistry during the past year and a half. After some experience the analyst should have little difficulty in the identification of aloë, cascara, rhubarb, and senna. Frangula responds to the same tests as cascara.

PREPARATION OF SAMPLE

In the case of liquids evaporate about 10 cc. to a pasty consistency in a porcelain dish, acidulate with hydrochloric or sulfuric acid, and extract the contents of the dish several times with ether, stirring with a glass rod and pouring off the ether into a test tube. With pills or other solid material it is necessary only to powder, acidulate and extract with ether as described.

BORNTRÄGER REACTION¹

To a portion of the ether extract is added ammonia water or dilute alkali. If emodin or other anthraquinone compounds are present a red color develops in the water layer.

Phenolphthalein also gives this reaction, but if some of the ether solution is evaporated to dryness and sodium or potassium hydroxide solution (5-10 per cent) added, the color given by phenolphthalein disappears after a short time (an hour or two), while the color of the anthraquinone compounds is permanent. If phenolphthalein and anthraquinone compounds are both present the method of Warren⁴ should be used for separating them. It is as follows:

"The preparation in the form of a syrup is diluted with water, faintly acidified and filtered to remove most of the phenolphthalein. The filtrate is neutralized with ammonia water, evaporated to a very thick syrup which is extracted while warm with acetone, and rendered slightly acid with hydrochloric acid. The extraction is made by stirring with successive portions of the solvent⁵ and decanting from the residue. The acetone fractions are united, evaporated to dryness on the water bath, the residue twice moistened with alcohol and the alcohol evaporated in order to remove the last traces of acetone.⁶ The residue is taken up in diluted sodium hydroxide solution, filtered, and a slight excess of iodine test solution added, allowed after a few minutes by the addition of a slight excess of hydrochloric acid. The compound is cooled below 15° C. for an hour and the contents filtered. The phenolphthalein is thus precipitated as tetraiodophthalein, a substance which is very insoluble in water. The solution is then treated with a slight excess of sodium sulfite, to remove free iodine, and shaken with chloroform. The chloroform is evaporated to dryness and the residue treated with a dilute solution of sodium

¹ *J. Chem. Soc.*, **99** (1911), 946; *Report 186* (1911), Wellcome Research Laboratories.

² *J. Chem. Soc.*, **103** (1913), 2006; *Report 187* (1913), Wellcome Research Laboratories.

³ *Ann. J. Pharm.*, **87** (1915), 148.

⁴ *J. Ind. Eng. Chem.*, **19** (1888), 168.

⁵ *Ind. Eng. Chem.*, **25** (1913), 434.

⁶ The carbon prefers ether instead of acetone.

⁷ If ether is used these evaporations are unnecessary.

hydroxide which develops a red color in the presence of anthraquinone compounds."

Another method, described by E. M. Bailey,¹ is of about equal value for the elimination of phenolphthalein and also eliminates curcumin (the coloring substance of *Curcuma longa*) and haematoxylin. The solution is treated with zinc dust in the presence of 25 per cent sodium hydroxide and the anthranol is oxidized back to chrysophanic acid by means of hydrogen peroxide. In a later paper² Bailey states that, "The reaction utilized to identify chrysophanic acid in the presence of phenolphthalein serves also as a test for oxymethylanthraquinones, generally, and is much more specific for this group than the Bornträger reaction."

The procedure is, however, so complicated that it would rarely be used in place of the Bornträger reaction. Since all the emodin-bearing drugs discussed in this paper contain oxymethylanthraquinones, the reaction described does not help to distinguish between the individual emodin-bearing drugs.

BORAX TEST³

After the presence of an anthraquinone compound is shown by the Bornträger test and phenolphthalein is shown to be absent or is eliminated by one of the methods given, the borax test is applied. To a portion of the ether extract in a test tube is added an equal amount of saturated borax solution.⁴ In the presence of aloes a green fluorescence develops in the aqueous layer. It sometimes requires half an hour for the fluorescence to become noticeable. With the borax solution rhubarb shows an old rose color, cascara a brown and senna sometimes a light brown but usually no color. With a little experience there is no difficulty in distinguishing between cascara and senna. From this borax test an idea is obtained of the particular drug present, and confirmatory tests are then applied.

ALOES

The borax test is carried out as described in the U. S. Pharmacopoeia, 9th Ed. (1916), p. 37. The test is best conducted in a 100 cc. graduated cylinder and allowed to stand at least an hour before deciding that there is no fluorescence. One might be led to believe from the pharmacopoeia that this test is distinctive for the species recognized, but as a matter of fact it applies to all species of aloes.

Alotin⁵ gives the fluorescence test of aloes either directly or when shaken out with ether. It does not give the Bornträger reaction, but if ammonia or other alkali is added directly to the alotin a red color develops. It is found that in carrying out the Bornträger reaction by addition of ammonia directly to the ether a fluorescence develops after standing a short time.

¹ THIS JOURNAL, 6 (1914), 320.

² Am. J. Pharm., 87 (1915), 153.

³ Pharm. Weekblad, 26, Maart, 1892, L. Schouteten. The author claims the test to be sensitive one part in ten thousand. In searching for this reference, the name has been found spelled three different ways, and in no place has the correct reference been given to the original. In one case [Jahrb. der Pharm., 27 (1892), 112], the reference gives the correct publication but the wrong year.

⁴ The original test was for an aqueous solution of aloes.

U. S. Pharmacopoeia, 9th Ed., 1916, 38.

It is said that aloes are sometimes found which do not contain emodin¹ but so far as the author can ascertain this is very rare. It has no bearing on the borax test. If emodin is absent it will of course fail to give the Bornträger reaction.

Other tests for aloes have been proposed: Klunge's reaction² by the addition of copper sulfate gives a yellow color and after addition of salt and alcohol a red color develops. This is not distinctive for aloes.

Kremel's Chrysaminic Acid Test³ by the transformation of alotin to chrysaminic acid by evaporation with nitric acid and addition of ammonia or other alkalis. This reaction is also given by substances other than aloes.

The Hirschsohn's test⁴ is applied after purification with basic lead acetate. To 10 cc. of the filtrate add a few drops of copper sulfate solution and hydrogen peroxide and warm, but not to boiling. In the presence of aloes a deep red color appears, which increases in intensity on standing. This is not distinctive for aloes.

Mossler⁵ describes a method to avoid the precipitation of alotin with foreign oxyanthraquinones, etc., by lead acetate whereby the Hirschsohn⁶ and borax test for aloes are more distinctive. It is claimed that 0.2 g. of aloes can be detected in a mixture containing 5 g. of rhubarb, frangula or cascara. The method is rather tedious and must be followed very carefully to obtain satisfactory results.

RHUBARB

An aqueous solution of chlorinated lime is added to a portion of the ether extract and in the presence of rhubarb a red color appears in the water solution. Sometimes only a red ring forms at the point of contact of water and ether, and if large quantities of rhubarb are present a red precipitate is formed between the ether and water. Chlorine water will not react. Both calcium chloride and calcium oxide give a pink to red color with aloes, cascara and senna, as well as with rhubarb. If a saturated aqueous solution of ferric or ferrous sulfate is used instead of the solution of chlorinated lime, the water layer assumes a blue color, sometimes quite faint, but evident when viewed with a white background. Aloes, cascara and senna do not respond to this test. At the present time the causes of these two reactions are not known and the questions are being studied. It is necessary to have both of these tests positive before reporting rhubarb, for samples of senna have been found on two occasions which gave the test with chlorinated lime. St. John⁷ has found that *Acer spicatum* gives the test with the iron salt. There has been recently imported into this country, previous to the European war, a preparation of 1,8-dioxanthraquinone, called "Istizin," used for the same general purpose as aloes, cascara, rhubarb, and senna. It gives the Bornträger reaction

¹ H. Herissey, J. Pharm. Chim., 5 (1912), 393.

² Through Pharm. Post, 46 (1913), 313.

³ Pharm. Post, 1895, 421.

⁴ Pharm. Zentralhalle, 1901, 64.

⁵ Pharm. Post, 46 (1913), 313.

⁶ Loc. cit.

⁷ Am. Pharm. Jour., January, 1917.

and the reaction with a solution of chlorinated lime, but does not give the test with the iron salt or borax solution.

ALOES AND RHUBARB

When these substances are present in about equal amounts, or rhubarb in excess, it is well to extract the acidified material with ether until practically no more yellow color is removed. The residue is then extracted with hot water and tested according to the directions given in the U. S. Pharmacopoeia.¹ If the aloes is in excess, rhubarb does not interfere.

CASCARA AND ALOES

The cascara solution sometimes gives a fluorescence which need not be confounded with aloes since the fluorescence of the former has a brown color; neither need it be confused with a mixture of rhubarb and aloes, for the presence of rhubarb produces a reddish color and is easily identified by the special tests already described. If, however, aloes and cascara are both present, the fluorescence and brown color will both appear, in which case it is best to carry out the test according to the directions given in the U. S. Pharmacopoeia, 9th Edition,¹ and carry the dilution to 500 cc. in a cylindrical graduate, at which concentration the fluorescence of aloes will be very prominent and that of cascara will have disappeared. Preparations containing "cascarin" may be identified as cascara, for it has been shown that "cascarin"² is not a definite chemical compound and contains the anthraquinone compounds as well as the active constituents.

The colors produced by an aqueous solution of the following chemicals on the ether extractions of these drugs were found to be as follows:

AMMONIUM THIOCYANATE

Senna—yellow to brownish color in water layer.
Rhubarb—green to yellowish color in water layer.
Cascara—brownish to rose-red color in water layer.
Aloes—red in ether and brown in water layer.

AMMONIUM MOLYBDATE

Aloes and cascara—no color change.
Rhubarb—mahogany-brown in water layer.
Senna—very light brown to yellowish in water layer.

Ammonium sulfate, ammonium persulfate and ammonium oxalate give no color change.

URANIUM ACETATE

Aloes, cascara and senna—no color change.
Rhubarb—reddish mahogany color in water layer.

SUMMARY

Aloes can be identified by the fluorescence with borax solution no matter what combination of emodin-bearing drugs may be present.

Rhubarb can be identified by obtaining a positive reaction with both chlorinated lime and iron sulfate solutions. No other substance, so far as known, will give both reactions.

Cascara is identified by the brown color imparted to the water solution on the addition of borax solution to the ether extract provided the two tests for rhubarb are negative. Cascara can be identified in any combination of the emodin-bearing drugs if rhubarb is absent.

Senna is the most difficult to detect and is identified by its failure to respond to any except the Bornträger reaction. It is sometimes difficult to get senna to respond even to the Bornträger reaction and this is no doubt due to the fact that glucosides of the anthraquinone compounds are present in greater quantity than the compounds themselves. Senna cannot be identified in combination with any of the other drugs.

DEPARTMENT OF AGRICULTURE
BUREAU OF CHEMISTRY, WASHINGTON

THE DETERMINATION OF ALCOHOL AND WATER IN ETHER FOR ANAESTHESIA

By R. L. PERKINS

Received December 29, 1916

The Pharmacopoeia (U. S. P. IX, p. 32) describes ether for anaesthesia as containing between 2.5 and 4.5 per cent of alcohol and a little water. No method is given for determining either of these substances and there has been much uncertainty in the past as to the amounts of them present in anaesthetic ether.

Quite recently Mallinckrodt and Alt¹ have published a method in which the water is determined by absorbing it with potassium carbonate and weighing the latter and the alcohol is determined in the dehydrated mixture by specific gravity.

This method appears to give satisfactory results but it seemed to the writer simpler to determine water by the specific gravity of the original mixture.

Regnault and Adrian² suggested this method in 1864. They worked out a table of densities of ether-alcohol-water mixtures. By means of this table, alcohol was determined from the specific gravity of the sample after dehydration with potassium carbonate. Water was then determined from the specific gravity of the original mixture. Their results were expressed only to the third decimal place. Since it requires a change of about 1 per cent of alcohol or 0.2 per cent of water to affect the third decimal place, the results obtained by the use of their table would be crude at best.

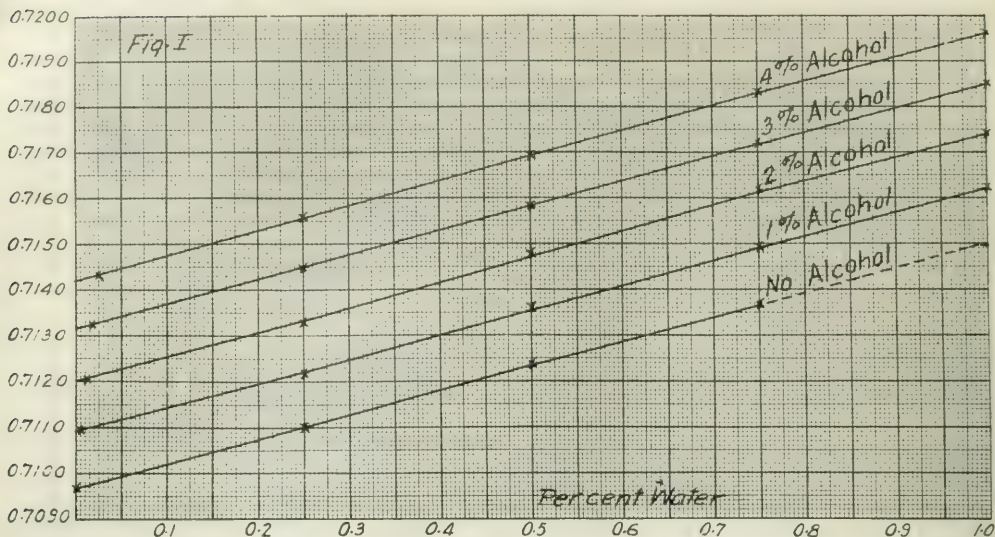
So far as is known to the writer no better data have since been published. The work described below was, therefore, undertaken for the purpose of supplying more satisfactory figures.

SPECIFIC GRAVITIES OF MIXTURES OF ETHER, ALCOHOL AND WATER

Pure ether was prepared as follows: Anaesthetic ether was shaken out three times with water and twice with alkaline permanganate solution. It was then dried several times over calcium chloride, and distilled. The specific gravity was still high (about 0.7100 uncorrected), evidently due to incomplete dehydration. It was, therefore, allowed to stand over calcium peroxide for several days. The specific gravity was now 0.7085 uncorrected or, corrected to 15°C. and 760 mm., 0.7081 on the hydrogen scale (density). This mixture was very favorably with the alkaline ether prepared by Mallinckrodt and Alt and others.

¹ *Loc. cit.*

² H. A. D. Jowell, *Report* 47, 1903, Wellcome Research Laboratories.



Mixtures of this pure ether with different amounts of absolute alcohol (99.2 per cent by weight) and water were made by weighing the water and alcohol into a graduated flask and diluting up to the mark with the ether.¹ The flask was immersed in the thermostat for some time before the final dilution was made. Amounts of alcohol and water were taken which would correspond to definite volumes, so that the percentages were all by volume.

The specific gravity determinations were made by means of pycnometers. These consisted of flasks holding a little less than 50 cc. and having a narrow neck (about 2 mm. bore). These were filled with the ether solutions and immersed in the thermostat

level was kept constant by means of an overflow. The stirrer was a bent piece of glass tubing with holes at the bends. It was rotated by means of a water motor.

The temperature was indicated by a Fahrenheit thermometer which was carefully compared, at 25° C., with a Centigrade thermometer which had been standardized by the Bureau of Standards. The determinations were made at 25°/25° on the mercury scale. The temperature of the bath could be maintained within about 0.02° to 0.03° C. of this temperature. This amount of variation in temperature makes a variation in specific gravity of about ± 0.00002 or ± 0.00003 .

The results are given in Table I. They are uncorrected for the buoyancy of the air. These re-

PER CENT Alc. Water	SPECIFIC GRAVITY Detns. Mean	PER CENT Alc. Water	SPECIFIC GRAVITY Detns. Mean	PER CENT Alc. Water	SPECIFIC GRAVITY Detns. Mean	PER CENT Alc. Water	SPECIFIC GRAVITY Detns. Mean	PER CENT Alc. Water	SPECIFIC GRAVITY Detns. Mean
0 0	0.70970 0.70968 0.70967 0.70968	1 0.006	0.71092 0.71092	2 0.012	0.71205 0.71205	3 0.018	0.71322 0.71322	4 0.025	0.71428 0.71428 0.71427 0.71429
0 0.25	0.71100	1 0.25	0.71218 0.71220 0.71219	2 0.25	0.71334 0.71333 0.71333	3 0.25	0.71447 0.71448 0.71447	4 0.25	0.71553 0.71557 0.71556
0 0.50	0.71242 0.71239 0.71240	1 0.50	0.71358 0.71359 0.71358	2 0.50	0.71473 0.71475 0.71474	3 0.50	0.71580 0.71582 0.71581	4 0.50	0.71690 0.71693 0.71691
0 0.75	0.71368 0.71372 0.71370	1 0.75	0.71490 0.71490 0.71490	2 0.75	0.71612 0.71613 0.71612	3 0.75	0.71720 0.71720 0.71720	4 0.75	0.71838 0.71828 0.71828
0 1.00	(a)	1 1.00	0.71622 0.71622 0.71622	2 1.00	0.71743 0.71741 0.71742	3 1.00	0.71848 0.71853 0.71850	4 1.00	0.71955 0.71959 0.71957

(a) Water is not soluble in ether to this extent.

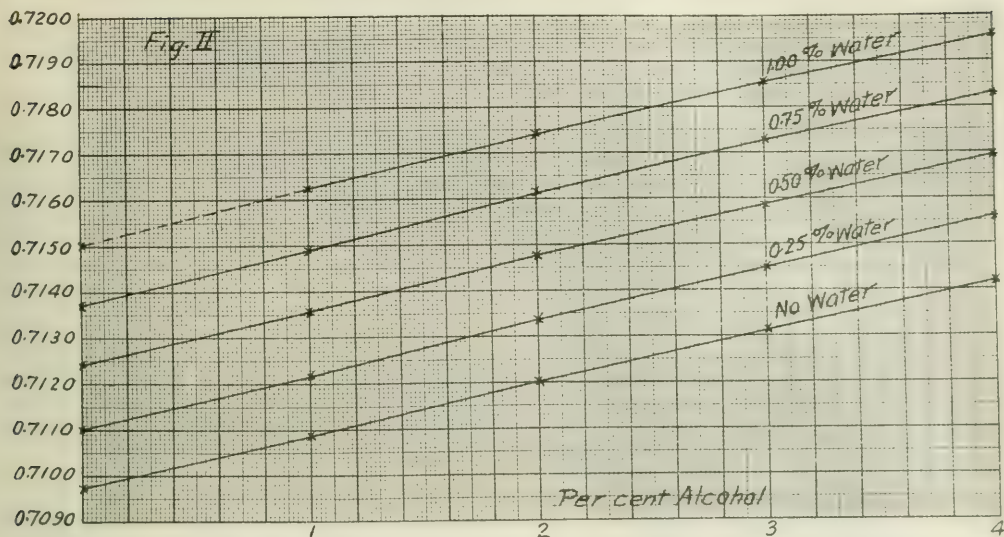
until the meniscus level was constant. The level was then brought to the mark on the neck and the flask dried and weighed to the nearest half milligram.

A granite ware dish holding about 10 quarts served as a thermostat. It was wrapped in asbestos paper to prevent too great radiation. The heat was furnished by a small gas flame controlled by a regulator filled with ether. The gas was supplied through a constant pressure apparatus. In the bottom of the bath was placed a coil of glass tubing through which cold water circulated from a reservoir in which the

sults are represented in graphic form in Figs. I and II. Fig. I represents the water as being varied and the alcohol kept constant for each curve. It will be noticed that the points representing ether-alcohol mixtures are not on the Y axis but are somewhat displaced to the right. This is due to the fact that there was a small amount of water (0.8 per cent by weight) in the absolute alcohol. The intersection of the extended curves with the Y axis are thus the true values for anhydrous mixtures.

Fig. II represents the alcohol as being varied and the water kept constant. The corrected values obtained from Fig. I were used for the alcohol-ether curve in Fig. II.

¹ Allowance was made in weighing alcohol and water for the amount of water in the alcohol so that the percentages are correct except in the case of the ether-alcohol mixtures. This is corrected as explained later.



DIRECTIONS FOR ANALYSIS—The specific gravity of the ether is determined at 25°/25°. From 100 to 200 cc. are then placed in a flask, 30–50 g. K_2CO_3 added and the sample allowed to stand 24 hrs., shaking occasionally. The specific gravity is then determined as before.

This latter value, referred to the lowest curve in Fig. II, gives the per cent of alcohol in the dehydrated ether, which is very close to that in the original sample.¹

The intersection of a vertical line through this point with the horizontal line representing the specific gravity of the original sample corresponds to the amount

¹ A correction could be made for the amount of water removed, but since this correction would always be less than 0.05 per cent, it will probably not usually be required.

of water in the ether. If this point falls on a curve, the per cent is known from the fact that it is on that particular curve. If it falls between two curves, the per cent is obtained by interpolation of the vertical distance between them.

The amount of water can also be determined by use of Fig. I. Starting with the specific gravity of the dehydrated mixture, on the Y axis, an imaginary curve is drawn parallel to the nearest curve until it intersects the horizontal line representing the specific gravity of the original sample. These intermediate curves could, of course, be actually drawn, using values read from the curves in Fig. II.

751 HAMILTON AVENUE, DETROIT, MICHIGAN

LABORATORY AND PLANT

THE MEASUREMENT OF THE ABSOLUTE VISCOSITY OF VERY VISCOUS MEDIA

By S. E. SHEPARD

Received November 4, 1916

The determination of the viscosity, specific or absolute, of extremely viscous fluids, *e. g.*, rubber, cements, nitrocellulose solutions, etc., is a matter of some difficulty. The usual transpiration (tube) viscosimeters are not suitable, and shearing viscosimeters of the Couette type are only beginning to be developed sufficiently in this direction, while the various commercial or industrial viscosimeters introduced in the oil industry have, perhaps happily, not been applied to any considerable extent.

The methods actually employed are mostly based either on the fall of a suitable heavier body (plummet) through the liquid or the rise of a suitable lighter body, *e. g.*, oil, globule or air-bubble (Cochius). The values obtained have usually been taken as *arbitrary empirical standards*, and little data exist on the tech-

nical application of these methods, either for relative (specific) or absolute measurements of the viscosity coefficients.

None the less, the fall of an accurately spherical body of suitable density and size depending upon the absolute viscosity offers, by way of Stokes' law for the terminal velocity of fall of such a spherical body, a ready and fairly precise method for absolute measurement. The ground for this was broken in the investigation of Stokes on fluid motion. In the case of a sphere falling under gravity in a viscous liquid, Stokes showed that the terminal or steady velocity when the viscous resistance just balances the force of gravity depends only on the viscosity and radius of the sphere and the inner friction or viscosity of the fluid. If X be the force acting on the sphere and just balancing the resistance in its steady state,

$$X = 6\pi KRV \quad (1)$$

where K = Coefficient of Viscosity

R = Radius of sphere and V = Velocity of Fall

Now, X , the force acting on the sphere,

$$= \frac{4}{3}\pi R^3(s - s')g \quad (2)$$

where s = Density of Sphere,
 s' = Density of Liquid, and g = Gravitational Constant.

$$\text{Substituting in (1) } K = \frac{2gR^2(s - s')}{9V} \quad (3)$$

Stokes' theoretical work was done in 1840-5, but the first experimental discussion of Formula (3) of any value appears to have been made by H. S. Allen¹ in 1900. An extensive theoretical and experimental investigation on Stokes' law was made by R. Ladenburg,² with results which will be noted immediately. H. D. Arnold³ has made a valuable investigation of the same problem, which is best discussed in connection with Ladenburg's work. I have been unable to obtain access to a paper by Flower.⁴

Arnold points out in the paper cited that in the mathematical deduction of the original formula certain assumptions are made, notably:

- (1) That the discontinuities of the fluid are small compared with the size of the sphere.
- (2) That the fluid is infinite in extent.
- (3) That the sphere is smooth and rigid.
- (4) That there is no slip at the surface between sphere and fluid.
- (5) That the velocity of the sphere is small.

As regards the first assumption, Cunningham⁵ has investigated theoretically and Millikan⁶ experimentally the effects of a violation. They have shown that in the case of a very small sphere, falling in a gas, there is a considerable departure from the value by the simple formula. Arnold, working only with fairly simple liquids (oils of low viscosity) and comparatively large spheres, considered that for his work the assumption was sufficiently justified. In the case, however, of complex fluid media, of colloidal nature, such as those referred to, starch sols, gelatine and other albuminoid solutions, the industrial chemist frequently requires a fairly accurate mean value of the viscosity for solutions which may readily have internal discontinuities of considerable magnitude. If spheres very much larger than these discontinuities are used, he may yet not have such ample quantities of the material at his disposal as to be able to approach, with these larger spheres, fulfillment of the second assumption either in the absolute limit proper to the simple Stokes' law, or in the restricted form obtained by Ladenburg. The latter found⁷ that if the liquid is contained in a cylinder of circular cross-section of radius R' and of length L , that the following modified form held up to a certain limit.

$$K = \frac{2}{9} R^2 \frac{g}{V}$$

$$\text{where } V = \frac{S(1 + 2.4R/R')(1 + 3.3R/L)}{T}$$

S = Length of Fall in Steady State

T = Time of Fall of Length S

$$R/R' = \frac{\text{Radius of Sphere}}{\text{Radius of Cylinder}} = \frac{\text{Diameter of Sphere}}{\text{Diameter of Cylinder}}$$

$$R/L = \frac{\text{Radius of Sphere}}{\text{Height of Liquid Column}}$$

Using this corrected form he obtained for the viscosity of Venice turpentine, with a series of steel spheres, the value $K = 1343$, whereas the value by Poiseuille's law and the capillary tube method at the same temperature was $K = 1325$. This appears to have been the first direct comparison of these two methods, and the agreement to within 1.3 per cent shows, Arnold points out, the validity of the corrected formula in the case of liquids of high viscosity. We shall return to Ladenburg's formula immediately. With regard to surface slip, the position is as follows. Following Arnold, we may modify Stokes' law by an expression for the coefficient of sliding function, when we have for the terminal velocity V

$$V = \frac{2gR^2(s - s')}{9K} \left(1 + \frac{K}{\beta R + 2K} \right)$$

which for $\beta = \infty$ reduces to the original form, but for $\beta = 0$ gives a value 50 per cent higher. Experimentally, to test this factor, it is necessary to use a sphere of sufficiently small radius in a liquid of high viscosity. The simplification of the mathematical analysis, allowing terms of the order of the square of the velocity (so-called inertia terms) to be neglected, is only permissible when assumption (5) is obeyed. This can be shown to hold only when the velocity is small compared with $\frac{K}{R}$. The value of R for which

$V = \frac{K}{R}$ is called the critical radius and may be designated R_c . Various observers have assumed that the upper limit of radius for which the simple formula may be used is of the order

$$\frac{R_c}{10} \text{ (Ladenburg) to } \frac{R_c}{\sqrt{10}} \text{ (Zeleny).}$$

EXPERIMENTAL

The experimental results detailed in the following were not made with a view to precision determination of the validity of Stokes' law, simple or corrected, but to find under what conditions it could be used for approximate determinations of the absolute viscosity of the very viscous media referred to. It may be pointed out that the determination of an absolute value involves in itself no greater *precision* than that of a specific or relative value of a physical constant. The essential point is that the value is obtained directly from a function of the variables and in terms of absolute units, as (M), (L), (T) = grams : centimeters; seconds. The requirements as to precision depend upon the purpose of the determination, and may be less than, equal to, or greater than, those for a determination of a *specific* or *relative* value of a constant according to the requirements in view.

As readily obtainable rigid spheres of considerable precision of figure, steel ball bearings were used. Their dimensions were as follows:

¹ Phil. Mag., 1900, 323.

² Ann. phys., 22 (1907), 287, 23 (1907), 447.

³ Phil. Mag., 22 (1911), 755.

⁴ Proc. A. S. T. M., Part II, 14 (1914), 591.

⁵ Proc. Roy. Soc. (A) 83 (1910), 357.

⁶ Phys. Rev., April, 1911.

⁷ Loc. cit.

No.	Diameter Inches	Diameter Mm.	Precision Per cent	Weight Grams	Volume Cu. in.	Density 18° 18°
1.....	1/4	6.35	±0.04	1.0472	0.13406	7.811
2.....	3/4	9.525	±0.03	3.4754	0.45246	7.681
3.....	1 1/2	12.70	±0.02	8.3170	1.07249	7.754

The specific gravity of hardened steel is stated to be 7.6-7.8.

As corroborating the truth of the spherical figure, the average deviation in weight of 6 balls of each size was determined. The results showed that while the mean deviation was nearly constant, the per cent deviation was as follows:

Diameter.....	1/4 in.	3/4 in.	1 1/2 in.
Per cent Deviation.....	±0.72	±0.23	±0.09

that is, the deviation increases as the radius diminishes. Remembering the note on the increment of importance of rotational movements with other than true spheres, it will be evident that diminution in radius may be pushed too far, in that sphericity is liable to become steadily diminished with decreasing radius, as well as less amenable to direct determination.

METHOD OF EXPERIMENT

In all the experiments the liquid, a very viscous solution of nitrocellulose, was contained in a graduated cylinder of some 40 cm. height, standing in a water jacket at 20° C. \pm 0.2. The spheres were allowed to drop axially, a variety of releases being employed as, *e. g.*, iris diaphragms, etc., but these were found to be without influence on the time of fall in the liquid.

Time was recorded with a stop-watch reading to 1/5 sec. and checked on a standard chronometer. Parallax in observing the transit of the sphere past the selected upper and lower graduation marks on the cylinder was avoided by having fore- and hind-sight-lines outside the cylinder aligned in the same planes with the marks in question.

INFLUENCE OF THE DIAMETER

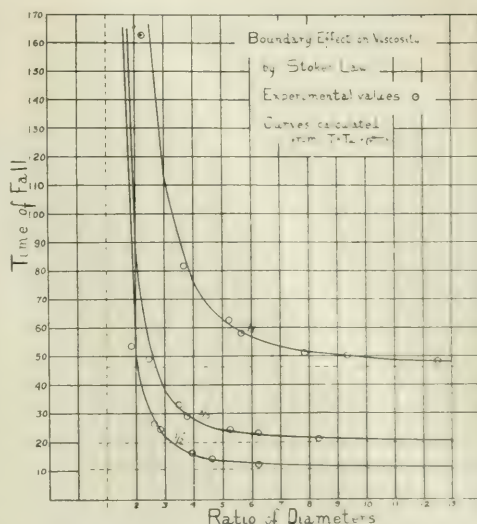
The next factor investigated was the influence of the cylinder wall or boundary, upon the time of fall, other things being equal, or more exactly, the influence of the ratio, diameter of cylinder to diameter of falling sphere, upon the experimentally obtained "time of fall" through a fixed measured height, *i. e.*, upon the steady velocity. It was soon apparent that this influence is very considerable, only becoming negligible when the ratio in question becomes very large, or approaches infinity. This is shown in fact by the following figures for a 1/4 in. sphere and 19.5 cm. "fall" distance.

Ratio.....	1.810	2.235	3.670	5.248	8.672	7.875	9.340	12.81
Time (Sec.)	270.0	162.7	81.7	62.6	58.0	51.0	50.0	48.3

It will be evident that as R'/R = ratio of cylinder diameter (or radius) to sphere diameter (or radius) increases, that the "time of fall" or the "velocity value" tends to approach a constant value. Compare the curves for the three spheres of different diameters.

As already stated, Ladenburg¹ has introduced a correction term for the influence of this factor, into the Stokes equation, which makes this become:

$$K = \frac{2R^2(\gamma - \gamma')T}{9S(1 + 2.4/r)}$$



Where $r = R'/R$, ratio of cylinder to sphere diameters, and the other symbols have the significance already defined. This expression was found satisfactory by both Ladenburg and Arnold within the limits of r which they employed. In the present case, the expression was found to have only a very limited range of validity, as will be seen from the following data:

1/4 IN. DIAMETER Reciprocal of r	3/4 IN. DIAMETER Reciprocal of r	1 1/2 IN. DIAMETER Reciprocal of r
0.0798	311	0.1198
0.107	305 Mean	0.1198
0.127	300 K'	0.1905
0.1762	312	0.2645
0.1922	328	0.286
0.2723	378.5	0.408
0.4465	603	0.670
		276.7 Mean
		0.1597
		264.1
		281.5
		0.254
		353.5
		397.0
		330.5
		0.381
		422.5
		705.0

The only factor varied in each set being r , the variation of K' , the viscosity constant must be attributed to the insufficiency of Ladenburg's correction for anything but a limited upper range of values of r approaching ∞ ; actually in all Ladenburg's experiments r was greater than 10. Further, it will be seen that his expression will not satisfy the condition that T' (corrected time of fall) becomes infinite for $r = R'/R = 1$, but instead, as T' (Ladenburg) = $T/1 + 2.4/r$ approaches a constant fixed value $T/3.4$ which is entirely incorrect, and gives real values for $r = R'/R \geq 1$, which is absurd. While then his formula is satisfactory under the condition employed both by him and by Arnold, it does not appear to be for the wider range used in the present experiments. A further correction worked out by Ladenburg for the influence of the total height of liquid in the cylinder, will be dealt with subsequently; it is independent of the factor and data first discussed.

The data obtained with the three spheres and a considerable range of cylinders of the same height but varying diameter, were plotted as graph with T = time of fall as ordinate, $r = R'/R$ as abscissa. Since the values for each sphere fall on a single curve, and

SERIES I—DIAM. OF SPHERE = $\frac{1}{4}$ IN. = 6.35 MM. Fall Length $S = 19.5$ cm. Corrected Time of Fall over Length $S = T_{\infty} = T - \frac{268.45}{(r-1)^2}$. Viscosity Coefficient = $K = \frac{2R^2}{9S} (s-s') \cdot g \left(T - \frac{C}{(r-1)^2} \right)$

SERIES II—DIAM. OF SPHERE = $\frac{3}{8}$ IN. = 9.525 MM. Fall Length $S = 19.5$ cm. Corrected Time of Fall over Length $S = T_{\infty} = T - \frac{72.28}{(r-1)^2}$. Viscosity Coefficient = $K = \frac{2R^2}{9S} (s-s') \cdot g \left(T - \frac{C}{(r-1)^2} \right)$

SERIES III—DIAM. OF SPHERE = $\frac{1}{2}$ IN. = 12.7 MM. Fall Length $S = 19.5$ cm. Corrected Time of Fall over Length $S = T_{\infty} = T - \frac{43.86}{(r-1)^2}$. Viscosity Coefficient = $K = \frac{2R^2}{9S} (s-s') \cdot g \left(T - \frac{C}{(r-1)^2} \right)$

No.	Ratio r	TIME IN SECONDS Found	Calc.	T Secs.	K	ΔK	ΔK Per cent
1	2	175.5	(314.6)	(88.8)
2	3	110.5	113.32	46.55	361	+3	+0.8
3	4	75.0	76.04	49.10	380	+22	+6.0
4	5	63.6	62.97	45.80	355	-3	-0.8
5	6	57.2	56.92	43.75	339	-19	-5.5
6	7	53.1	53.64	45.20	352	-8	-0.2
7	8	51.0	51.67	47.00	364	+6	+1.6
8	9	50.1	50.38	47.00	364	+6	+1.6
9	10	49.5	49.51	46.55	360	+2	+1.0
10	11	48.9	48.87	45.40	352	-6	-1.2
11	12	48.2	48.41	45.52	353	-5	-1.3
12	13	47.8	48.05	46.187	358	+8	+2.0
Mean value $T_{\infty} = 46.19$ secs.				Mean value of $K = 358 \pm 8$.			

No.	Ratio r	TIME IN SECONDS Found	Calc.	T Secs.	K	ΔK	ΔK Per cent
1	2	83.0	(94.28)	(23.26)
2	3	38.2	38.06	22.38	379	+44.0	+10
3	4	29.4	28.03	19.59	332	-7	-2
4	5	25.1	24.51	19.82	336	-3	-0.9
5	6	23.2	22.89	19.32	327	-12	-3
6	7	22.0	22.01	18.61	316	-23	-6
7	8	21.1	21.48	20.23	343	+4	-1
8	9	20.9	21.13	19.93	338	-1	-0.3
9	10	20.4	20.89	20.15	342	+3	+0.9
10	11	20.6	20.72	20.00	339	0	0
11	12	20.5	20.59	20.00	339	0	0
12	13	20.4	20.50	20.03	339.1	+9.3	+2.7
Mean value of $T_{\infty} = 20.03$ secs.				Mean value of $K = 339 \pm 9$.			

No.	Ratio r	TIME IN SECONDS Found	Calc.	T Secs.	K	ΔK	ΔK Per cent
1	2	44.5	(56.55)	(15.97)
2	3	23.1	22.15	10.68	325	-5	-1.5
3	4	16.2	15.78	10.18	325	-5	-1.5
4	5	13.1	13.55	10.05	306	-24	-7.0
5	6	12.0	12.52	11.69	356	+26	+7.0
6	7	11.9	11.96	11.51	350	+20	+6.0
7	8	11.8	11.62	10.95	334	+4	+1.3
8	9	11.6	11.41	10.70	326	-4	-1.3
9	10	11.4	11.25	10.81	329	-1	-0.3
10	11	11.3	11.15	10.75	327	-3	-0.5
11	12	11.2	11.07	10.61	323	-7	-2.0
12	13	11.1	11.01	10.685	330	+9.9	+2.8
Mean value of $T_{\infty} = 10.685$ secs.				Mean value of $K = 330.1 \pm 9.9$.			

the curves are quite similar for the three spheres, it appeared possible that an empirical formula for the function $T = f(R'/R)$ might be obtained, giving a satisfactory expression for the influence of the cylinder wall upon the terminal velocity. It is evident from inspection of the curves and consideration of limiting conditions, that the function sought must satisfy:

T approaches ∞ for $R'/R = r = 1$

T approaches constant for $R'/R = r = \infty$

These conditions would be satisfied by a function of the type:

$$T = T_{\infty} + \frac{C}{(r-1)^n}$$

where T_{∞} = constant value of T for $r = \infty$

$r = R'/R$ (ratio of diameters)

C and n are constants

Taking the exponent n as 1, 2, 3, etc., in turn, the formula reduces to a 2-constant interpolation formula, easily tested by trial. Actually, with a value $n = 2$, the expression $T = T_{\infty} + C/(r-1)^2$ was found to represent the results very satisfactorily, as will be seen from the accompanying tables and the curves given.

The three correction equations for the time of fall are:

$$(1) \quad T = 46.19 + \frac{268.45}{(r-1)^2} \text{ for } \frac{1}{4} \text{ in. sphere}$$

$$(2) \quad T = 20.03 + \frac{72.28}{(r-1)^2} \text{ for } \frac{3}{8} \text{ in. sphere}$$

$$(3) \quad T = 10.685 + \frac{43.86}{(r-1)^2} \text{ for } \frac{1}{2} \text{ in. sphere}$$

The constant C of the correction equation may be conveniently termed the "lag." As will be seen, it diminishes as the diameter of the sphere increases, and in fact, within the range investigated, appears roughly to approach inverse proportionality to the mass of the sphere.

No.	Diameter	Wt. in grams	C	C X Weight
1	6.35 mm.	1.0472	268.45	281
2	9.525 mm.	3.4754	72.28	252
3	12.70 mm.	8.3170	43.86	380

INFLUENCE OF THE TOTAL HEIGHT OF LIQUID

The values compared for the viscosity-coefficient K using Stokes' formula, with the time of fall corrected to T_{∞} by the expression just discussed, *i. e.*,

$$K = 2/9 \frac{R^2(S - S')g}{V}, \text{ where } V = S/T, \text{ were:}$$

Sphere Diam.	K Abs. viscosity at 20° C.	K/ k_w relative to water at 20° C.
$\frac{1}{4}$ in.	358 \pm 8.0	3.58 $\times 10^4$
$\frac{3}{8}$ in.	339 \pm 9.0	3.39 $\times 10^4$
$\frac{1}{2}$ in.	330 \pm 9.9	3.30 $\times 10^4$

It will be seen that the values of K although constant in the same series for one diameter of sphere and varying cylinder radius, show some tendency to diminish as the diameter of the sphere is increased. Now in all the experiments the total height of liquid was the same, *viz.*, 40 cm., and it appears probable that this falling off may be due to a similar effect to that from the wall, but in this case due to "reflection" from the bottom of the cylinder and the surface layer of the liquid.

This effect was in fact taken up by Ladenburg in the second of his two papers cited, and he applies a second, independent correction term similar in form to the one for the cylinder wall:

$$V' = \text{steady velocity} = S \left(\frac{1}{T} + 3.3 \frac{R}{L} \right)$$

where S = fall length

T = time of fall

R = radius of sphere

L = total height of liquid.

The multiplier of the term R/L depends considerably upon the experimental conditions—in Ladenburg's case, the cylinders were 24 cm. long and the fall length was the middle 10 cm. In the present investigation, the height of liquid was 40 cm., the fall length 19.5 cm., in all except certain special experiments at nearly 10 cm. from top and bottom of the liquid column respectively. The values of R/L for the three spheres were:

Sphere Diam.	R/L	L/R
6.35 mm.	1/126	126
9.525 mm.	1/84	84
12.70 mm.	1/63	63

$L = 40$ cm.

In view of the order of magnitude of L/R , as compared with that of R'/R in these experiments (see previous section) it appeared probable that a correction of the linear form, as used by Ladenburg, would be satisfactory; that is, the values of K found are multiplied by the terms $(1 + b.R/L)$ where b is a constant and R/L is the particular value of the ratio of radius of sphere to height of liquid column, to give the corrected value K . In this case three equations are obtained, for two unknowns, b and K . The mean value of b by solution of these was 11.65, and the corresponding values of K' were:

Sphere Diam.	R/L	K	K'	Mean K'
$1/4$ in.	$1/126$	358	391.2	389.7
$1/8$ in.	$1/84$	339	386.0	
$1/16$ in.	$1/63$	330	392.0	

On the other hand, by plotting K (uncorrected for height) as ordinate, R/L as abscissa, and extrapolating the closest fitting straight line to cut the K -ordinate, giving the value K for $R/L = 0$ or $L/R = \infty$, the value $K = 386.5$ was obtained. Hence, the corrected values are:

Ht. correction applied	K	k (viscosity relative to water at 20°)
By formula.....	389.7	3.9×10^4
Graphically.....	386.5	3.87×10^4

The correction for the length of height of the tube appears rather large, and further work is planned using a wider range of values of L/R , to test the validity of the linear correction more precisely, as well as a comparison of the method with the "shearing" type of viscosimeter.

While the viscosity found is very high, it is less than that of the turpentine solution of colophony used by Ladenburg (K 1343) and was shown to be of the right order by a comparison with castor oil, at the temperature given 20°C ., which made our medium to be 3.1 times the viscosity of castor oil which, at $20^\circ = 10,000 K_w$.¹

Hence by this the viscosity of our medium would be some 31,000 times water. The viscosity of "castor oil" varies considerably but the comparison shows the result is of the right order.

SUMMARY

I—The application of Stokes' law to viscosimetry is discussed, particularly for very viscous media, and with special reference to the influence of the wall or boundary of the containing vessel.

II—An empirical formula correcting for the influence of the wall of a cylinder is obtained which is valid over a wide range.

III—Using this formula and a linear correction for the influence of the total height of the liquid column, determinations of the absolute viscosity of very viscous media may be made with relatively simple apparatus, by application of Stokes' law.

The author's thanks are due to Mr. W. H. Davis for help in the experimental work, and to Mr. S. Tompkins for assistance in the computations.

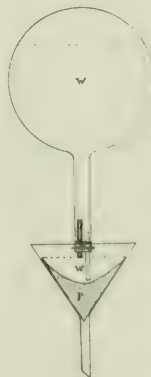
RESEARCH LABORATORY
EASTMAN KODAK COMPANY
ROCHESTER, NEW YORK

A SIMPLE DEVICE FOR THE AUTOMATIC AND INTERMITTENT WASHING OF PRECIPITATES

By ELBERT C. LATHROP

Received January 31, 1917

The accompanying illustration shows a simple and efficient form of apparatus for the automatic, intermittent washing of precipitates. The feature which distinguishes this apparatus from the well-known constant level device is the capillary tube (represented in the figure by heavy black lines), the function of which is not only to permit air to enter the inverted flask, but also to produce an intermittent flow of solvent from the flask. The principle underlying the use of the capillary tube may perhaps be best explained by a description of the operation of the apparatus. Suppose that the apparatus is set up as shown, with the end of the capillary tube, which is full of solvent, just touching the surface of the solvent in the funnel, and the other tube, which in the apparatus used has been about 5 mm. in diameter, just touching the surface of the settled precipitate. As the solvent passes through the precipitate and out of the funnel the level of the liquid above the precipitate will fall below the end of the capillary tube. Air will not pass into the inverted flask, however, until the level of liquid in the funnel has fallen to a point such that the resulting differences of hydrostatic pressure in the two tubes is sufficient to overcome the force of capillarity, which tends to keep the capillary tube filled with water. In the apparatus as drawn, this point lies just above the end of the large tube, so that the precipitate is almost bare of solvent, thus permitting each addition of solvent to drain from the precipitate, the most efficient method of freeing a precipitate from soluble substances. When this point on the large tube is reached the air rushes into the flask through the capillary tube, the funnel fills again with solvent, which finally reaches the end of the



capillary tube and cuts off the air supply, the tube filling with liquid due to diminished pressure within the flask. The process then repeats itself.

Experiment has shown that the vertical distance from the end of the capillary tube to the point on the other tube, at which the pressure just overbalances the capillarity, is just a little greater than the height of capillary rise. The pressure required to pull air through a capillary tube full of liquid depends on the size of the capillary opening and on the nature of the liquid. In practice, the author, after allowing the precipitate to settle on the filter, measures the vertical distance from the lowest point on the surface of this precipitate to the top of the filter paper, and selects for use a capillary tube having a capillary rise for the given solvent equal in length to this distance. The total length of the capillary tube should be a little greater than the capillary rise. The author has

¹ Landolt-Börnstein, 4 Auflage, p. 25.

used this apparatus for the past two and a half years with entire success in washing large amounts of gelatinous precipitates, working with as much as three pounds of precipitate in one funnel and washing with ten liters of water at one filling of the flask.

BUREAU OF PLANT INDUSTRY
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

AN IMPROVED COMPENSATOR¹ FOR GAS ANALYSIS

By E. T. GREGG

Received February 10, 1917

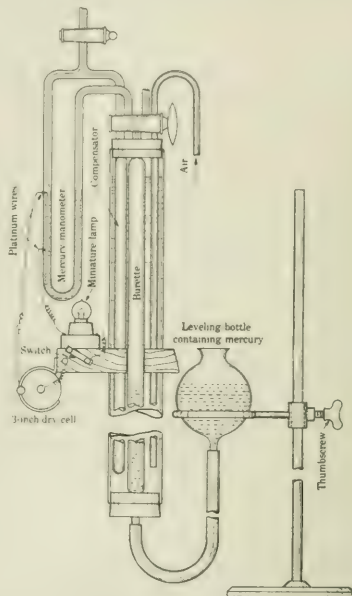
An improved compensator, described below, has been used with most satisfactory results in connection with the Hempel apparatus for gas analysis in the fuels efficiency laboratory of the Federal Bureau of Mines.

As shown in the accompanying drawing, two platinum wires are sealed into the compensator side of the mercury manometer. The upper wire which is sealed about $\frac{3}{8}$ in. above the mercury when level, is bent downwards at right angle and just touches the surface of the mercury. The lower platinum wire enters far enough to make electrical contact with the mercury. In series with the two platinum wires are a small dry cell, switch and miniature lamp.

To use the compensator for adjusting the volume of a gas before making a reading, the contact between the mercury and upper platinum wire is broken by means of the leveling bulb containing mercury, the switch is then closed and the compensator adjusted till the break in the circuit at the mercury platinum contact is just closed, whereupon the lamp lights and the compensation is completed. Rough adjustment is made by sliding the mercury bulb and its support upon the iron rod by hand. The fine adjustment is made by taking up the sag in the arm supporting the bulb by means of the thumb screw. The switch is then opened to prevent sparking at the mercury sur-

face when breaking the contact and to prevent deterioration of the battery. Compensation should always be made with a rising mercury column at point of contact.

In practice this compensator checks the gas volume consistently and accurately and does it in less time than the old optical method of adjusting the height



of the mercury to a mark. It removes the difficulty of adjustment due to poor or changing light and decreases the strain upon the eyes of the operator. Where many analyses are made it removes one of the chief sources of fatigue.

U. S. BUREAU OF MINES
EXPERIMENT STATION, PITTSBURGH

¹ Petterson, "O. Luftanalyse nach einem neuen Princip," *Z. anal. Chem.*, **25** (1886), 467; also Hempel's "Gas Analysis," translated by L. M. Dennis from 3rd German Edition, 1902, 59.

ADDRESSES

ONE BILLION GALLONS OF SYNTHETIC GASOLINE IN 1918¹

By WALTER F. RITTMAN

Received April 9, 1917

The market value of synthetic gasoline produced by cracking in the United States during 1917 will be sufficient to supply the navy with ten superdreadnaughts. In other words, one-fifth of the 3,000,000,000 gallons to be produced will be made by cracking.

By July 1 of the present year there will be in operation in the United States 4,000,000 automobiles. Financial men, in considering the investment value of motor stocks, have for several years been dwelling upon the saturation point, but despite this consideration the demand for machines still keeps well ahead of the 40 per cent average yearly increase of past years. When the saturation point will be reached nobody knows. Responsible and successful automobile men maintain that the present increase in rate of production will keep up for years, and that

after the present high prices of materials the price of cars can be so reduced that every family having an income over \$1,000 may own a car. On this basis, the United States will have in the neighborhood of 10,000,000 automobiles, two and one-half times the present number. Assuming an annual life of five years per machine, 10,000,000 cars means an annual replacement number equal to 2,000,000; i. e., our present rate of production. When one questions the correctness of the opinion of the automobile man who suggests the above figures, one is answered with the statement that every prediction which the automobile man has heretofore made has been too conservative. An important consideration is the greatly increasing number of motor trucks necessary to replace the shortage in horses. As to the influence on this industry of the United States' entrance into the European war, time will tell.

Only the steel, lumber, and clothing industries exceed the automobile business in importance today. Detroit, the center of this new industry, has risen as a manufacturing center from sixteenth place in 1900 to sixth place in 1914. In the United States over 500 factories are to-day engaged in making different

¹ Paper read at the Spring Meeting of the American Chemical Society, Kansas City, April 10-14, 1917.

types of automobiles, and new companies of varying stability are announced each week. As a sidelight, it is interesting to observe the approximate annual upkeep involved in America's automobile bill which is as follows:

Gasoline.....	\$500,000,000
Tires.....	\$500,000,000
Accessories.....	\$300,000,000
Garage hire.....	\$150,000,000
Repairs.....	\$150,000,000

The number of automobiles in use in this country on January 1st over the period of the past fifteen years is as follows:

Year	Number of Cars
1905.....	85,000
1910.....	400,000
1911.....	600,000
1912.....	677,000
1913.....	1,010,483
1914.....	1,253,875
1915.....	1,754,570
1916.....	2,225,000
1917.....	3,250,000
1918 (estimated).....	4,750,000

In addition, gasoline requirements are not limited to the above automobiles, for tremendous quantities are used in motor boats, motor cycles, farm engines, chemical manufacture, cleaning establishments, etc. The requirements per machine per annum vary with different users, some using on an average of less than a gallon a day, whereas, the public vehicle often uses as high as 10 gallons a day. Statistics would indicate that the average consumption per car per annum approaches 500 gallons.

Of the various problems confronting the automobile industry, the motor fuel problem of the future has loomed up as the most important, but it would seem that this problem will temporarily at least be solved. Much discussion and attention is paid to the use of gasoline substitutes, such as alcohol, benzol, gasoline from natural gas, electricity, etc. All of these materials are very valuable sources of power, and the extent of their use is entirely a question of quantity produced, and price. Alcohol is commercial when gasoline exceeds 35 cents per gallon. This price, however, is based on ante-war prices, as every one realizes that the present price of alcohol makes it prohibitive. Benzol, when mixed with gasoline, makes a superior type of motor fuel, and here again it is entirely a question of the supply available. The figures of the best informed people in this field indicate a supply of benzol and light oils available equal to 100,000,000 gallons, which it is observed will fulfill less than 10 per cent of our motor fuel requirements even though none of the benzol and similar materials were used for explosives and other chemical purposes.

Casing-head gasoline (gasoline from natural gas) is an item of considerable importance because it is so volatile and has such wide explosive limits that it can be blended with naphthas and thereby makes available for motor use materials which were not available. The production of this material has been as follows, but this production, it may be remarked, will hardly supply more than one-tenth of our fuel requirements:

Year	Gallons
1911.....	7,435,849
1912.....	12,081,179
1913.....	24,060,817
1914.....	42,685,683
1915.....	68,561,668
1916.....	128,000,000
1917.....	200,000,000

Much is heard of the kerosene carburetor, and the patent office holds thousands of carburetor patents. Prof. Lucke of Columbia University rightly believes that in the development of a commercial kerosene carburetor it will not be a new invention, but a matter of a design utilizing parts from various patents or designs already developed that will solve the problem. Practically no consideration has been paid to what is perhaps the most important factor militating against the use of kerosene, *i. e.*, the question of explosive limits. This will be discussed later. The carburetors already invented surely embody all possible principles, so it would seem that from this time forward

the problem is one of a design wherein ideas from different carburetors are brought together in a new form. A partial way out of the difficulty may be by reversion to the steamer type of automobile in which heavier oil is used to generate steam.

The crude oil production and the gasoline production in the United States, during a period corresponding to the automobile figures previously given, is shown as follows in barrels of 42 gallons:

Year	Crude Oil Production	Year	Gasoline Production
1905.....	134,717,580	1904.....	6,920,000
1910.....	209,557,248	1909.....	12,900,000
1911.....	220,449,391	1914.....	34,915,000
1912.....	222,935,044	1915.....	41,600,000
1913.....	248,446,230	1916.....	54,760,000
1914.....	265,762,535	1917 (estimated).....	70,000,000
1915.....	281,104,104		
1916.....	292,300,000		

From these figures it will be observed that during the period from 1910 to 1917 when the number of automobiles increased eightfold, crude oil production grew but a little over one-third, and gasoline production increased four times, an order of magnitude comparable with the growth in production of automobiles. This increased production of gasoline from a relatively constant quantity of crude oil is obviously the result (1) of taking a larger portion of motor fuel from the crude oil and calling it gasoline and (2) of producing gasoline from heavier oils by cracking.

The question naturally arises as to how much further into crude oil the petroleum man can cut in order to increase the supply of motor fuel. We have all observed the Baumé gravity of gasoline decrease from the seventies to the fifties, which means an increase in the specific gravity from 0.700 to 0.778. But practical motor men to-day believe that, with the present automobile carburetor and engine, gasoline containing heavier portions of the crude oil below 50° B.é. does not work efficiently.

Scientific explanation of the fact can be found in a consideration of the explosive limits of various hydrocarbons. For every mixture of hydrocarbons and air, as produced in the carburetor, there is a proportion below which the mixture contains too small a percentage of hydrocarbons to explode. There is also an upper limit above which the mixture contains too large a percentage of hydrocarbons to explode. Between these two limits is the desired range in which the proper explosive mixture is formed. For instance, a mixture of natural gas and air containing below 5 per cent of gas will not explode; also a mixture containing more than 11.5 per cent of gas will not explode. Hence, the explosive limits for mixtures of natural gas and air are between 5 and 11.5 per cent of gas. Similarly, the explosive limits for mixtures of gasoline vapor and air lie approximately between 1.4 and 6 per cent of gasoline vapor.

When the size and weight of petroleum molecules increase, the boiling point is raised. In other words, the higher the molecular weight, the heavier and less volatile is the material. Furthermore, as the volatility of these hydrocarbons decreases, the limits for their explosive mixtures with air, below which nothing happens and above which there is a burning rather than an explosion, come closer and closer together.

Consequently, as we go from lighter petroleum products, such as gasoline to heavier petroleum products, such as kerosene and up to materials boiling above 425° F., the range for explosive mixtures of air and heavy hydrocarbon vapors becomes more and more narrow, until a point is reached where there is great difficulty in adjusting the mechanical parts of the carburetor, so that they deliver the proper explosive mixture. For example, suppose a mixture of 1 per cent hydrocarbon vapor and 99 per cent of air is the only possible explosive mixture for the vapors of a certain substance, how difficult it is not impossible, it would be to adjust a carburetor to deliver accurately and continuously that exact mixture. The point then is that when this heavy material with narrow

explosive limits, is used for fuel, there is slow burning rather than explosion, and only a part of the combustion occurs in the cylinder where it can be utilized. Therefore, it is questionable whether an efficient carburetor for heavy kerosene can be devised.

Other suggested solutions of the motor fuel problem involve the use of oil derived from coal, shale, peat, and lignite. These will be immensely important sources of liquid fuel in the more remote future. Passing over the large supply of light oil possible from coal now burned without coking, which may amount to as much as a billion gallons of fuel per annum, there are immense shale deposits in America, containing a volume of oil many times greater than that now known. Here the problem of obtaining motor spirits from the oil will arise again and the solution of it, as of our present problem, will necessitate cracking processes.

Then, as now, the demand for motor spirits will run ahead of the supply obtainable by straight distillation; and the logical solution of our present motor fuel problem will be the logical solution in future problems. The fundamental proposition is that when the demand for gasoline doubles or trebles, while the amount of petroleum remains nearly constant, we must make more gasoline from a given volume of crude oil. The best evidence that this proposition furnishes the answer to our problem, is the fact that cracking processes are now solving the problem. In other words, since 20 per cent of our gasoline is now being made by cracking, the price of gasoline would of necessity be much higher without this increased supply.

The chemical phenomena involved in the cracking of heavy oils into lower boiling oils have been discussed in considerable detail in *Bulletin 114*, United States Bureau of Mines. Broadly

speaking, and without consideration of relative merits, cracking processes may be classified under the five heads:

- 1—Liquid condition processes wherein oil is cracked as a liquid;
- 2—Gaseous condition processes wherein oil is cracked as a gas;
- 3—Processes wherein cracking is aided through the use of catalyzers;
- 4—Processes wherein the oil is mixed with steam, hydrogen, or other materials;
- 5—Combinations of the above four methods.

The object of the present paper is not to discuss the technical nor the research side of cracking, but to indicate how real is this industrial operation to-day. During the present year, 1917, approximately 600,000,000 gallons of cracked gasoline are being produced in the United States. It is estimated by competent authorities that the production of cracked gasoline in 1918 will be 1,000,000,000 gallons, and that by 1920 more gasoline will be produced by cracking than by all other methods. Many people have been disappointed because cracking processes have not reduced the price of gasoline materially, but fail to consider their tremendous benefit in keeping the price of gasoline from going 10 cents a gallon higher: 7,000 automobiles a day require a cumulative supply of motor fuels. Our crude oil production is not increasing. Kerosene carburetors as yet are not a factor. The entire load is falling on the shoulders of cracked gasoline, and cracked gasoline promises to make light of its load.

PITTSBURGH, PA.

CURRENT INDUSTRIAL NEWS

BEET SUGAR INDUSTRY

The report of the Incorporated English Beet Sugar Pioneer Association on its second year's experimental culture in Montgomeryshire, England, states that, taking into account the shortage of labor owing to the war and the consequent inability of growers to give proper attention, the crops generally as regards shape, size of roots, heads and estimated weight per acre were entirely satisfactory and, in the opinion of experts, in many cases equal to the growing crops in Holland and Germany in 1910. From the one-acre plots, the estimated yield was from 17 to 18 tons. On analysis, the following results were obtained: 17.75 per cent sugar in root, 18.68 per cent sugar in juice and 89.70 per cent coefficient of purity. German roots, which are considered a good type, contain 16 to 16.5 per cent sugar, while the average of the English roots was 16.48 per cent.—A. MACMILLAN.

NEW METHOD OF EXTRACTING VAPOROUS CONSTITUENTS FROM COAL GAS

At a recent meeting of the Society of Chemical Industry, London, a paper was read by Dr. R. Lessing on the above subject. The author said that, so far, the method had been used only for research purposes but it was hoped that, before long, it would be available on a commercial scale. The principle of the process is that of a dry scrubber filled with solid absorbent material which will strip the benzene from the gas without the employment of running wash oil and from which the volatile products can be recovered by steam distillation *in situ*. At first, it seemed that crushed pitch would serve the purpose of the absorbent matter, but it was found that its viscosity decreased to such an extent by the absorption of the solvents from the gas, that it began to run after a while and was liable to consolidate and block the passages of the apparatus. Finally, it was decided to use a rigid material and broken fire-brick was found to answer the purpose very well.—M.

ITALIAN CHEMICAL INDUSTRY

According to a report in a contemporary, great activity characterizes the chemical industry in Italy at the present time. The war has caused great changes both in the materials used and in the methods of production. During last year one of the leading companies produced 35,000 tons of sulfate of copper, 200,000 tons of superphosphates, 270,000 tons of sulfuric acid and 12,000 tons of fine sulfur, and was able to furnish 80,000 tons of sulfuric acid to France.—M.

MOLYBDENUM

Some years ago, says *Engineer*, 123 (1917), 109, molybdenum looked very promising as an alloy in tool steel but, unfortunately, it was found that, while the steel had very often remarkably efficient cutting qualities, it frequently ran with fine hairline seams, and, very peculiarly, the molybdenum seemed to volatilize out of the surface of the steel on heat treatment. In the case of magnet-steel, also, it has not proved as satisfactory as tungsten. Metallurgically considered, molybdenum should have about twice the efficiency of tungsten.—M.

BARIUM-RADIUM CARBONATES

The Golden, Colorado, Experiment Station of the Bureau of Mines, Department of the Interior, reports that it has been found that, by fusing-radium barium sulfates carrying a considerable proportion of silica with a mixture of caustic soda and sodium carbonate, the whole of the barium and radium are converted into carbonates. The amount of sodium carbonate required is comparatively small, 10 to 15 per cent only being required. The reaction goes at a low temperature, and the difficulties of fusing with carbonate alone are entirely eliminated. The product is also much more easily washed free from sodium silicate.

The equipment and installation of the technologic laboratory at Golden have been almost completed. The laboratory is designed to handle rare metal ores in quantities from 10 to 500 lbs. It is designed to make any kind of an acid leach; any kind of an alkaline or salt leach; and any kind of a fusion. In addition a small Wedge type roasting furnace has been installed as well as a tube furnace which can be used either for oxidation purposes or for reduction.

STATUS OF PATENTS UNCHANGED

Mr. Thomas Ewing, U. S. Commissioner of Patents, announced on April 17th that he did not believe it would become necessary for the United States to take over any patents held in this country by residents of foreign countries now at war with the United States. It is well known that in an emergency the government can take over and make use of any patents held in that if the output of any manufactured article controlled by a patent is inadequate, the government can authorize manufacture by another concern, the amount of damages to be adjusted later in the courts. Mr. Ewing further stated that all the warring powers except Russia and Germany have agreed to keep in force patents already granted to enemies, and that he thought the status of patents held by Americans in Germany would remain unchanged.

FRANCE DEVELOPING WATER POWER TO AID INDUSTRIES

The Journal of Commerce, April 17, 1917, reports great development of water power in France since the outbreak of the war, particularly in the southwestern part of the country, which will, upon the conclusion of peace, result in France's entrance into the economic competition of the future with a large number of new factories, equipped with the most modern machinery and appliances and prepared to manufacture chemicals and other products for which before the war Germany held a virtual monopoly, according to a communication just received by the Philadelphia Bourse from the Chamber of Commerce of Paris.

The Paris trade body, which at intervals furnishes the Bourse with information as to the economic and commercial developments of the war, says in part:

"One of the good results of the war will be to have aroused throughout France intense industrial activity, and consequently a considerable increase in electrical power works, formerly scarce in this country. Electro-metallurgy has been rapidly improving during the war, as well as chemical manufactures, so that most of the plans for development in these industries have either already been carried out or are now in course of execution.

"The manufacture of large calibre shells and armor plate is assured by the help of water power. Thanks to the facilities that the transporting of electrical power offers, the works which undertake to produce it can combine the advantages of water descending from the glaciers of the Alps, very plentiful in summer time, with the force to be obtained from the waters of the rivers, which are swollen by the snowfalls of winter and autumn. Such is the system as a whole, adopted by the Société de l'Énergie Électrique du Centre, which supplies electrical power to the towns and factories of the Loire, the Haute Savoie and the Allier, and exceeds 20,000 horse power.

"Before 1914 factories were scarce in the Southwest. One of the most remarkable results of the war will be the industrial activity produced in the regions of Languedoc, Gascogne and Guyenne, which indirectly causes the development of electrical power works and enterprises. The Société Pyrénéenne d'Énergie Électrique has seen its custom among manufacturers vastly on the increase since hostilities began. Its reserves are constituted by more than 50,000 horse power obtained by the falls of water from the lakes and rivers of the Pyrenees mountains.

"These new factories, fitted with the most modern appliances, and whose capital, to a large extent, will be covered by war

profits, will one day—and immediately after peace is signed—be called upon to play a considerable rôle in the economic struggle of the future. They will enable France to become a large producer of matter and materials for which Germany had formerly almost exclusively held the monopoly in manufacture, such as chlorine, bromine, magnesium and the products required in the dyeing industries. They also allow a very great economy in coal and will become a fresh source of inexhaustible wealth and prosperity to the country."

TO PROMOTE CLOSER TRADE RELATIONS WITH RUSSIA

Manufacturers' Record, April 19, 1917, states that an effort is to be made to interest American universities in studying and investigating the economical conditions in Russia and the best methods by which the United States can assist in the economical transformation which will come after the war.

This is an important part of the work proposed to be done by the Russian Information Bureau, promotion of which has recently been announced. Dr. B. E. Shatzky, of Petrograd, a personal and political friend of Dr. Rodzianko, President of the Russian Duma, and Paul Miliukoff, Minister of Foreign Affairs, has come to this country as the authorized delegate of the new Russian Government to furnish accurate information as to financial, commercial and industrial conditions in Russia and to assist in promoting and developing the closest bonds of friendship and sympathy as well as trade relations between the two countries.

This information bureau will work in connection with the American-Russian Chamber of Commerce, and will have headquarters in New York and a branch office in Chicago. A. J. Sack, staff correspondent for the publications of the Russian Ministry of Finance, will assist in the development of this work, and E. C. Porter, executive secretary of the American-Russian Chamber of Commerce, will cooperate in carrying out the work of this new information bureau. Prominent and representative Americans representing many different lines of interest will be associated with the information bureau in an advisory capacity.

Russia is looking to America for capital and organizing ability for the development of Russian railroads and industries after the war. The Russian Government has already outlined a program for the expenditure of \$300,000,000 for railway construction during the next few years, and American capital should play an important rôle in the development of these railroad enterprises. As compared with the United States, Russia at the present time has approximately 46,000 miles of railroad track to 256,000 miles of track in the United States.

For a period after the war Russia will require immense quantities of almost every kind of merchandise. An opportunity for America to meet a considerable portion of these requirements is indicated in the fact that while American exports to Russia ranged between \$23,000,000 and \$32,000,000 annually before the war, the total for the year ending June 30, 1916, footed up \$330,000,000.

Cooperation by the United States Government in the plan outlined herewith has been assured. A recent proof of the Government's interest is afforded in an announcement of the appointment of William A. Russell, of New York, to the position of special agent to investigate Russian investment opportunities in behalf of the Bureau of Foreign and Domestic Commerce of the Department of Commerce.

Mr. Russell is a native of Petrograd, received his education there and gained valuable experience as a consulting engineer in Russia, Siberia and China before coming to this country. In New York he has been engaged as an advisory engineer and has devoted much of his time to analyzing investment propositions. He will consult with interested American firms before sailing for Russia.

SCIENTIFIC SOCIETIES

FIFTY-FOURTH MEETING AMERICAN CHEMICAL SOCIETY, KANSAS CITY, MISSOURI APRIL 10 TO 14, 1917

PROGRAM OF PAPERS

GENERAL SESSION

Address of Welcome. HON. GEORGE H. EDWARDS, Mayor of Kansas City, and DR. FRANK STRONG, Chancellor of the University of Kansas.

Response. JULIUS STIEGLITZ, President of the American Chemical Society.

The Economic Resources of the Kansas City Zone. A. J. BOYNTON.

PUBLIC SESSION—PETROLEUM AND NATURAL GAS

H. P. CADY, *Chairman*

1. The Geology of the Mid-Continent Oil and Gas Fields. RAYMOND C. MOORE.

2. Variations in the Composition of Gases of the Mid-Continent Field. H. C. ALLEN AND E. E. LYDER.

3. Helium and Associated Elements in Kansas Natural Gases. C. W. SEIBEL.

4. Some Experience in the Use of Oxy-Acetylene Welding in Long Distance Natural Gas Transportation. E. P. FISHER.

5. The Cracking of Petroleum in the Liquid Phase. ROY CROSS.

6. One Billion Gallons of Synthetic Gasoline in 1918. WALTER F. RITTMAN.

7. The Chemical Work of the Petroleum Division of the Bureau of Mines. HARRY H. HILL.

AGRICULTURAL AND FOOD CHEMISTRY DIVISION

T. J. BRYAN, *Chairman*

G. F. MASON, *Secretary*

1. A New, Rapid and Accurate Method for the Determination of Lime and Potash in Soils. T. E. KEITH AND C. J. KING.

2. The Examination of Malted Milk. JACOB JAY.

3. The Mineral Elements of the Avocado. M. E. JAFFA AND MR. ALERO.

4. A Study of the Reichert-Meißl Number with a View to Its Modification. W. F. COOVER AND ANSON HAYES.

5. Vinegar Investigations. A Study of the Changes that Cider Undergoes during Fermentation and Prolonged Storage and Its Subsequent Conversion into Vinegar in Rotating Generators. B. G. HARTMANN AND L. M. TOLMAN.

6. An Improved Method for Determining Citral in Lemon Extracts.

R. S. HILTNER AND C. E. PARKER.

7. Arsenic, Copper and Zinc in Oysters. R. S. HILTNER.

8. A Method for the Determination of Starch. W. S. LONG.

9. The Practical Use of Alfalfa Flour. ELIZABETH C. SPRAGUE.

10. Composition of the Dwarf Chestnut (Chinquapin). (By title.) W. A. WHITAKER AND W. A. GOLDTRAP.

11. Carbon Dioxide Production as a Measure of the Rate of Decomposition of Manures in Soil. R. S. POTTER AND R. S. SNYDER.

12. The Effect of Prolonged Production of Alfalfa on the Nitrogen Content of the Soil. C. O. SWANSON.

13. Variations in the Ether Extract of Silage. L. D. HAIGH.

14. The Occurrence and Action of Molds in Soils. P. E. BROWN AND W. V. HALVERSON.

15. Sulfonation in Manure and Its Influence on the Production of Available Phosphorus from Floats. P. E. BROWN AND H. W. WARNER.

BIOLOGICAL CHEMISTRY DIVISION

C. L. ALSBERG, *Chairman*

I. K. PHELPS, *Secretary*

1. The Toxicity of Galactose and Mannose for Green Plants and the Antagonistic Action of Certain Other Sugars toward These. LEWIS KNUDSON.

2. The Effect of Three Annual Applications of Boron on Wheat. F. C. COOK AND J. B. WILSON.

3. The After-Ripening of Fruits. F. W. MUNICH AND W. P. JAMES.

4. Quantitative Determination of Carbohydrates in Plant Tissues. F. W. MUNICH AND D. T. ENGLISH.

5. The Proteins of the Peanut, *Arachis hypogaea*. II. The Distribution of the Basic Nitrogen in the Globulins Arachin and Conarachin. C. O. JOHNS AND D. B. JONES.

6. A Physical and Chemical Study of the Kafr Kernel. C. L. BIDWELL.

7. Oil from the Avocado. Preliminary Report. H. S. BAILEY AND L. B. BURNETT.

8. Oil from *Sitlingia Sebeferi*. H. S. BAILEY AND L. B. BURNETT.

9. A Noteworthy Effect of Bromides upon the Action of Malt Amylase. A. W. THOMAS.

10. Availability of the Energy of Food for Growth. C. R. MOULTON.

11. Investigation of the Kjeldahl Method for Determining Nitrogen.

I. Influence of Reagents and Apparatus on Accuracy. I. K. PHELPS AND H. W. DAUDT.

12. A Study of the Estimation of Fat in Condensed Milk and in Milk Powder. C. H. BIESTERFELD AND O. L. EVENSON.

13. Schmeyer's Method for the Determination of Lactic Acid in Urine. MARY E. MAYER.

14. Tissue Transplantation as a Biochemical Method. LEO LOEB.

15. On the Optimum Reaction for Tryptic Proteolysis. J. H. LONG AND MARY HULL.

16. On the Normal Reaction of the Intestinal Tract. J. H. LONG AND F. FENGER.

17. Studies of the Gastric Residuum. III. The Relation of Total Phosphorus to Acidity. C. C. FOWLER.

18. Studies of Food Utilization. I. The Utilization of Carbohydrates on a Relatively High and Low Cereal Diet. ZELMA ZENTMIRE AND C. C. FOWLER.

19. The Nature of the Inositol Phosphoric Acid of Some Important Feeding Materials. J. B. RATHER.

20. Determination of the Proteolytic Action of Papaya Latex and the Detection of Enzyme Adulterants. V. K. CHESNUT.

21. The Formation of Ester Hydrolyzing Substances by the Action of Alkali on Casein. FLORENCE H. FRANKEL.

22. Factors Influencing the Proteolytic Activity of Pepsin. E. M. FRANKEL.

23. Variations in the Chemical Composition of Alfalfa at Different Stages of Growth. H. S. GRINDLEY AND H. E. ECKSTEIN.

24. Physical and Chemical Constants of Some American Tomato Seed Oils. H. S. BAILEY AND L. B. BURNETT.

25. A Laboratory Method for the Hydrogenation of Oils. H. S. BAILEY AND L. B. BURNETT.

26. An Electrically Heated Melting Point Apparatus. H. S. BAILEY.

27. The Alkaloids of *Bocconia frutescens*. EMERSON R. MILLER.

28. On the Presence of Free Hydrocyanic Acid in Cassava. EMERSON R. MILLER.

29. The Effect of the Ingestion of Certain Organic and Mineral Acids upon Growing Swine on a Normal Level of Protein Intake. A. R. LAMB AND JOHN M. EVVARD.

30. Effects of Various Substances on the Auto-Oxidation of Brain Cephalin. (By title.) CHARLES G. MACARTHEUR.

31. Microchemical Studies on the Mosaic Disease of Tobacco. G. W. FREIBERG.

32. Some Peculiarities of Plant Decoctions as Nutrient Media for Fungi. R. M. DUGGAR.

33. Isolation of Parahydroxy-benzoic Acid from Soil. E. H. WALTERS.

INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION

H. E. HOWE, *Chairman*

S. H. SALISBURY, JR., *Secretary*

1. The Production of Ferro-Uranium. H. W. GILLET AND E. L. MACK.

2. Chemical Examination of Industrial Brines. O. R. SWEENEY AND JAMES R. WITTEBROW.

3. Contribution to the Industrial Chemistry of Chicle and Chewing Gum. FREDERICK DANNERTH.

4. Apparatus for Determining the Specific Gravity of Natural Gas. CHARLES K. FRANCIS.

5. Comparative Results from Experiments in the Distillery with Open and Closed Fermenters. NIELS C. ORTVED.

6. The Effects of Exposure of Some Fluid Bitumens. CHARLES S. REEVE AND RICHARD H. LEWIS.

7. The Thermal and Pressure Decomposition of an Absorbent Oil. GUSTAV EGLOFF.

8. The Formation of Benzene and Toluene by the Action of Aluminum Chloride on Solvent Naphtha. GUSTAV EGLOFF.

9. The Determination of Available Oxygen in Oxidized Manganese Ores. O. L. HARNEY.

10. Some Relations of the Effect of Overheating to Certain Physical and Chemical Properties of Asphalts. (Illustrated.) A. W. HIXON AND HAROLD E. HANDS.

11. Chemical Industry in Canada. H. E. HOWE.

12. Chemical Laboratory of the Youngstown Sheet and Tube Co. D. A. RUSSELL.

13. The Availability of Nitrogen in Fertilizers. A New Method Based on the Nitrogen Rendered Water-Soluble by Incubation with a Fertile Soil. J. P. SCHROEDER.

14. I. The Fertilizer Value of City Wastes. II. Garbage Tankage, Its Composition, the Availability of Its Nitrogen and Its Use as a Fertilizer. J. P. SCHROEDER.

Symposium on the Chemistry and Metallurgy of Zinc

JOHN JOHNSTON, *Presiding*

1. A New Method of Separating Zinc from Cadmium and the Determination of the Latter Iodometrically. ERIC JOHN ERICSON.
2. The Determination of Cadmium in Brass. EDWARD SCHRAMM.
3. The Electrometric Determination of Zinc. F. R. VON BICHOWSKY.
4. The Occurrence of Germanium in Missouri and Wisconsin Blendes. E. H. BUCHANAN.
5. The Vapor Pressure of Zinc and Related Metals. JOHN JOHNSTON.
6. The New Zinc Fields of Kansas-Oklahoma. (Illustrated.) P. HAYNES.
7. Results of Recent Investigations on Smelter Smoke Problems. A. E. WELLS.
8. Notes upon the Hydro-Metallurgical and Electrolytic Treatment of Zinc Ore. E. E. WATTS.

ORGANIC CHEMISTRY DIVISION

J. R. BAILEY, *Chairman*H. L. FISHER, *Secretary*

Joint Meeting with Physical and Inorganic Chemistry Division

1. Some Oxidation Reactions. H. D. GIBBS.
2. The Action of Aluminium Chloride upon Aromatic Hydrocarbons. G. EGLOFF and R. J. MOORE.
3. A Study of the Nitrogen Distribution in Different Soil Types. C. A. MORROW.
4. 1. New Derivatives of Arsanilic Acid. 2. Tetraphenylmethane. O. KAMM.
5. The Rotatory Powers of Some New Derivatives of Gentibiose. C. S. HUDSON and J. M. JOHNSON.
6. Sedoheptose, a New Sugar from *Sedum Spectabile*. (Communication.) F. B. LAForge and C. S. HUDSON.
7. Picryl-Phenyl Ether. ALFRED N. COOK.
8. The Oxidation Product of Lactose. W. LEE LEWIS.
9. The Oxidation of Ethyl Alcohol by Means of Alkaline Potassium Permanganate. W. L. EVANS and J. E. DAY.
10. The Oxidation of Acetaldehyde by Means of Alkaline Potassium Permanganate. W. L. EVANS and H. B. ADKINS.
11. The Preparation of Quinone from Aniline. C. E. BOORD and E. H. LOEB.
12. The Preparation of Some New Acetyl Arylhydrazines. C. E. BOORD and C. E. SENSEMANN.
13. A Study of the Constitution of Hydrasino-Quinones. EDWARD SCHMIDT and C. E. BOORD.
14. The Attractions between Various Organic Groups and Water. (By title.) WILLIAM D. HARKINS.
15. A Further Study of Chloro Ethers. FRIEND E. CLARK and E. MACK.
16. On the Preparation of Dichloroether. G. B. FRANKFORTER and S. J. REICHERT.
17. The Oxidation Products of Pinene. G. B. FRANKFORTER and M. B. CHITTICK.
18. Further Reactions between the Carbohydrates, Benzene and Its Homologues in the Presence of Aluminium Chloride. G. B. FRANKFORTER and V. R. KOKATNIK.
19. The Cross-Cross Addition on Conjugate Systems. J. R. BAILEY, N. H. MOORE and A. T. McPHERSON.

PHARMACEUTICAL CHEMISTRY DIVISION

I. F. KEBLER, *Chairman*G. D. BEAL, *Secretary*

1. Standards for the Official and Popular Aromatics. G. N. WATSON and L. E. SAYRE.
2. Investigation of the Practicability of the U. S. P. Method for Manufacturing Magma Magnesia by the Retail Pharmacist and Comments on Other Methods. L. E. SAYRE.
3. Analysis of Preparations for the Hair, Containing Arsenic, and Comments on Same. L. E. SAYRE.
4. Analysis of Tablets of Secret Composition. I. F. KEBLER.
5. An Interesting Prescription. I. F. KEBLER.
6. The Relative Alkaloidal Value of the Rhizome and the Rootlets of Hydrastis. L. D. JUVENSTON.
7. Lessons from the New York Meeting of the American Chemical Society. I. F. KEBLER.
8. Analysis of Ragweed Pollen. FREDERICK W. HELL.
9. The Volatile Oil of *Monarda fistulosa*. EMERSON R. MILLER.
10. The Volatile Oil of *Nepeta cataria*. EMERSON R. MILLER.
11. The Kinetic Properties of Pepsin. HOWARD T. GARDNER.
12. The Action of Phenol on Tin Containers. HARPER F. ZOLLER.
13. Some Constituents of the American Grapefruit. HARPER F. ZOLLER.

PHYSICAL AND INORGANIC CHEMISTRY DIVISION

H. P. TALBOT, *Chairman*E. B. MILLARD, *Secretary*

Joint Meeting with Division of Organic Chemistry

1. Negative and Positive Specific Heat of Saturated Vapor. F. P. STEINDEL.

2. The Dependence of Ion Conductance upon the Viscosity of the Medium. (Lantern.) E. W. WASHBURN and KARL A. CLARK.

3. The Effect of Colloids on the Velocity of Crystallization of Water. (Lantern.) J. H. WALTON and ALBERT BRANN.

4. The Separation of Erbium from Yttrium. B. S. HOPKINS and EDWARD WICHERS.

5. A Study of the Ratio $\text{Er}_2\text{O}_3 : 2\text{ErCl}_3$. CLARENCE W. BAKER and EDWARD WICHERS.

6. Thermal Studies of Some Members of the System $\text{PbO}-\text{SiO}_2$. L. I. SHAW and B. H. BALL.

7. Preliminary Studies on the Change of Conductivity with Time in the System Methyl Alcohol-Iodine-Water. L. I. SHAW.

8. Use of "Cupferon" (Ammonium Nitrosophenylhydroxylamine) in the Analysis of Zirconium Minerals. JAMES BROWN.

9. The Solubility of Pure Radium Sulfate. S. C. LIND, C. F. WITTE-MORRE and J. E. UNDERWOOD.

10. Studies in Pseudo-Isotropy. I. S. C. LIND.

11. Silicic Acid Gels. HARRY N. HOLMES.

12. Rhythmic Banding. HARRY N. HOLMES.

13. Peptization and Gel Formation of Ferric Arsenate and Phosphate. HARRY N. HOLMES.

14. Differential Iodimetry. IV. Determination of Manganese Dioxide in the Presence of Ferric Iron. O. L. BARNEBEY and G. M. BISHOP.

15. Reactions in Non-aqueous Solvents. III. Some New Double Univalent Halides. O. L. BARNEBEY.

16. Density of the Transition Layer between Liquid and Vapor. (By title.) F. H. MACDOUGALL.

17. Dieterici Equation of State. (By title.) E. H. MAC DOUGALL.

18. Colors of Second Order. (Blackboard.) JEAN PICCARD.

19. Precipitation, Stability and Constitution of Hydrous Ferric Oxide Sols. (By title.) MARKS NEIDLE.

20. Oxidation-Reduction Reactions without the Addition of Acid. IV. Ferrous Chloride-Potassium Dichromate and Ferrous Chloride-Hydrogen Peroxide. (By title.) MARKS NEIDLE and JACOB BARAB.

21. Studies on Dialysis. III. Mixtures of the Chlorides of Ferric Iron, Aluminium and Chromium. (By title.) MARKS NEIDLE and JACOB BARAB.

22. Emulsification as Related to the Orientation of Molecules in the Surfaces of Liquids. (By title.) WILLIAM D. HARKINS.

WATER, SEWAGE AND SANITATION DIVISION

E. H. S. BAILEY, *Chairman*H. P. CORSON, *Secretary*

1. Seasonal Distribution of Soil and Fecal Strains of the Colon Aerogenes Group in Surface Waters. MYRTLE GREENFIELD and W. N. SKOURUP.

2. Legal Status and Character of the Work of the Water and Sewage Laboratory of the Kansas State Board of Health. C. C. YOUNG.

3. The Problems of Water Supply of a Great Railroad System. ORTON T. REES.

4. Well Waters of Chicago. EDWARD BARTOW.

5. The Vertical Distribution of Dissolved Oxygen and the Precipitation by Salt Water in Certain Tidal Areas. J. W. SALE and W. W. SKINNER.

CALENDAR OF MEETINGS

American Electro-Chemical Society: Spring Meeting, Detroit, Mich., May 2 to 5, 1917. Autumn Meeting, Pittsburgh, October 3 to 6, 1917.

Interstate Cotton Seed Crushers' Association Convention: Dallas, Texas, May 14 to 16, 1917.

Technical Textile Conference (Second Annual): Washington, D. C., May 21, 1917.

Technical Association of the Pulp and Paper Industry: Annual Spring Meeting, Neenah, Wisconsin, May 24 and 25, 1917.

American Iron and Steel Institute: New York, May 25 and 26, 1917.

American Institute of Chemical Engineers: Ninth Semi-Annual Meeting, Buffalo, N. Y., June 20 to 22, 1917.

First Industrial Exposition and Export Conference: Springfield, Mass., June 23 to 30, 1917.

American Society for Testing Materials: Atlantic City, June 26 to 30, 1917.

American Chemical Society: Annual Meeting, Boston, September 16 to 19, 1917.

National Exposition of Chemical Industries (Third): Grand Central Palace, New York City, September 24 to 29, 1917.

SECOND ANNUAL TECHNICAL TEXTILE CONFERENCE WASHINGTON, D. C., MAY 21, 1917

The Second Annual Conference of those interested in the consideration of problems relating to the testing and general technology of textiles and the closely allied materials, cordage, thread and felt, will be held at the National Bureau of Standards, Washington, D. C., commencing May 21, 1917 and continuing for one, two, or three days, as required. All persons interested are cordially invited to attend.

It has been suggested that at the meeting the conferees might consider the advisability of forming a permanent society for the promotion of research. The functions of such a society might include some of the following, as well as others:

1—To maintain a library for assembling and disseminating printed information of all kinds about the textile and allied industries.

2—To publish a periodical, devoted exclusively to technical considerations, in which original papers would be printed in full and abstracts given of current articles and books.

3—To hold regular meetings for the discussion of technical work in progress or completed.

4—To offer prizes for the satisfactory solution of specific problems.

5—To give university scholarships to competent men desiring to equip themselves for textile research.

6—To maintain laboratories for the general investigation of the physical and chemical theory of textiles.

Any comments or suggestions regarding any of the above matters will be greatly appreciated. Those wishing to attend the conference or to present papers are requested to advise the Bureau of Standards at the earliest possible date.

PERSONAL NOTES

A commission of scientists, appointed by President Wilson on the initiative of the National Research Council and upon the recommendation of the National Academy of Sciences, has been sent to England and France to cooperate with the scientists of those countries in the study of war problems. The members of the commission and their respective subjects are: (Chairman) Dr. Joseph S. Ames, Johns Hopkins University, aeronautics; Dr. Harry F. Reid, Johns Hopkins University, scientific map making and photography from airplanes; Dr. Richard P. Strong, Harvard University, epidemics and sanitation; Dr. Linsley R. Williams, assistant health commissioner of New York State, camp investigations; Dr. George A. Hulett, Princeton University, chemistry of explosives; and Dr. George K. Burgess, Bureau of Standards, munitions, metals suitable for guns and rigid dirigibles.

The Bureau of Mines, in cooperation with the American Institute of Mining Engineers and the American Chemical Society, is taking a preparedness census of the mining engineers, chemists, and metallurgists of the United States, at the request of the Council of National Safety. Cards calling for specific qualifications of technical men are being mailed to all names available to the Bureau, and anyone who does not receive a card may obtain one from the Director of the Bureau of Mines, Washington, D. C. The work is urgent, and immediate cooperation will yield information of the greatest value.

A joint meeting of the New York Sections of the Society of Chemical Industry, the American Chemical Society and the American Electrochemical Society, was held on April 13th with the following program: "Recent Advances in Leather Manufacture," by Allen Rogers, Pratt Institute, Brooklyn, N. Y.; "Some Technological Aspects of Colloid and Emulsion Chemistry," by Prof. Martin H. Fischer, University of Cincinnati; "Ultra-Microscopic Demonstration of Zsigmondy-Brownian Motion," by Jerome Alexander. In the election of officers, Mr. Alexander was re-elected chairman, and Mr. Rogers and Mr. Hemingway were re-elected secretary and treasurer, respectively. The new committeemen are: Messrs. W. M. Grosvenor, A. C. Langmuir, Henry Wigglesworth, Utley Wedge, Charles Baskerville, S. R. Church, Allen Rogers, H. S. Miner, J. M. Matthews, T. B. Wagner, P. C. McIlhiney, J. R. M. Klotz, C. H. Herty and John Teeple.

An International Conference of the executives of the Technical Section of the Canadian Pulp and Paper Association and the Technical Association of the American Pulp and Paper Industry, was held at Erie, Pa., March 22 and 23, 1917, at which various steps were taken towards increased technical cooperation between the two associations. It was decided to arrange

for annual meetings of their committees on standard processes and tests, alternately in the United States and Canada. The first conference of this kind will occur at the Joint Meeting of the two Associations to be held at Holyoke, Mass., in September, 1917, at the time of the Annual Meeting of the American Chemical Society in Boston.

Mr. C. F. Carrier, Jr., is now department manager and chemical engineer with the Rollin Chemical Company and will have charge of the chemical engineering connected with the additions now being made to their plant at Charleston, W. Va.

David H. Browne, chief metallurgist of the International Nickel Company, died at his home in Montclair, N. J., on March 30, 1917, at the age of fifty-two years.

Dr. Ralph E. Hall, assistant professor of inorganic chemistry at the Iowa State College, has resigned to accept a position in the Geophysical Laboratory of the Carnegie Institution, Washington, D. C.

Dr. E. A. Letts has resigned from the chair of chemistry in Queens University, Belfast.

Prof. W. S. Hendrixson, of Grinnell College, Iowa, is at the University of Illinois this semester, assisting in the work in general chemistry. Dr. H. F. Lewis, of the University of Illinois, has taken charge of Prof. Hendrixson's classes at Grinnell, during his absence. The exchange is only for this semester.

The Legislature of the State of Ohio has appropriated \$85,000 to the Ohio State University at Columbus, for an additional wing to the chemistry building. This will be largely devoted to chemical engineering. The appropriation made includes the building only and does not take into account the equipment.

The Annual Spring Meeting of the Technical Association of the Pulp and Paper Industry will be held at Neenah, Wis., on May 24 and 25, 1917, with headquarters at The Valley Inn. Mr. Ernst Mahler, of the Kimberly-Clark Company, Neenah, has charge of the arrangements for the meeting. The second day of meeting (25th) will be spent in an inspection of all departments of the Kimberly-Clark Mill, including the alcohol and bleach plants. The National Textile Fiber Company, manufacturer of paper textile goods, have invited the members to visit their experimental station in which paper rugs are made on a commercial scale.

By legislative enactment the scientific departments of Rutgers College have been designated as the State University of New Jersey.

At the meeting of the New York Section of the American Electrochemical Society held at the Chemists' Club on April 13th, the following officers for the next session, 1917-18, were elected: *Chairman*, J. V. N. Dorr; *Vice-Chairman*, E. D. Kingsley; *Secretary-Treasurer*, J. Malcolm Muir. Mr. Dorr has attained a world-wide reputation through his cyanide machinery. He is one of the organizers of "Belgian Kiddies, Ltd." Mr. Muir is manager of *Metallurgical and Chemical Engineering*, and Dr. Kingsley is President of the Electro-Bleaching Gas Company and of the Niagara Alkali Company.

The department of chemistry of the University of New Mexico, whose chemical laboratories were lost by fire a few years ago, are now housed in their new chemistry building. This building has a capacity of two hundred students, and has been constructed around a patio, as so many buildings in that section were made years ago. Within the patio are concrete laboratory desks, so that during the nice weather (which is about three-fourths of the time there) students may work in an open-air laboratory. The rest of the building is like the usual run of such structures and contains the usual rooms and offices, laboratories and stock-rooms.

Prof. Henry B. Cornwall, emeritus professor of Princeton University, died on April 1st, at his home in Princeton, N. J., in his seventy-third year. Prof. Cornwall was a graduate of Columbia and was professor of applied chemistry and mineralogy at Princeton University from 1873 to 1910.

Dr. Wm. M. Barr has been appointed consulting chemist to the Oregon Short Line Railroad Company, in addition to his present work as consulting chemist of the Union Pacific Railroad Company. Dr. Barr's headquarters are at Omaha, Neb.

Charles V. Bacon, consulting and analytical chemist, announces the removal of his office and laboratory to 3 Park Row, New York City.

Mr. Walter Arthur, formerly chief chemist of the Frankford Arsenal, has left the Government service and is now connected with private interests in Pittsburgh.

Dr. E. M. Chamot, of Cornell University, gave an illustrated lecture on "Chemical Microscopy," at the April 20th meeting of the Chicago Section of the A. C. S. The meeting of the Section on May 18th will be the occasion of the Willard Gibbs Medal Award to Prof. E. W. Morley.

S. T. Mather has been promoted from assistant to the Secretary of the Interior to the position of Director of National Parks in the Interior Department.

The Annual Smoker and Entertainment of the Philadelphia Section of the A. C. S. was held on April 12th.

Prof. M. A. Rosanoff, of the Mellon Institute, and Prof. W. D. Harkins, of the University of Chicago, are acting as exchange professors this spring for a period of six weeks. Dr. Rosanoff's lectures are on stereo-chemistry and on his theory of chemical reactions. Dr. Harkins is lecturing on thermo-chemistry.

We learn from *Science* that "Gilman Hall" will be the name of the first unit, now being built at a cost of \$200,000, of the future group of permanent buildings for chemistry at the University of California. The name was chosen in honor of Daniel Coit Gilman, president of the University from 1872 to 1875, and later president of Johns Hopkins University.

Dr. William C. Moore, of the Research Laboratory, National Carbon Company, Cleveland, gave two lectures on April 5th, at the Case School of Applied Science, on "Research as an Industrial Tool" and on "The Arc as an Illuminant." These talks will be followed by three others on Arc Technology.

C. M. Hargrave has left the Prest-O-Lite Company, of Indianapolis, and is now with the Ault & Wiborg Company, of Cincinnati.

The April Meeting of the Indiana Section of the A. C. S. was held on the 20th at the German House, Indianapolis. Edgar B. Carter, director of scientific work, Swan-Myers Company, addressed the Section on "Immuno-Chemistry," the earlier part of which was presented at their February Meeting. Dr. E. V. McCollum, of Wisconsin, will address the Section at the next meeting on May 11th.

The United States Civil Service Commission announces the following open competitive examinations: *Micro-analyst*, salary \$1200-\$1400 a year, on May 16, 1917; *Junior Chemist*, salary \$1200-\$1740 a year, on May 16-17, 1917; *Chemist (male)*, salary \$1400 a year.

A symposium on "The Theory and Practice of Distillation," was held by the Northeastern Section of the A. C. S., in Boston, on March 30th. The following papers were read: "The Elements of Distillation," by C. S. Robinson; "Free Energy Relations Involved in Distillation," by W. K. Lewis; "Commercial Practice in Distillation," by C. L. Campbell.

The eighth meeting of the Ames Section of the A. C. S. was held on March 29th with the following program: "The Relation of Chemistry to Preparedness," by Prof. W. F. Coover; "The Synthesis of a Naphtholtetrazine," by Dr. A. W. Dox; "A Study and Modification of the Reichert-Meissl Method for the Determination of Soluble Acids in Edible Fats," by Anson Hayes.

A dinner was given in honor of Professors M. C. Whitaker and F. J. Metzger by the Columbia University Chemical Engineering Society on Wednesday evening, April 25th, at the Chemists' Club, New York City.

Professor C. R. Richards, professor of mechanical engineering and head of the department since 1911, has been appointed Dean of the College of Engineering and Director of the Engineering Experiment Station of the University of Illinois, to succeed Dr. W. F. M. Goss, who has resigned to become President of the Railway Car Manufacturers' Association of New York. Since entering the University of Illinois Prof. Richards has served two years as acting Dean of the College of Engineering during an absence of Dean Goss.

Duell, Warfield & Duell, counselors at law, of New York City, announce the removal of their offices from 2 Rector Street to the Berkeley Building, 25 West 44th Street. Announcement is also made that Royal W. France has become a member of the firm.

The Kansan Chemist announces the following changes in the chemistry staff of the University of Kansas: Prof. Clarence Estes recently joined the Empire Gas and Fuel Company of Bartlesville, Okla.; Ivan T. Parkhurst will go with the company on June 15th. O. L. Maag left the University February 1 to accept a position as chemist with the Kansas City Testing Laboratory. J. B. Whelan has purchased an interest in the White & Whelan Chemical company, with which he plans to be actively associated next year. A. H. Henson joined the staff of the Division of State Chemical Research at January 1. R. N. Harger will probably enter the Yale Graduate School next September. Ray Q. Brown is considering the University of Chicago for studying advanced chemistry. W. M. Tatum has under consideration a fellowship at the University of California for the coming year.

Mr. C. E. Thies has severed his connection with Harnet & Amend and is now with the Paley Gas and Meters Co., New York City.

A new course in chemical laboratory organization and management will be given during the Summer Session, July 9 to August 17, 1917, of Columbia University, New York City, by Prof. Thomas B. Freas of Columbia University, and Prof. W. L. Estabrooke of the College of the City of New York. The purpose of this course is to fit men to equip and maintain a chemical laboratory efficiently. Inspection trips will be made to educational institutions, manufacturing plants and supply houses, in or near New York City, Boston, Washington, D. C., Rochester, Philadelphia, and points en route.

George A. Ferguson, formerly professor of chemistry in the New York College of Pharmacy, died at his home in Brooklyn, N. Y., in his forty-ninth year. Prof. Ferguson was well known for his bacteriological researches and was for several years head of the Ferguson laboratories in New York City and at Blue Point, L. I.

M. C. Whitaker, head of the Department of Chemical Engineering, Columbia University, was elected Vice-President of the U. S. Industrial Alcohol Company at the meeting of their Board, on April 19th. In this capacity, Mr. Whitaker will serve as Chairman of the Manufacturing Committee in charge of plants and operations, Chairman of the Research Committee in charge of the new laboratories at Baltimore, and as a member of the Sales Committee of the Company.

The following papers have been recently presented before The Franklin Institute of Philadelphia:

March 29—"The Chemistry of Cellulose and Its Important Industrial Applications," by H. S. Mork, of Arthur D. Little, Inc., Boston.

April 5—"Analysis of Commercial Products by Microscopic Means," by Prof. E. M. Chamot, of Cornell University.

April 12—"The Electron Theory," by Prof. W. A. Noyes, of the University of Illinois.

April 18—"Hydrogenation of Oils," by Prof. Charles Baskerville, of the College of the City of New York.

April 26—"Whirlwinds and Sunspots," by Dr. Geo. E. Hale, director of the Mount Wilson Solar Observatory, Pasadena, Cal.

Prof. Marston Taylor Bogert, of Columbia University, chairman of the Chemistry Committee of the National Research Council, addressed the Pittsburgh Section of the A. C. S. on "Research and Development Work Expected of Chemists in War Times," on April 5th; and the Chemical Society of Washington on "Chemistry and the War," on April 20th.

Prof. Hugh Stott Taylor, of Princeton University, has left for England to accept an appointment with the Munitions Inventions Department of the British Ministry of Munitions. He will probably be located at University College, London.

George Mallet MacNider died at the Davis and Fisher Sanatorium at Atlanta on Tuesday afternoon, February 27, of pneumonia, after an illness of but ten days.

Dr. MacNider was born in 1884 and graduated from the University of North Carolina with the Class of 1903. He then took a post-graduate course at Cornell University and became assistant state chemist of the Department of Agriculture at Raleigh, N. C.

While in this position he became interested in research work and prepared several monographs on commercial starches. These were printed in *THIS JOURNAL*, 4 (1912), 417, the *Journal of the Elisha Mitchell Scientific Society* for December, 1912, and in *Cotton*, in August, 1912, and February, 1913. These articles attracted wide-spread attention and in June, 1913, he was offered and accepted a position as chemist with the Corn Products Refining Company of New York.

In March, 1914, he was sent to Greenville, S. C., as manager of the Southern office of the company and occupied this position until July, 1915, when he was made textile chemist for the company and looked after their interests throughout the whole textile field, although still retaining Greenville as his headquarters. This position he retained up to the time of his death.

A further step toward the practical correlation of education with industry is to be seen in the action just taken by a number of Akron rubber factories in establishing at the Municipal University of Akron, thirty scholarships in the engineering college under the following unique conditions: The candidate will be chosen from high school graduates ranking in the upper third of the class, preference being given to graduates of Akron High Schools, although others will also be received. The scholarships will cover all tuition, incidental and laboratory fees. Upon entrance the scholarship holders will be assigned to a course upon the cooperative basis, working alternate two-week periods in factory and college. In the factory they will become a part of the regular factory training squadron, proceeding step by step through every department of the industrial organization. In the college they will receive training in basic engineering and business-training subjects, this work being related to their practical experience by a regular system of coordination. Each student will receive from the company employing him the sum of \$37.50 for each two-week period during which he is employed. At the end of the four-year course the graduate will have the opportunity of a permanent position in the organization in which he has been trained. Among the cooperating firms are the Firestone Tire and Rubber Co. and the Goodyear Tire and Rubber Co., both of which have recently established industrial graduate fellowships in rubber chemistry at the Municipal University.

The plan just outlined is a decided innovation in the development of the part-time system, in that it offers the opportunity for a high school graduate to procure an education practically without expense to himself—a condition now scarcely to be found outside such institutions as West Point and Annapolis. The cooperating firms are acting on the same sound economic basis on which the government itself proceeds, namely, that money spent in training men for its own service is well invested.

NEW ENGINEERING SOCIETY ORGANIZED

At a Convention held in El Paso, Texas, on March 8, 9, and 10, the SOUTHWESTERN SOCIETY OF ENGINEERS was organized with more than one hundred charter members. Membership is open to civil, mechanical, mining, electrical, or chemical engineers, or architects or other persons belonging to a technical profession, who are not less than 27 years of age, and who have been in active practice of their profession for at least six years. Provision is also made for Associated, Honorary, and Affiliated Members.

The great distance from centers of population makes it difficult for southwestern engineers to attend meetings of the national engineering organizations, so it is believed that the new Society will fill a real need. It is planned to hold at least two Conventions of the Society each year for the reading and discussion of professional papers and for social intercourse.

A. F. Barnes, Dean of the School of Engineering, New Mexico College of Agriculture and Mechanic Arts, is President of the New Society and Forrest E. Baker, of El Paso, Texas, is Secretary.

RESEARCH COMMITTEE APPOINTMENTS TO COÖPERATE WITH THE NATIONAL RESEARCH COUNCIL

BROWN UNIVERSITY—John E. Bucher, of the chemistry department; J. B. F. Herreshoff, of the Nichols Chemical Company; John C. Hebdon, of the Federal Dyestuffs Corporation; and others.

COLLEGE OF THE CITY OF NEW YORK—Chas. Baskerville, *Chairman*; T. A. Storey, F. G. Reynolds, G. G. Scott, J. G. Coffin, F. E. Breithut and A. N. Goldsmith.

UNIVERSITY OF PITTSBURGH—Geo. H. Clapp, *Chairman*; Messrs. Bacon, Brashear, Griffin, Guthrie, Holland, Lincoln, Schlesinger and Thorpe.

INDUSTRIAL NOTES

\$20,000,000 DYESTUFF CONSOLIDATION TO MEET FOREIGN COMPETITION AFTER WAR

The coal-tar color and chemical industries of this country have now agreed upon a form of amalgamation, not by any means a trust or combination in the accepted sense of the word, but a centralization of productive effort and of capital, utilizing the sources of supply, the mines, coke-oven by-products plant, manufacture of intermediates and acids, etc., with the sole purpose of meeting the post bellum competition with a united front and with the strength of resource which can be found alone in such industrial coöperation.

The amalgamated company—which will be known as the National Aniline and Chemical Company, Inc.—will have among its executives J. F. and C. P. Hugo Schoellkopf, of the Schoellkopf Aniline and Chemical Works, I. Frank Stone, president National Aniline and Chemical Company and Dr. William Beckers, of the W. Beckers Aniline and Chemical Works, and will control the entire works of the Schoellkopf Aniline and Chemical Works, Inc., of Buffalo, the W. Beckers Aniline and Chemical Works of Brooklyn, the Benzol Products Company, of Marcus Hook, Pa., and such sections of the plants of the Semet-Solvay Company of Syracuse, the Barrett Company works at Frankfort, Pa., the General Chemical Company of New York, and other factories, as produce those coal-tar intermediates entering into the manufacture of the finished colors.

The entire business of this new amalgamation will be under the control and known by the name of the National Aniline and Chemical Company, Inc., and the present company bearing that name, of which Mr. Stone has been president since its formation will be reorganized. The executives will include those already associated with the companies entering into the new productive alliance, together with such new research and manufacturing chemists and other experts as shall be necessary to the carrying out of the plans for such a nationalization of dyestuff production as is contemplated.

The Schoellkopf and Beckers Companies are manufacturers of dyestuffs, the Benzol Company aniline oils, salts and certain intermediates, while the General Chemical, Semet-Solvay and the Barrett Company production entering into the plans of the new organization is in the line of coal, coke oven by-products and intermediates.

The combined output of the Schoellkopf and Beckers concerns is about 75 per cent of the aniline color production of the country. It is interesting to note, however, that the lines are not competitive to any extent, since the Beckers colors are successfully employed in the woolen trade, while the Schoellkopf Company has specialized more in cotton, silk, leather, paper colors, etc.

The Beckers Company bought the Standard Aniline Company recently, the second producer of sulfur black in the country in point of output. The Schoellkopf company leads the country in sulfur black production and the combined output of both concerns totals about 75 per cent of the total production to day. The competition from other makers in this line is increasing steadily, however.

There is another interesting factor in the color production of the Schoellkopf and Beckers Companies. While the number of such colors produced prior to the war was about 150, this has now been considerably reduced, primarily because of a lack of those intermediates not yet made in this country. The Beckers Company produces about 50 colors, and it will be noted that the total by the two companies is but 115, or about 50 per cent of the 250 or so colors of commerce, which will re-enter American consumption soon after the close of hostilities.

The Benzol Company is the only branch of the new organization manufacturing aniline oils and salts, of which it is the

principal producer in this country. With the expansion of its modern plant on the Delaware River it has increased its output to a large extent and has now begun the manufacture of various intermediates and is experimenting with the production of others. This business had its inception before the war and was the result of ante-bellum demands. It is owned equally by the General Chemical Company, the Semet-Solvay Company and the Barrett Company, makers of acids, and of benzol and other coal-tar distillates, respectively. There is marked competition in these lines of production, for there are many makers of acids in quantity and there are other producers of large quantities of coal-tar distillates.

As an indication of the policy of the new organization it is stated that no agreements have been entered into with the three concerns last mentioned, for the supplies of raw materials produced since the amalgamation will be free to buy supplies in the open market just as the other companies will be free to sell the other color makers.

One of the best evidences that the new association will not enjoy a monopoly—the first cry raised whenever the exigencies of business demand a conservation of supply and productive effort, although in this instance the conservation is for the interests of the dye industry as a whole against the united effort of foreign competitors when the war-time embargo shall again be lifted—is the fact that some 35 manufacturers of aniline colors in this country, many of whom are among the best-known concerns, are coming to the fore with the demand for increased production following war-time scarcity of coal-tar colors.

In addition to its purpose of placing the color industry of this country upon a more permanent basis, this proposed \$20,000,000 consolidation offers the opportunity through plant production possibilities, the availability of acids, bases and intermediates, the laboratory facilities to be provided and the economic advantages due to centralization of production and marketing effort for the rapid development of production until they shall be prepared to market all the colors necessary to meet the demands, instead of about one-half the varieties as at present. In addition the organization will also produce pharmaceutical and photographic chemicals and explosives, as a natural development of their production of coal-tar products.

AETNA EXPLOSIVES COMPANY BUSINESS TO BE CARRIED ON UNDER COURT ORDERS

Judge Mayer, of the Federal District Court, on April 19, named ex-Judge George C. Holt and ex-Governor Benjamin B. Odell as receivers of the Aetna Explosives Company with orders to continue the business. Each receiver must furnish a \$25,000 bond. They will be represented by the law firm of Winthrop & Stimson.

The company is an \$18,000,000 concern, and has large contracts for furnishing the Allies with explosives. It has fallen in financial difficulties for some time for lack of capital to carry on its contracts.

Application for receivers was made by Henry M. Ait, the General Chemical Company, of Cleveland, Ohio, a creditor for \$100,000.

At all times since its organization, the defendant now, the defendant company has been pressed as a very heavy weight in the manufacture of explosives, particularly for the use of the Allied governments of Europe, and it is now assumed it had had further large contracts which are or will amount to a large portion of the war.

These contracts, the company says, are among the most important assets of the Aetna Explosives Company, Inc., and

to interfere with their performance would be altogether ruinous to the company.

The plants and other assets, the complaint states, are of such nature that their value depends largely upon the continuance of the defendant company as a going concern, and further adds that if the business were to be interrupted their value would be greatly impaired. Such derangement, the complaint asserts, would also be very detrimental to the public welfare by preventing the delivery of explosives called for by contract with the Allied Powers, and by removing a most important source of supply for explosives necessary to the United States.

The complaint explains that, while the company's property, at a fair valuation, aggregates more than enough to pay all debts, by reason of pending litigation, its credit is so impaired that it is unable to obtain sufficient money to conduct its business in an efficient manner.

Upon the filing of the suit, Stanchfield & Levy, counsel for the Aetna Explosives Company, Inc., submitted the company's answer, in which it admitted all allegations of the complainant.

The company will be continued and later authority probably will be given by the court for certificates so that money may be speedily raised. Quick funds are needed for the payment of employees and purchase of materials. The lawyers representing interests involved are Sullivan & Cromwell, Paul D. Cravath, George Gordon Battle, ex-Senator James A. O'Gorman, ex-Justice George L. Ingraham, and John B. Stanchfield.

DU PONT ACQUIRE NITRATE FIELDS

Du Pont de Nemours & Co. announced to-day they had acquired from the government of Chile two large nitrate fields in the northern part of that country and would begin at once to develop them. Shipments, it is expected, will begin in a year.

A railroad runs from the new du Pont fields, in the Tarapaca district, forty miles to the port of Iquique, whence vessels will come north through the Panama Canal.

It was stated at the du Pont offices that the purchase would increase the annual supply of nitrate of soda for use in the

United States more than one hundred million pounds. Although that is only one-sixtieth of the Chilean output last year and one-tenth of the quantity used by the du Ponts, it is said in the announcement it is deemed ample to meet commercial demands for several years.

A joint stock company with a capital of \$500,000 has been formed to manufacture soda ash in Nagoya, Japan, and land has been acquired at Nagoya harbor to erect factories. An electrochemical company with a capital of \$500,000 will build factories at the river Arakawa for the manufacture of bleaching powder, etc.

The Braemer Air Conditioning Corporation of Philadelphia, announces the opening of a New York office at 90 West Street, with G. P. Uppington as district manager. Mr. Uppington is a graduate engineer with eleven years' practical experience in heating, ventilating, air-conditioning and sales work.

Detailed plans are now completed and in course of execution for rebuilding the burned portion of the plant of The Hydraulic Press Manufacturing Company, in Mount Gilead, Ohio. The plans give the Company facilities for doubling their manufacturing capacity and cover the erection of four new buildings, planned to be in full operation by July 1st.

The First Industrial Exposition and Export Conference will be held at Springfield, Mass., June 23 to 30, 1917. F. H. Page, president of the National Equipment Company, has been made chairman of the General Committee to have charge of the Exposition. John C. Simpson is general manager; address, Eastern States Exposition, Springfield, Mass.

The Rollin Chemical Company, Inc., manufacturers of barium chemicals, with works at Charleston, W. Va., have increased their capital stock from \$1,600,000 to \$2,000,000 and have begun a proposed expansion of their plant. The National Aniline & Chemical Company are their general sales agents.

The German-American Stoneware Works, Jersey City, N. J., has been changed to the General Ceramics Company and its capital increased from \$450,000 to \$2,000,000.

GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

BUREAU OF STANDARDS

Manufacture and Properties of Sand-Lime Brick. WARREN E. EMLEY. Technologic Paper 85. 39 pp. Paper, 10 cents. Processes of manufacture, raw materials, influence of methods of manufacture on properties, properties of brick and tests of product are discussed.

Standard Substances for the Calibration of Viscometers. EUGENE C. BINGHAM AND RICHARD F. JACKSON. Scientific Paper 298, 28 pp. Paper, 5 cents. "The existing data on the viscosity of water has been reviewed in order to correct it so far as possible according to our present knowledge. The viscosity and fluidity of water for every degree Centigrade from 0 to 100

has been calculated. Several liquids suitable for calibration of viscometers are recommended, particularly sucrose solutions of 20, 40, and 60 per cent by weight have been investigated.

"The advantages and disadvantages of expressing viscosity in absolute or specific units have been compared. The suggestion has been made that by expressing all data in terms of the centipoise (the one-hundredth part of the cgs. unit), the absolute viscosity of substances would be practically also the specific viscosity, provided that we take water at 20° as the standard. We find the most probable value for the viscosity of water at 20° C. to be 1.005 cp."

GEOLOGICAL SURVEY

Bismuth in 1915. FRANK L. HESS. From Mineral Resources of the United States, 1915, Part I, pp. 847-848. Published March 13, 1917.

"The only bismuth known to have been produced in the United States during 1915 was that isolated as a by-product by the American Smelting & Refining Co., at Omaha, and by the United States Metals Refining Co., at Grasse, Ind. Both companies refine lead bullion electrolytically and save the bismuth from the anode muds.

"The American Smelting & Refining Co. obtains a considerable quantity of bismuth in flue dusts saved by the Cottrell process

at its Garfield (Utah) plant and from lead bullion from Leadville, Colo. It is said that at Leadville a special furnace is run at times upon ores carrying bismuth, in order that the bismuth may be collected in comparatively concentrated form. Both flue dusts and bullion are shipped to Omaha for treatment.

"The United States Metals Refining Co.'s bismuth-bearing lead comes largely from Tintic, Utah.

"Only one lot of bismuth ore is known to have been sold as such during 1915.

"The imports of bismuth have dwindled almost steadily since 1910, but the reduction in 1915 was undoubtedly much more than normal and was caused by the European war.

"As quoted by the *Engineering and Mining Journal* (New York), the price of bismuth during the year was from \$2.75 to \$3.00 a pound."

Selenium and Tellurium. FRANK L. HESS. From Mineral Resources of the United States, 1915, Part I, pp. 849-850. Published March 13, 1917.

"No new use and no new developments in the selenium industry came to light during 1915. The quantity produced was smaller than in the two preceding years and was made by only two companies, so that the figures may not be given. As usual, the selenium was obtained as a by-product in the electrolytic refining of copper. No tellurium is known to have been produced."

Cobalt in 1915. FRANK L. HESS. From Mineral Resources of the United States, 1915, Part I, p. 805. Published March 22, 1917.

"No cobalt or cobalt minerals are known to have been produced in the United States in 1915, but a certain quantity of cobalt was used by manufacturers of tool steel and in the making of stellite, all of which is thought to have been imported, although no imports of the metal are recorded separately. The price of the metal during the year seemed to range between \$1.25 and \$2.00 a pound."

Molybdenum in 1915. FRANK L. HESS. From Mineral Resources of the United States, 1915, Part I, pp. 807-811. Published March 22, 1917.

"The output of molybdenum ore in 1915 was the largest yet recorded in the United States, but it was still small compared with that of other metals, and only one company, the Arizona Rare Metals Co., seems to have operated steadily through the remainder of the year after having started operations. The production is estimated at 3,498 tons of raw ore. The concentrates and the unconcentrated portion of this ore contained 181,769 pounds of molybdenum and were valued at \$114,866. These figures show a total of nearly 91 tons of metal in ores and concentrates, but the loss in smelting is said to be considerable.

"The world's production in 1915 may be recapitulated thus

COUNTRY	ORE MINERAL	Estimated		Wt. of molybdenum (short tons)
		Quantity (short tons)	percentage of molybdenum (per cent)	
Canada	Molybdenite	14.3	82.2	7.2
New South Wales	Molybdenite	45.8	84.0	19.2
Norway	Molybdenite	87.0	45.0	39.1
Peru	Molybdenite	3.0	49.0	1.5
Queensland	Molybdenite	109.0	54.0	58.8
Spain	Wulfenite	9.1	20.0	5.8
United States	Molybdenite and wulfenite	3,498.0	2.6	31.1

1994

The molybdenum situation is always very hard to define because the demand is small, most buyers are very secretive about the disposition of their purchases or manufactured products, and inquirers for the ore usually surround their dealings with an air of mystery.

The actual use as now developed for the metal are small. In the country the use of molybdenum in tool steel, according to reports received by the Geological Survey from various sources, has decreased. A small quantity is used in electric work, to

supports for tigten filaments in incandescent lamps, in Roentgen ray apparatus, and in small resistance furnaces; number of tons of ore is consumed in making ammonium molybdate for use in chemical work, and a little is used in some textile; but outside of these practically no uses are known. Efforts have been made to use the blue oxide in dyes, but the process is not known to have been adopted on a commercial scale, although stated in certain papers as a prominent use. Statements that molybdenum is used in smokeless powder, gun steels, and armor plate are constantly reiterated and as positively denied.

"Abroad molybdenum is apparently used in steel much more than in this country, and it is commonly accepted that the decided rise in prices was caused by German buyers taking available supplies a few months before the beginning of the war. French and English steel makers are apparently now using the metal to some extent."

Tin in 1915. FRANK L. HESS. From Mineral Resources of the United States, 1915, Part I, pp. 813-818. Published March 22, 1917. "The only tin mined and sold in the United States in 1915 was that produced in Alaska and consisted of 102 tons of metallic tin having a value, at the average price of tin for the year, of \$78,846.

"The United States is the greatest user of tin among the nations, using about 40 per cent of the world's production in 1915, and as it is almost a nonproducer, its imports of tin are, of course, large. Hitherto the imports have been almost wholly of smelted tin, but in the next few years ores may be expected to cut a considerable figure in the imports."

The average monthly price of Straits tin in New York during 1915 was 38.66 cents per pound as compared with 35.70 cents in 1914 and 44.225 cents in 1913.

Titanium in 1915. FRANK L. HESS. From Mineral Resources of the United States, 1915, Part I, p. 821. Published March 22, 1917.

"In 1915 the American Rutile Co. produced 250 short tons of rutile (titanium dioxide) at its plant at Roseland, Va. In the concentration of the rutile, a considerable quantity of ilmenite (titanium iron oxide) was produced as a by-product. The value of both was about \$27,500. For many years the company has been the sole producer of rutile in this country. Attempts have been made by others to develop deposits in Hanover and Goochland counties, Va., and near Magnet, Ark., but no commercial production has yet been made at these places.

"Rutile and menite are both used in making ferrotitanium, which is employed in making steel and cast iron and both are used in making electrodes for arc lamps, but for some reason ilmenite from other sources than the Roseland deposits does not seem to give the same satisfaction. Rutile is the source of titanium for making cyprotitanium for use in brass and other copper bearing alloys and for making potassium titanium oxalate and titanium sulfate for use in dyeing, leather and textiles. A little rutile is also used in ceramics."

Tungsten in 1915. FRANK L. HESS. *Iron, Manganese Resources of the United States, 1915*. Part I, pp. 811-817. Published March 22, 1917.

*The production of tungsten ore in the United States in 1962 was larger than in any previous year and, according to the figures collected by the United States Geological Survey, was equivalent to 0.55 tons of concentrate, carrying 10 per cent WO_3 and valued at about \$2,100,000. The production was more than 500 tons larger than the largest previous output, that of 1930, when 4,841 tons were produced, and was nearly two and a half times as much as the production of 1949, which was 200 tons, valued at \$240,000, only a little more than one-fifth the value of the output in 1962.

The transient production of the 4 seed states by an individual is negligible—less than 1 percent of the total. The latter are pure well-seeds (86.7%), and barren seeds (8.3%).

It is probable that at least 40 tons of the wolframite should be classed as hübnerite, but as no analyses are at hand and as the application of the term hübnerite to the ore mineral has been resented, it will be called wolframite until more definite knowledge is at hand. It seems probable, therefore, that wolframite, the commonest tungsten mineral in most countries, is the least common of the commercially valuable tungsten minerals in this country.

"In 1914 the tungsten industry had been temporarily nearly paralyzed by the beginning of the European war, but before the end of the year \$9 or more a unit was paid for ores carrying 60 per cent WO₃. The demand was not steady, however, and early in 1915 ores were sold as low as \$5.80 a unit, so that many properties were idle. As already stated, large orders from Europe for munitions caused a sudden inflation of prices until \$40 a unit was a common price and more than \$50 a unit was reported. Some producers were tied up with contracts at low prices, and had it not been for this fact values would have shown a still greater total.

"The price of tungsten as metal or ferrotungsten rose from \$1 a pound in January to \$8 a pound in December. In the same period tungsten steels increased in price from 60 or 75 cents to \$3 a pound."

Radium, Uranium and Vanadium. FRANK L. HESS. From *Mineral Resources of the United States, 1915, Part I*, pp. 831-836. Published March 22, 1917.

"Radium, uranium and vanadium are closely connected in occurrence in the principal fields, Colorado and Utah. In 1915 the European war caused a great decline in the production of ores of radium and uranium, but it caused a considerable increase in the production of ores of vanadium.

"According to reports received by the United States Geological Survey, the output was 47,000 tons of ore containing 19.9 tons of uranium and 6.1 g. of radium contained in the carnotite ores produced and 627 tons of vanadium contained in the carnotite ores shipped and in the chemical concentrates from the roscolite ores. The vanadium is arbitrarily valued at \$600,000, though the vanadium in the carnotite ores was practically without value in the ore and the roscolite was all mined and reduced by the owner, the Primos Chemical Co., so that it would probably be difficult for the company itself to assign a value to the ore. The uranium ores were valued at \$93,750, which covered the value of the uranium and radium contained. In 1914 the ores produced contained 87.2 tons uranium oxide (U₃O₈) containing 74 tons of uranium, 22.3 g. radium, and 435 tons vanadium. Nearly all of the ores were from Colorado."

Artificial Gas and By-Products in 1915. C. E. LESHNER. From *Mineral Resources of the United States, 1915, Part II*, pp. 1031-1060. Published March 20, 1917. This report gives a large number of statistics by tables and diagrams, covering the production of various kinds of gas, fuels used, number and kinds of plants operating, and by-products, including coke, tar, ammonia, etc.

The Enrichment of Ore Deposits. WILLIAM HARVEY EMMONS. Bulletin 625, 493 pp. Paper, 45 cents. "This paper is an amplification of an earlier Survey bulletin on the enrichment of sulfide ores (Bulletin 529). It is a discussion of representative deposits, especially of the paragenesis of their ores and of the principles that underlie the processes of enrichment."

DEPARTMENT OF AGRICULTURE

Changes in Fresh Beef during Cold Storage Above Freezing. RALPH HOAGLAND, CHARLES N. MCBRYDE and WILMER C. POWICK. Bulletin 433. Contribution from the Bureau of Animal Industry. 100 pp. Paper, 10 cents. Published February 15. This reports an investigation of commercial practices in the cold storage of beef and the chemical changes in the muscular tissues of the meat while in storage from 14 to 177

days. The factors upon which successful storage depends are also discussed.

Separation and Identification of Food-Coloring Substances. W. E. MATHEWSON. Bulletin 448. Contribution from the Bureau of Chemistry. 56 pp. Paper, 10 cents. Published February 15. This reports methods for chemical detection of about 130 coal-tar colors which are commonly used in dyeing food.

Production of Sugar in the United States and Foreign Countries. PERRY ELLIOTT. Bulletin 465. Contribution from the Bureau of Biological Survey. 40 pp. Paper, 10 cents. Published February 23.

Digestibility of Some Vegetable Fats. C. F. LANGWORTHY AND A. D. HOLMES. Bulletin 505. Contribution from the States Relations Service, 20 pp. Paper, 5 cents. Published February 13. This bulletin records studies of the digestibility of olive oil, cottonseed oil, peanut oil, coconut oil, sesame oil, and cocoa butter, and is primarily of interest to students and investigators of food problems.

Some American Vegetable Food Oils, Their Sources and Methods of Production. H. S. BAILEY. Separate 691, Yearbook, 1916. 18 pp. Paper, 5 cents.

COMMERCE REPORTS—MARCH, 1917

The prospects for petroleum in Bolivia are very promising. (P. 840)

Efforts are being made to develop a paper industry in Australia and New Zealand, using straw as the raw material. (P. 841)

A cement plant in Ontario is now adding feldspar to the raw material, and producing 15 tons per day of 80 per cent potash, besides considerable dust and gases containing 5 per cent potash, and suitable as fertilizer. (P. 903)

A great shortage of ammonium sulfate is reported in Japan. (P. 921)

A process has been devised in Sweden for making textiles for wearing apparel from peat fiber. (P. 971)

A large natural deposit of soda in East Africa is estimated to contain from 50 to 200 million tons of sesquicarbonate of soda. Efforts are being made to market this product. (P. 1011)

Efforts are being made in Canada to develop the smelting of low-grade iron ores. (P. 1047)

Large deposits of clay in New Brunswick have proven suitable for brick, tile and other structural clay products. (P. 1062)

Six large British firms have combined for the manufacture of chemical glass and porcelain ware, each plant concentrating on certain lines. (P. 1080)

A plant is to be erected in Chile for smelting Bolivian tin ores. (P. 1092)

The annual output of tungsten ore from Siam has increased to nearly 1,000,000 lbs. (P. 1118)

The mineral resources and metal industries of the Far East are to be studied thoroughly by a representative of the Bureau of Foreign and Domestic Commerce. (P. 1128)

The seeds of "Sim-sim," an annual plant growing in East Africa, contain a high percentage of an edible oil, used as a substitute for olive oil. (P. 1155)

In the ceramic industry of Japan, various substitutes for kaolin are used, which are essentially aluminum silicates, containing some alkali and iron. (P. 1203)

STATISTICS OF EXPORTS TO THE UNITED STATES

SINGAPORE—978	MOSCOW—1114
Gambier	Cashu
Gum copal	Santonin
Gum damar	Hides
Gutta jelutong	Sugar beet seed
Gutta percha	CBYLON—1160
Mangrove bark	Copra
Rubber	Coconut oil
Tin	Graphite
	Rubber

NEW PUBLICATIONS

By IRVING DeMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

Analysis: Principles of Quantitative Analysis. W. C. BLASDALE. 2nd Ed. 12mo. 402 pp. Price, \$2.50. D. Van Nostrand Co., New York.

Analysis: Standard Methods of Chemical Analysis. W. W. SCOTT and OTHERS. 8vo. 864 pp. Price, \$6.00. D. Van Nostrand Co., New York.

Atoms: JEAN PERRIN. Translated by D. L. HAMMICK. 8vo. 211 pp. Price, \$2.50. D. Van Nostrand Co., New York.

Color and Its Distribution in Printing; How to Estimate Ink. E. C. ANDREWS. 8vo. 42 pp. Price, \$5.00. Inland Printer Co., Chicago.

Engineering Ethics. CARNEGIE LIBRARY OF PITTSBURGH. 17 pp. The Library, Pittsburgh.

Engineer's Manual. W. P. JAMES. 12mo. 444 pp. Price, \$2.50. W. P. James Publishing Co., Louisville, Ky.

Electric and Magnetic Measurements. C. M. SMITH. 12mo. 368 pp. Price, \$2.40. The Macmillan Co., New York.

Electrical Equipment. H. W. BROWN. 8vo. 229 pp. Price, \$2.00. McGraw-Hill Book Co., New York.

German: Exercises in Scientific German. R. M. IHRIG. 12mo. 31 pp. Price, \$0.18. D. C. Heath & Co., New York.

Glass: A Memoir on British Resources of Sands Suitable for Glassmaking. (American Edition.) P. G. H. BOSWELL. 8vo. 92 pp. Price, \$0.50. Longmans, Green & Co., New York.

Hydraulic Power: Service des grandes forces hydrauliques dans la région des Alpes. Vol. 7. 8vo. 481 pp. Imprimerie nationale, Paris.

Inorganic Chemistry: Introduction to Inorganic Chemistry. ALEXANDER SMITH. 3rd Ed. 8vo. 925 pp. Price, \$2.60. The Century Co., New York.

Mechanical Equipment of School Buildings. H. L. ALT. 4to. 111 pp. Price, \$2.50. Bruce Publishing Co., Milwaukee.

Mineralogy: Elements of Mineralogy, Crystallography and Blowpipe Analysis. A. J. MOSHES and C. L. PARSONS. 5th Ed. 8vo. 631 pp. Price, \$3.00. D. Van Nostrand Co., New York.

Nature of Matter and Electricity. D. F. COMSTOCK and L. T. TROLAND. 12mo. 203 pp. Price, \$2.00. D. Van Nostrand Co., New York.

Physical Laboratory Experiments for Engineering Students. S. SHELDON and ERICH HAUSMANN. 12mo. 104 pp. Price, \$1.15. D. Van Nostrand Co., New York.

Roads: Modern Road Construction. A. T. BYRNE. 8vo. 200 pp. Price, \$1.00. American Technical Society, Chicago.

Science: An Introduction to the History of Science. W. LIBBY. 12mo. 288 pp. Price, \$1.50. Houghton, Mifflin Co., Boston.

Steam Turbines. W. S. LILAND. 8vo. 137 pp. Price, \$1.00. American Technical Society, Chicago.

Steam Turbines. J. A. MOYER. 8vo. 468 pp. Price, \$3.50. John Wiley & Sons, New York.

Steam Turbines: A Treatise Covering U. S. Naval Practice. C. J. MEYERS. 246 pp. Price, \$4.50. U. S. Naval Institute, Annapolis.

Sulfuric Acid Tables. H. C. MOORE. 8vo. 36 pp. Price, \$2.00. Commercial Fertilizer, Atlanta, Ga.

Ventilation: Some Modern Methods of Ventilation. R. GRIFFITHS. 12mo. 187 pp. Price, \$3.00. D. Van Nostrand Co., New York.

Water Supply. W. P. MASON. 8vo. 538 pp. Price, \$3.75. John Wiley & Sons, New York.

Wool Industry. P. T. CROOKINGTON. 8vo. 256 pp. Price, \$2.50. A. W. Shaw Co., Chicago.

RECENT JOURNAL ARTICLES

Air Supply for Laboratory Tests. A. W. ALLEN. *Engineering and Mining Journal*, Vol. 103 (1917), No. 13, p. 585.

Analysis of Aluminum Dust. J. E. CLENNELL. *Engineering and Mining Journal*, Vol. 103 (1917), No. 12, pp. 496-499.

Analysis of Nickel Chromium. E. D. KOPPEL. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 6, pp. 319-321.

Bleaching: Details of Bleaching and Finishing. DRUMAN. *Textile World Journal*, Vol. 52 (1917), No. 18, p. 27.

Coefficient Curves for Stack and Oven Gas. T. G. ESTER. In *The Blast Furnace and Steel Plant*, Vol. 5 (1917), No. 4, pp. 147-149.

Comparative Metals Showing Resistances. W. TRINKS. *American Iron Worker*, Vol. 3 (1917), No. 3, pp. 35-36.

Draft in Steam Boiler Practice. J. D. MORGAN. *Power*, Vol. 45 (1917), No. 12, pp. 374-375.

Dyeing Light Weight Wool Dress Goods. L. J. MARY. *Textile World Journal*, Vol. 52 (1917), No. 18, pp. 55-57.

Electric Furnaces: The Regulation of Electric Furnaces. HUBERT WILBY. *The Electric Journal*, Vol. 14 (1917), No. 1, pp. 138-140.

Electric Furnace Practice. T. S. QUINN. *The Electric Journal*, Vol. 14 (1917), No. 4, pp. 140-141.

Electric Furnace Steel. W. H. COMBES. *The Electric Journal*, Vol. 14 (1917), No. 4, pp. 142-143.

Electrical Endosmose. T. R. BRIGGS. *Journal of Physical Chemistry*, Vol. 21 (1917), No. 3, pp. 198-237.

Electrolytic Equivalents of Gases. CARL HERING. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 7, pp. 383-384.

Electrometric Titration of Zinc with Ferrocyanide. F. R. V. BICHOWSKY. *Journal of the Washington Academy of Sciences*, Vol. 7 (1917), No. 6, pp. 141-143.

Exploration of Metalliferous Deposits. W. H. EMMONS. *Mining and Scientific Press*, Vol. 114 (1917), No. 13, pp. 436-440.

Explosives: The Application of Nitro Aromatics in Explosive Industry. J. R. MARDICK. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 6, pp. 303-305.

Fuel: Equivalent Cost of Coal and Oil as Fuel. R. L. WALES. *Power*, Vol. 45 (1917), No. 11, pp. 347-348.

Gas Power: Is Not Gas Power Cheaper than Water Power? H. G. H. TARR. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 7, pp. 373-374.

Gases: Influence of Gases in Cast Metal. J. E. FLETCHER. *The Iron Trade Review*, Vol. 60 (1917), No. 11, pp. 617-621.

Insulation of Boiler Furnaces. JOSEPH HARRINGTON. *Power*, Vol. 45 (1917), No. 13, pp. 410-413.

Iron Ore from Range to Furnace. E. A. ANDERSON. *The Iron Trade Review*, Vol. 60 (1917), No. 12, p. 674.

Linseed Oil: Commercial Linseed Oil. C. D. HOLLEY. *Paint and Varnish Record*, Vol. 12 (1917), No. 5, pp. 24-25.

Metal Mining in Russia. S. H. BALL and BELA LOW. *Engineering and Mining Journal*, Vol. 103 (1917), No. 10, pp. 403-417.

Metallurgy and Electrochemistry at the University of Cincinnati. E. E. THUM and A. W. DAVISON. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 7, pp. 367-373.

Mining Industry of Brazil. F. L. GARRISON. *Mining and Scientific Press*, Vol. 114 (1917), No. 10, pp. 329-333.

Mining Laws of Brazil. HENRY THOMAS. *Engineering and Mining Journal*, Vol. 103 (1917), No. 12, pp. 489-490.

Mining Methods Illustrated in Miniature. W. R. CRANE. *Engineering and Mining Journal*, Vol. 103 (1917), No. 14, pp. 563-566.

Nitrate Industry in Chile. I. B. HOSSAWAY. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 5, pp. 253-259.

Paint and Its Application to Exposed Structures. A. H. SABIN. *Electrical Age*, Vol. 50 (1917), No. 2, pp. 35-36.

Pavements: The Design of Bituminous Pavements. C. C. BROWN. *Municipal Engineering*, Vol. 52 (1917), No. 2, pp. 42-46.

Pitch in Sulfite Pulp. R. E. COOPER. *Paper*, Vol. 20 (1917), No. 1, pp. 13-15.

Pyrites Cinder: Using Pyrites Cinder in Blast Furnaces. W. W. TAYLOR. *The Iron Trade Review*, Vol. 60 (1917), No. 10, pp. 581-582.

Pyrometers: Past, Present and Future. R. P. BROWN. *The Iron Trade Review*, Vol. 60 (1917), No. 12, pp. 671-673.

Recovery Products of Black Liquor. A. H. WHITE and J. D. RUE. *Paper*, Vol. 19 (1917), No. 23, pp. 56-64.

Refractory Linings and Materials No. 1. J. W. HAULM (N.). *Blast Furnace and Steel Plant*, Vol. 5 (1917), No. 4, p. 159.

Refrigerating Troublesman's Job. J. W. MILLER. *Power*, Vol. 45 (1917), No. 8, pp. 249-250.

Röntgen Rays from Sources Other than the Focal Spot in Tubes of the Pure Electron Discharge Type. W. D. COLEMAN and C. N. MARR. *Electrical Review*, Vol. 20 (1917), No. 4, pp. 272-284.

Rubber Works: Electrical Equipment of Rubber Works. W. H. EASTON. *Electrical Age*, Vol. 50 (1917), No. 3, pp. 13-16.

Silica Brick and Some New Uses for Them. W. J. GILLES. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 1, pp. 1-10.

Soils: Effect of Irrigation Water and Manure on the Nitrate and Total Soluble Salts of the Soil. F. S. HERR. In *Proceedings of the American Society of Agronomy*, Vol. 8 (1917), No. 1, pp. 1-10.

Stokers and Condensers in the Power Plant. J. J. GILLES. *The Engineering Magazine*, Vol. 52 (1917), No. 1, pp. 1-10.

Sulfite: Studies in the Sulfite Process. J. J. GILLES. *Power*, Vol. 45 (1917), No. 4, pp. 13-14.

Surface Combustion: Some Results of Recent Work in Surface Combustion. H. J. RAY. *Power*, Vol. 45 (1917), No. 5, pp. 21-22.

Tungar Rectifier. R. E. COOPER. *Electrical Review*, Vol. 20 (1917), No. 1, pp. 909-914.

Water in the Anhydrous Charge. J. W. MILLER. *Power*, Vol. 45 (1917), No. 10, pp. 110-112.

Wood: A Portable Plant for the Distillation of Wood. J. J. GILLES. *Journal of the American Chemical Society*, Vol. 39 (1917), No. 1, pp. 68-70.

Zinc: The Determination of Zinc. J. H. HENDERSON. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 5, pp. 253-259.

MARKET REPORT—APRIL, 1917

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON APRIL 20

INORGANIC CHEMICALS

Acetate of Lime.....	100 Lbs.	4 50	@	4.55
Alum. lump ammonia.....	100 Lbs.	4.00	@	4.25
Aluminum Sulfate, high-grade.....	Ton	70.00	@	75.00
Ammonium Carbonate, domestic.....	Lb.	10 1/2	@	11
Ammonium Chloride, white.....	Lb.	18	@	18 1/2
Aqua Ammonia, 26°, drums.....	Lb	5 1/2	@	6 1/2
Arsenic, white.....	Lb.	16 1/2	@	17
Barium Chloride.....	Ton	85.00	@	90.00
Barium Nitrate.....	Lb.	10 1/2	@	11
Barytes, prime white, foreign.....	Ton	30.00	@	40.00
Bleaching Powder, 35 per cent.....	100 Lbs.	3.95	@	4.00
Blue Vitriol.....	Lb.	9 1/2	@	10
Borax, crystals, in bags.....	Lb.	7 3/4	@	8 1/2
Boric Acid, powdered crystals.....	Lb.	12 1/2	@	12 1/2
Brimstone, crude, domestic.....	Long Ton	45.00		
Bromine, technical, bulk.....	Lb.	80	@	1.00
Calcium Chloride, lump, 70 to 75% fused.....	Ton	24.00	@	25.00
Caustic Soda, 76 per cent.....	Lb.	4.80	@	4.85
Chalk, light precipitated.....	Lb.	4 1/2	@	4 1/2
China Clay, imported.....	Ton	18.00	@	30.00
Feldspar.....	Ton	8.00	@	15.00
Fuller's Earth, foreign, powdered.....	Ton	35.00		
Glauber's Salt, in bbls.....	100 Lbs.	62	@	65
Green Vitriol, bulk.....	100 Lbs.	1.10	@	1.15
Hydrochloric Acid, commercial, 18°.....	Lb.	1 3/4	@	1 1/2
Hydrochloric Acid, C. P., conc., 22°.....	Lb.	1 3/4	@	1 7/8
Iodine, resublimed.....	Lb.	3.50	@	3.55
Lead Acetate, white crystals.....	Lb.	14 1/2	@	15
Lead Nitrate.....	Lb.	15 1/4	@	16
Litharge, American.....	Lb.	8 1/2	@	9 1/2
Lithium Carbonate.....	Lb.	1.25		
Magnesium Carbonate, U. S. P.....	Lb.	24	@	26
Magnesite, "Calced".....	Ton	60.00	@	62.50
Nitric Acid, 36°.....	Lb.	6	@	6 1/4
Nitric Acid, 42°.....	Lb.	6 1/2	@	7
Phosphoric Acid, sp. gr. 1.710.....	Lb.	33	@	34
Phosphorus yellow.....	Lb.	1.05	@	1.10
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, casks.....	Lb.	34 1/2	@	36
Potassium Bromide (granular).....	100 Lbs.	1.00	@	1.10
Potassium Carbonate, calcined, 80 @ 85%.....	Lb.	32	@	34
Potassium Chlorate, crystals, spot.....	Lb.	49	@	50
Potassium Cyanide, lump, 98-99 per cent.....	Mixture	1.20	@	1.25
Potassium Hydroxide, 88 @ 92%.....	Lb.	85	@	87
Potassium Iodide, bulk.....	Lb.	2.90		
Potassium Nitrate.....	Lb.	30	@	32
Potassium Permanganate, bulk.....	Lb.	3.65	@	4.75
Quicksilver, flask.....	75 lbs	113.00	@	114.00
Red Lead, American, dry.....	Lb.	10	@	10 1/2
Salt Cake, glass makers'.....	Ton	16.50	@	20.00
Silver Nitrate.....	Oz.	47 1/2	@	
Soapstone in bags.....	Ton	10.00	@	12.50
Soda Ash, 58%.....	100 Lbs.	3.25	@	3.30
Sodium Acetate.....	Lb.	8 1/2	@	9
Sodium Bicarbonate, domestic.....	100 Lbs.	1.90	@	2.00
Sodium Bichromate.....	Lb.	14 1/2	@	15 1/2
Sodium Chlorate.....	Lb.	23 1/2	@	24 1/2
Sodium Fluoride, commercial.....	Lb.	—	@	—
Sodium Hyposulfite.....	100 Lbs.	1.80	@	2.00
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	3.70	@	3.75
Sodium Silicate, liquid, 40° Bé.....	100 Lbs.	1.20	@	1.46
Sodium Sulfide, 30%, crystals, in bbls.....	Lb.	2 1/2	@	2 1/2
Sodium Bisulfite, liquid, 32 s. g.....	Lb.	.01 1/2	@	.01 1/2
Strontium Nitrate.....	Lb.	28	@	30
Sulfur, flowers, sublimed.....	100 Lbs.	3.05	@	3.45
Sulfur, roll.....	100 Lbs.	2.75	@	2.80
Sulfuric Acid, chamber, 66° Bé.....	Ton	29.00	@	30.00
Sulfuric Acid, oleum (fuming).....	Ton	38.00	@	40.00
Talc, American white.....	Ton	10.00	@	12.00
Terra Alba, American, No. 1.....	100 Lbs.	85	@	90
Tin Bichloride, 50°.....	100 Lbs.	17.50		
Tin Oxide.....	Lb.	59	@	60
White Lead, American, dry.....	Lb.	25 1/2	@	26 1/2
Zinc Carbonate.....	Lb.	25	@	27
Zinc Chloride, commercial.....	Lb.	15	@	15 1/4
Zinc Oxide, American process XX.....	Lb.	12 1/4	@	12 1/4
Zinc Sulfate.....	Lb.	6 1/2	@	6 1/2

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	45	@	50
Acetic Acid, 56 per cent, in bbls.....	Lb.	7 1/2	@	8
Acetic Acid, glacial, 99 1/4%, in carboys.....	Lb.	24	@	26
Acetone, drums.....	Lb.	22	@	23

Alcohol, denatured, 180 proof.....	Gal.	70	@	72
Alcohol, grain, 188 proof.....	Gal.	3.02	@	3.03
Alcohol, wood, 95 per cent, refined.....	Gal.	1.00	@	1.02
Amyl Acetate.....	Gal.	4.50	@	4.75
Aniline Oil.....	Lb.	28 1/2	@	30
Benzoin Acid, ex-toluol.....	Lb.	7.50	@	8.00
Benzol, 90 per cent.....	Gal.	58	@	60
Camphor, refined in bulk, bbls.....	Lb.	89	@	90
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	42 1/2	@	45
Carbon Bisulfide.....	Lb.	6	@	6 1/2
Carbon Tetrachloride, drums, 100 gals.....	Lb.	15	@	16
Chloroform.....	Lb.	60	@	61
Citric Acid, domestic, crystals.....	Lb.	74	@	75
Cresosote, beechwood.....	Lb.	2.00	@	2.10
Cresol, U. S. P.....	Gal.	1.25	@	1.30
Dextrine, corn (carloads, bags).....	100 Lbs.	5.30	@	5.54
Dextrine, imported potato.....	Lb.	16	@	17
Ether, U. S. P., 1900.....	Lb.	15	@	20
Formaldehyde, 40 per cent.....	Lb.	14 1/4	@	15
Glycerine, dynamite, drums included.....	Lb.	55	@	56
Oxalic Acid, in casks.....	Lb.	47	@	48
Pyrogallous Acid, resublimed bulk.....	Lb.	3.50	@	
Salicylic Acid.....	Lb.	85	@	90
Starch, cassava.....	Lb.	—	@	—
Starch, corn (carloads, bags) pearl.....	100 Lbs.	4.05	@	4.14
Starch, potato.....	Lb.	14	@	16
Starch, rice.....	Lb.	10	@	12
Flour, sago.....	Lb.	6	@	6 1/2
Starch, wheat.....	Lb.	6 1/4	@	6 1/2
Tannic Acid, commercial.....	Lb.	65	@	75
Tartaric Acid, crystals.....	Lb.	82	@	83

OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	51	@	53
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil, No. 3.....	Lb.	20 1/2	@	21
Ceresin, yellow.....	Lb.	14	@	18
Corn Oil, crude.....	100 Lbs.	14.81	@	14.82
Cottonseed Oil, crude, f. o. b. mill.....	Gal.	1.00	@	1.01
Cottonseed Oil, p. s. y.....	Lb.	15	@	15 1/2
Menhaden Oil, crude (southern).....	Gal.	nominal		
Neat's-foot Oil, 20°.....	Gal.	1.35	@	1.40
Paraffine, crude, 118 to 120 m. p.....	Lb.	6 1/2	@	6 1/2
Paraffine Oil, high viscosity.....	Gal.	29 1/2	@	30
Rosin, "B" Grade, 280 lbs.....	Bbl.	6.00	@	6.10
Rosin Oil, first run.....	Gal.	37	@	
Shellac, T. N.....	Lb.	57	@	58
Spermaceti, cake.....	Lb.	24	@	25
Sperm Oil, bleached winter, 38°.....	Gal.	24	@	nominal
Spindle Oil, No. 200.....	Gal.	24	@	25
Stearic Acid, double-pressed.....	Lb.	17	@	17 1/2
Tallow, acidless.....	Gal.	1.15	@	1.16
Tar Oil, distilled.....	Gal.	30	@	32
Turpentine, spirits of.....	Gal.	52	@	

METALS

Aluminum, No. 1, ingots.....	Lb.	60	@	62
Antimony, ordinary.....	Lb.	34	@	34 1/2
Bismuth, N. Y.....	Lb.	3.10	@	3.15
Copper, electrolytic.....	Lb.	31	@	
Copper, lake.....	Lb.	30	@	31
Lead, N. Y.....	100 Lbs.	91 1/2	@	91 1/2
Nickel, electrolytic.....	Lb.	55	@	56
Platinum, refined, soft.....	Oz.	105.00	@	
Silver.....	Lb.	73 1/2	@	
Tin.....	Lb.	55 1/2	@	
Tungsten (WOs).....	Per Unit	18.00	@	20.00
Zinc, N. Y.....	100 Lbs.	9.50	@	

FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	5.50	@	6.00
Blood, dried, f. o. b. Chicago.....	Unit	4.65	@	
Bone, 4 and 50, ground, raw.....	Ton	32.00	@	33.00
Calcium Cyanamid.....	Unit of Ammonia	—	@	—
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	nominal		
Phosphate, acid, 16 per cent.....	Ton	11.50	@	11.75
Phosphate rock; f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	2.00	@	2.10
Tennessee, 78-80 per cent.....	Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent.....	Ton	3.85	@	3.90
Pyrites, furnace size, imported.....	Unit	nominal		
Tankage, high-grade, f. o. b. Chicago.....	Unit	4.40	@	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

AT EASTON, PA.

Volume IX

JUNE 1, 1917

No. 6

Editor: CHARLES H. HERTY

Assistant Editor: LEOLA E. MARRS

Advertising Manager: M. A. WILLIAMSON

ADVISORY BOARD

H. E. BARNARD, H. K. BENSON, F. K. CAMERON, B. C. HESSE, A. D. LITTLE, A. V. H. MORY, M. C. WHITAKER

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly; single copy, 60 cents.
Price per single copy to American Chemical Society members, 50 cents. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.
Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

All communications should be sent to The Journal of Industrial and Engineering Chemistry.

Telephone: Vanderbilt 1930

35 East 41st Street, New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

The Platinum Situation.....	544
The Willard Gibbs Medal Award.....	544
In the Light of Experience.....	544
The Chemist as a Railway Industrial Agent.....	545
A Regrettable Failure to Cooperate.....	546
Prospective Enlargement of Chemists' Club Building.....	546
An Embarrassment of Riches.....	547
An Advance in Advertising Rates.....	547
Announcement.....	547
The Canadian Chemical Journal.....	548

CHEMICAL INDUSTRY IN CANADA

548

ORIGINAL PAPERS:

Factors Causing Variation in the Yield of Camphor in the Florida Camphor Tree. Samuel C. Hood.....	552
The Chemistry of Wood. I—Methods and Results of Analysis of Some American Species. A. W. Schorger.....	556
The Chemistry of Wood. II—Discussion of Methods and Results. A. W. Schorger.....	561
On the Toxicity to a Wood-Destroying Fungus of Maplewood Creosote and of Some of Its Constituents and Derivatives, Together with a Comparison with Beechwood Creosote. Ernest J. Pieper, S. F. Acree and C. J. Humphrey.....	566
The Determination of Phenol in Crude Carboic Acid and Tar Oils. John Morris Weiss and C. R. Downs.....	569
A Note on Silicon Coated Metal. W. E. Vawter.....	580
The Composition of Menhaden Oil Fatty Acids. E. Twitchell.....	581
Note on the Determination of Strontium and Lithium in Water. S. D. Averitt.....	584
Nitrate Determinations in the Presence of Chlorides. W. F. Gereke.....	585
A Note on the Phenolsulfonic Acid Method for Nitrates in Waters High in Magnesium Salts. M. Starr Nichols.....	586
Levulose the Preponderant Sugar of Apple Juices. John R. Boll, Jr.....	587
The Influence of Calcite Inclusions on the Determination of Organic Carbon in Soils. Edmund C. Shores and Wm. H. Fry.....	588
The Action of Solutions of Ammonium Sulfate on Micro-organisms. R. F. Gardiner and Edmund C. Shores.....	589

LABORATORY AND PLANT:

New Alloys to Replace Platinum. F. A. Fahrenwald.....	590
A Practical Method for Determining the Viscosity of Starch for Mill Purposes. G. M. MacNider.....	597
Fuller's Earth and Its Valuation for the Oil Industry. Theodore G. Richert.....	599
An Apparatus for the Purification of Mercury. Harrison E. Patten and Gerald H. Mains.....	600
Handling Laboratory Solutions by Suction. C. L. Beals.....	603
An Improved Bunsen Diffusion Apparatus. Jerome S. Marcus.....	603

FORMAL OPENING OF THE NEW CHEMICAL LABORATORY, UNIVERSITY OF CINCINNATI:

Presentation of the Building. Robert Hochstetter.....	604
Reply on Behalf of the Department of Chemistry. Lauder W. Jones.....	604
Reply on Behalf of the American Chemical Society. John Uri Lloyd.....	606
The Swing of the Pendulum in Chemistry. Charles H. Herty.....	608
Description of the New Chemical Laboratory, University of Cincinnati.....	611

ADDRESSES:

The Cheap Production of Alcohol. A. M. Breckler.....	612
--	-----

WILLARD GIBBS MEDAL AWARD. CHICAGO SECTION

613

CURRENT INDUSTRIAL NEWS

615

SCIENTIFIC SOCIETIES:

Calendar of Meetings.....	616
Analysis of Spelter.....	621
Division of Industrial Chemistry and Chemical Engineering—Minutes of Business Session, 34th Meeting, A. C. S.....	621
American Institute of Chemical Engineers—North Section—Annual Meeting.....	621
American Leather Chemist Association—Fiftieth Annual Meeting.....	621
Platinum in Jewels.....	621

NOTES AND CORRESPONDENCE

622

PERSONAL NOTES

624

INDUSTRIAL NOTES

625

GOVERNMENT PUBLICATIONS

625

NEW PUBLICATIONS

626

MARKET PRICES

627

EDITORIALS

THE PLATINUM SITUATION

The movement for the conservation of platinum, inaugurated at the recent Kansas City Meeting of the American Chemical Society, is making satisfactory progress. The phrase "conservation of platinum" is accurate, for by conservation is meant not the hoarding but the wise use of resources. In this case it signifies the diversion of large supplies of the precious metal, from decorative but unnecessary use in jewelry, into those chemical industries, such as the sulfuric acid industry, where it is essential. Fortunately the jewelers, in a spirit of patriotism, have endeavored to meet the situation by passing resolutions, printed elsewhere in this issue, pledging themselves to aid in this phase of conservation.

If confirmation of the wisdom and necessity of such conservation were needed it was furnished during the present month by Judge Sheldon Amos, the Munitions expert of the British Commission. At the luncheon given in his honor by the executive council of the National Civic Federation, Judge Amos said: "One of the first things we did, and which must be done in every country under such conditions, was to put a 'stopper' on certain kinds of trade; that is, stop speculation in munitions and army supplies and, in fact, all materials in connection with which there would be danger of the Government being embarrassed by competition. *The first on the list of such materials are the rare metals, notably platinum*" (our italics).

In the light of the appeals by scientific organizations, the testimony of the British expert, and the resolutions of the jewelers, we confess that we are surprised and puzzled by a statement attributed to the Secretary of Commerce. While commending the resolutions of the jewelers, as "wise, patriotic and unselfish action," he is quoted in the *New York Evening Sun*, of May 7, 1917, as saying: "The country will in no way be aided by the cutting down of purchases by the public, and the women of New York would be acting under a false impression if they accept as true the erroneous newspaper statements that they should stop buying platinum jewelry in order to show their patriotism."

Meanwhile, so far as laboratory utensils are concerned, chemists are busily engaged in trying to find suitable substitutes for platinum. The advance in recent years of 500 per cent in the price of platinum makes this search imperative. In this issue we print an article by Dr. Fahrenwald giving the results of tests on "rhotanium." Laboratory ware made of "palau," a palladium-gold alloy, is now being marketed. Mr. Haynes' tungsten-chromium-cobalt alloy, "stellite," presents interesting possibilities, and is being thoroughly tested. To coordinate work in this field, Prof. Bogert, Chairman of the Chemistry Committee of the National Research Council, has appointed Prof. James Lewis Howe, of Washington and Lee University, Lexington, Va., Special Committeeman in charge of substitutes for platinum. The Bureau of Standards is likewise actively at work on this subject. Necessity is still the mother of invention.

THE WILLARD GIBBS MEDAL AWARD

At the meeting of the Chicago Section on May 18, 1917, the Willard Gibbs medal was awarded to Dr. Edward Williams Morley. This event carries pleasure to the hearts of all American chemists. By his painstaking, accurate work on the densities of oxygen and hydrogen, Dr. Morley has made permanently valuable contributions to the very fundamentals of chemistry and has set an example of patience, skill and scientific integrity.

It is, however, not alone as one of our most distinguished chemists that we love to think of him, but also as a man who has endeared himself to all with whom he has ever been associated. Throughout a long life he has preserved always an innate simplicity and loveliness; toward his fellow-man his heart has been always deeply sympathetic, especially toward the younger men. We remember well an incident at an early meeting of the American Chemical Society. Dr. Morley made for us, in answer to a hesitating request, a sketch of a hand blowpipe. Long after the blowpipe had finished its day of usefulness the drawing was preserved as a valued souvenir of the generous response of a great man to the request of a very young chemist.

The Chicago Section is to be congratulated upon this happy occasion and upon the wise decision of its jury of award.

IN THE LIGHT OF EXPERIENCE

President Wilson, in his statement given to the press after signing the selective draft bill, said: "It is not an army we must shape and train for war; it is a nation." In this work of preparation we have just had the aid of the British and French High Commissions. Their visits were made for the avowed purpose of advising us of the mistakes made by their governments at the outbreak of the war. Through the testimony of these officials, both in the private conferences held in Washington and in their public addresses, we have undoubtedly profited greatly. Unfortunately the membership of the Commissions included no chemists who could speak to our people and to the authorities in Washington of early mistakes made as regards the position of their chemists in the plans for modern war. Fortunately abundant evidence exists concerning such errors and their tardy correction. A year passed before England realized that her chemists had rushed to "the front" among the early volunteers. Then began the recall from the spectacular and thrilling scenes of battle to those laboratories and plants, where through their special training they could render greatest service in that critical moment of national peril.

As a nation we would be foolish indeed did we not profit by that experience. If, however, we are so to profit, it is high time for the chemists of the country

to make their united voice heard, regardless of any possible misunderstanding of motive in so expressing themselves. We traveled a little last week and learned some things which gave rise to serious concern that already we may be well advanced in that same path of error, the disastrous effects of which have been so clearly pointed out.

Our military forces are to be raised by two methods: voluntary enlistment is now in daily progress; the selective draft system will soon be inaugurated. Under the volunteer system we found in our very limited journey one research in coke oven practice badly crippled by the absence of its leader, a member of the National Guard, now in service. At another place, a research, bearing probably on the solution of the submarine menace, had been discontinued—the student assistant had enlisted. Such men should not be allowed to enlist: Under the prospective draft system we found a commercial laboratory whose staff of well-trained assistants may be completely taken by the draft and yet that laboratory has been most successful in the construction of high explosives plants. Finally, we have watched closely all authorized statements as to probable exemptions under the draft system and we have as yet found no mention of the chemist.

A census of the chemists has been taken and we are informed that more than eleven thousand have replied, giving the information requested. Is this information to be used simply to secure the extra men who may be needed for the special problems which now confront our very much overworked government chemists? Should it not rather constitute in addition an official reserve for the adequate and uninterrupted output of the greater chemical industry which must immediately arise if this nation is to throw all of its resources into this war?

President Wilson has just said: "The business now in hand is undramatic, practical and of scientific definiteness and precision." This thought recalls a visit we had not long ago from two students of Lehigh University, representing their fellow students in chemistry in that institution. Both were former Plattsburgers and filled with eager enthusiasm for active service in the army, but they were also students in chemical engineering. Their question was—how can we best serve our country? Their final decision was to await the call to the colors by our country, meanwhile to organize their fellow students into groups according to raining, so that in case of need they can promptly offer their services to those industrial chemical plants for which they are best qualified, no matter how menial the work may be. Such a decision was essentially undramatic, thoroughly practical, marked by scientific definiteness and shot through with highest patriotism. It will be interesting to watch the subsequent career of these two young men as indicative of how we, as a nation, have met the problem of best utilizing chemists in this war which has so frequently been characterized as a war of chemists and engineers.

In this connection there is another problem which deserves the most serious consideration of our university executives, and that is, the provision of increased

facilities for instruction in chemical engineering, facilities both as to men and to means. The uncertainty as to student attendance next year, the absence of many professors and the probability of decreased funds have already led many institutions to formulate plans for curtailment of normal university activities. However strong the convictions which led to such contemplated restrictions, it is sincerely to be hoped that the outworking of the policy will not make itself felt in the chemistry courses, especially in the instruction in chemical engineering. On the contrary, it is sincerely to be hoped that ways may be found to increase rather than decrease this particular feature of the university curriculum.

Here again we may find guidance from British thought and conviction. In the *Journal of the Society of Chemical Industry*, Vol. 30, page 247, it was recently pointed out that "the chemists of this country were and are in the position of an army without reserves." That remark applies also to America. In such a war as we are now entering there will be increased work to be carried out at home by chemists in the peaceful arts and in the munition and directly related factories, while large numbers of chemists will be required in active field service. This country should at once proceed to train an adequate "reserve army" of chemists to meet the shortage that will be heavily felt beginning next spring and lasting until the end of the war, indeed until at least five years after peace is declared.

Whether or no that reserve army is to be supplied depends most largely upon the character of university budgets now in the making. The changes in the curricula of many educational institutions which are now being planned to admit of more intensive military training are fundamentally based upon the same necessity which demands increased chemical training. After nearly three years of bloodiest war, with more than five million men in service, and with the accompanying enormous tax on British resources, Sir Robert Hadfield, the President of the Faraday Society, said on March 6, 1917, during a discussion of the training and work of the chemical engineer: "It is most desirable that increased facilities should be given to training chemists to meet those conditions which will arise after the war."

THE CHEMIST AS A RAILWAY INDUSTRIAL AGENT

Congratulations to Mr. V. V. Kelley, the recently appointed industrial agent of the Carolina, Clinchfield and Ohio Railway! And congratulations to that Railway which, by this promotion from the laboratory to the broader executive field, has officially recognized that the chemist contributes as much more than analytical boiler waters and distillate slates or so specifications are met in purchase of coal, lubricating oil and paints, however important such themselves may be. We had this case as another subject mentioned in the constantly increasing *Journal of American Chemical Engineers*.

In itself this promotion is the natural outcome of the broad vision of a chemist as to his possibilities of usefulness to the railroad which employed him and to the country traversed by that railroad. In turn he has always received the generous support of officials in the adequate supply of laboratory equipment, services of assistants and freedom in the working out of his plans for industrial development. While the promotion is therefore perfectly logical, nevertheless it carries with it much food for profitable reflection, both on the part of railway officials and of the chemists in their employ.

This business of pioneering is not new to Mr. Kelsey, for he was the first chemist to be put in charge of an exhibit of natural resources, by a railway company, at the National Exposition of Chemical Industries. We beg to extend best wishes for his success in the new position and confidently predict that through his thorough surveys, interpreted by sound chemical common sense, many new industries will arise. From such industries the country will receive needed finished products, manufactured from raw materials which so long have lain dormant.

A REGRETTABLE FAILURE TO COÖPERATE

During the past two years we have continuously pleaded for coöperation as the most effective means for chemical progress. It has been our pleasure to record many forward-looking movements based primarily upon this rational principle. It is, therefore, with keen regret that we now record a failure to inaugurate an important work in which coöperation was the essential factor. We refer to the matter of coöperation on the part of the chemical industries with the U. S. Bureau of Foreign and Domestic Commerce in the compilation of a fully itemized census of chemicals other than dyestuffs during a typical pre-war fiscal year such as 1913-14. The importance of such a census was discussed in the editorial section of the March 1917 issue of *THIS JOURNAL*.

A committee was appointed by the American Chemical Society to raise \$2000 from the chemical industries. This amount was to be added to a similar sum which the Bureau of Foreign and Domestic Commerce agreed to set aside out of its present appropriations. The joint amount, \$4000, had been estimated by the Bureau as the cost of the preparation of the census from the Treasury records. The census was to be published by the Bureau and to be available to all at the usual price of such government publications—fifteen cents.

In order to raise the required \$2000 from the chemical interests, the committee asked by letter more than one hundred firms to contribute fifty dollars each, believing that sufficient favorable replies would be received to cover fully the amount needed. Any excess was to be returned to the contributors.

The committee's confidence, however, was not justified by the results, as only a little more than half the required amount was raised.

Having failed through this method, it was hoped that the balance might be subscribed by the National Association of Manufacturing Chemists. Its officers replied that as an Association it had no funds which could be used for such a purpose and that they considered this to be a matter for subscription by individual firms.

Loath to give up the effort we again conferred with Dr. Pratt, the Chief of the Bureau, laid the facts before him and urged that in view of the need of such government statistics the work be undertaken solely from government funds. In his courteous reply he pointed out that he would gladly authorize the undertaking if congressional appropriation could be obtained, but that present appropriations did not justify the favoring of the chemical industries with such expenditure of funds, while other industries were freely coöperating financially with the Bureau. The argument was sound, the position reasonable. So ended the effort.

We take pleasure in recording here the list of those who have subscribed to this fund:

The Barrett Company	Madero Brothers
The Calco Chemical Company	Mallinckrodt Chemical Works
Corning Glass Works	Merck & Company
The Dow Chemical Company	National Aniline & Chemical Company
General Chemical Company	National Gum & Mica Company
Globe Soap Company	The New Process Metals Company
Heller & Merz Company	Pfaudler Company
Alcan Hirsch	Chas. Pfizer & Company
Hooker Electrochemical Company	Smith, Kline & French Co.
The Institute of Industrial Research	Solvay Process Company
Eli Lilly & Company	Arthur H. Thomas Company

However deeply we are convinced of the fundamental need of such a census of imports and however important this step might prove as a preliminary to more adequate current statistics for the chemical industries, we do not feel that the raising of this \$2000 is a matter of a house-to-house canvass.

If, therefore, no further interest is developed in the matter, the committee will on June 15th return the subscriptions already made, which subscriptions were originally asked on the condition that the full amount be secured. We still have hopes!

PROSPECTIVE ENLARGEMENT OF CHEMISTS' CLUB BUILDING

The growth of the membership of the Chemists' Club, now numbering nearly fifteen hundred, and the large proportion of non-resident members, give to the record of the annual meeting of that organization on May 2, 1917, national rather than mere local interest.

The reports of its officers showed strength in all the departments of this unique organization. Under the wise and effective leadership of President M. C. Whitaker, the finances have been placed upon a sound basis, and his unanimous re-election for the ensuing year assures the continued growth of the Club and the safe administration of its affairs.

The most striking item in the report of the House Committee was the over-demand for bedrooms in the Club building. This feature of the Club, regarding the wisdom of which there was at first so much skepticism, has proved to be a success far beyond the highest expectations. For the visiting chemist, the isolation of New York Hotel existence has been changed to the more congenial atmosphere of club life. Indeed, so successful has this feature proved that it is seldom there is a vacant room, and many applications for rooms have to be denied.

To meet this condition, the trustees of the Club have, upon the recommendation of the members present at the annual meeting, promptly taken steps to secure by lease or purchase the four-story building adjoining on the west side. The two buildings could easily be thrown into one, and, by slight rearrangement of the annex, twenty-seven extra bedrooms could be provided. It is believed that the negotiations now in progress will be successfully terminated at an early date.

AN EMBARRASSMENT OF RICHES

The opening sentence of the last annual report of Secretary Parsons was as follows: "The growth of the American Chemical Society during the year 1916 has broken all precedents." In support of this statement it was shown that the membership had increased during the year from 7417 to 8355. All who have followed closely the growth of the Society felt that this increase probably would mark the high point in the curve of numbers of members, that 1916 would always be characterized as the "Banner Year" in the Society's growth.

On May 11th we were informed by the Secretary that the Society's membership had increased to 9325, exceeding even at that early date the increase for the entire previous year. What the final showing for 1917 will be is a purely speculative, but highly entertaining and interesting matter. As indicative, however, of the outcome it is extremely interesting to learn that the increase during the past month has been twice as great as during the corresponding period in 1916.

One result of this expansion is the complete upsetting of all estimates of the number of copies of each of the Society's publications which would be necessary to meet current demands. The necessity of such estimates will be readily recognized, especially at this time, in view of the increased cost of materials, labor, etc. Secretary Parsons now finds that it is impossible to supply new members with the early issues of this year, and writes us as follows:

"The half-year membership will begin for members elected after June 1, 1917, that is, dues will be five dollars and the journals will be furnished from July 1, 1917. Of course, all members elected on this basis will be expected to continue as regular members and pay ten dollars covering 1918 dues upon receipt of statement."

In connection with the question of new members we wish that some Local Section would attempt the

following simple experiment: get each member to agree to carry a membership application blank in his pocket for one month, provided he has not prior to the expiration of that month forwarded it to the Secretary filled out with the requisite data for action by the Membership Committee. We are confident that the psychological effect of the constant presence of that paper would result in stimulating initiative in getting new members where in many cases it had not previously existed. Such initiative is all that is needed to increase the membership far beyond the loyal hopes and expectations of even the most optimistic.

AN ADVANCE IN ADVERTISING RATES

At the Urbana Meeting, April, 1916, the Directors passed a resolution urging the Advertising Committee to advance the advertising rates as soon as practicable. In view of impending changes in the management of *THIS JOURNAL* the Committee felt that it would not be wise to make such advances until the new organization was completed and familiar with the details of the work.

At a meeting held on May 7, 1917, the Committee decided that an advance in rates should at once become effective and fixed the amount of the advance at a forty per cent increase over existing rates, providing, of course, that existing contracts should be filled as per contract.

The justification of this advance lay in the marked increase in the circulation of the journals incident to the rapid growth of the membership of the Society; its necessity was made evident by the cost sheets exhibited by the Advertising Manager.

Members of the Society can render valuable aid at this time by using their persuasive powers in holding all former advertisers to their appreciated connection with the Society's publications and by urging the establishment of such connections by those firms which at present do not utilize this valuable medium of publicity.

ANNOUNCEMENT

Beginning with the July issue we shall publish each month a Washington letter. Mr. Paul Wootton, Metropolitan Bank Building, Washington, D. C., has been engaged as our special correspondent. Mr. Wootton is an experienced journalist in thorough touch with matters legislative and scientific. Even under normal conditions, Washington news is of great interest to American chemists, and especially so at the present time when so much activity is centered there and when so many matters of deep concern to chemists are in process of development. Too often these topics are completely overlooked by the busy press correspondents. It is hoped through this monthly letter to furnish our readers with an accurate account of what is taking place in the National Capital of interest to chemists.

THE CANADIAN CHEMICAL JOURNAL

As indicative of the highly stimulated condition of the Canadian chemical industries incident to the war period, we have received the initial number of *The Canadian Chemical Journal*, published at Toronto, Canada, under the same management which founded *The Canadian Engineer*, *The Canadian Textile Journal*, *The Pulp and Paper Magazine*, *The Canadian Woodworker* and other technical publications.

The new journal, to be issued monthly, is "devoted to the chemical and metallurgical interests of Canada." The present issue contains interesting articles on Canadian water powers, the nickel industry of the Sudbury region, potash from Canadian feldspar, chemistry in Canadian woods, etc., and many up-to-date industrial notes. Confidence in the future of the Canadian industry is shown in the following excerpt from one of the leading articles: "Of course the present abnormally high prices of almost all kinds of chemicals make this an attractive field of investment, but it may fairly be

assumed that the natural resources of Canada are such that the Canadian chemical industries will stand the readjustment of peace conditions and that in many of the more important branches they will become permanent. This assumption is based mainly on three factors: First, the enormous water powers of Canada, as yet undeveloped, which are becoming more and more the deciding element in the cheap production of many chemicals—such, for example, as atmospheric nitrogen; second, the mineral deposits of Canada whose extent and variety are as yet scarcely comprehended by our own people; and third, the intelligence and energy of the younger generation of Canadian students, who will naturally turn their talents to the possibilities opened up under the new conditions."

We desire to extend best wishes to the new journal and to predict for it a career of marked usefulness in the industrial chemical life of our neighbors across the almost imperceptible northern border-line.

CHEMICAL INDUSTRY IN CANADA

Address delivered by H. E. HOWE at the 54th Meeting of the American Chemical Society, Kansas City, April 12, 1917

The force with which the importance of chemical industry has been brought home to the world since August 1914 has led to a stock-taking in various countries, and a review of the situation at present, followed by prophecies for the future. The extent to which our complex civilization depends upon chemical products and chemical processes is greater now than at any time in the world's history, and the accomplishments of chemical industry are in many cases so like magic that the popular press seizes upon the spectacular items and frequently overlooks extensive developments in localities which to the ordinary mind seem to lie outside the chemically active countries. We have had German chemists, German research and German efficiency thrust upon us until one can scarcely mention the subject of chemistry without seeming to hear "Die Wacht am Rhein" or "Deutschland über Alles." But Switzerland before the war was producing more dyestuffs per capita than was Germany, notwithstanding the fact that she had to import her raw materials, including coal itself. The world can learn much about advertising from Germany.

Since the war we have heard more of chemical industries in other countries, and steps have been taken to organize thoroughly and bring into a state of co-operation the many successful chemical laboratories, institutions, and individual chemists so as to place the British Empire and the United States upon a firm chemical foundation.

The work confronting chemical industry and chemical engineers in the production of enormous quantities of munitions is almost beyond our imagination. It may be measured in a way by the munitions production record of England. At the beginning of 1917 the production of high explosives was sixty-two times what it was in 1915. British munition factories are now making more heavy gun ammunition every 24 hours than they

manufactured during the entire first year of the war. The monthly output of heavy guns is more than six times what it was during the year 1915. The output of bombs increased thirty-threefold during the single year May 1915 to May 1916. Fourteen times the quantity of machine guns made during the period of August 1914 to August 1915 were made during the year 1915 to August 1916. The daily output of the twelve national projectile factories, which have as yet not developed their total capacity, would fill a train one mile long requiring eight engines to pull it. Where production is speeded up to this extent there are sufficient chemical and chemical engineering problems to tax the resources of a nation, not to mention the important work which England is doing on dyes, optical glass, refractory materials, porcelain, metallurgy, etc.

In France the organization is such that the chemical plants make only what is required for war and of a quantity and quality according to the specifications of the military departments.

You are so well acquainted with the active steps taken in America since 1914 that it is unnecessary for me to emphasize the importance of the work accomplished or under way, but in considering the position of the North American Continent, what attention has been paid to the achievements and potentialities of Canada, our neighbor to the north? Let me tell you something of what is being done there and suggest the possibilities in a brief account of the natural resources.

CHEMICAL PRODUCTION

In one locality, destined to become an electrochemical center of some magnitude, there will ultimately be available approximately 500,000 24-hour horse power. Here acetone is being made by a new process and the production of metallic magnesium in quantity is going forward, the metal being supplied in

bars and also in the variety of powders so necessary on the battlefields to-day for star shells. Aluminum, and carbon electrodes are also made, and other chemical products are now under serious consideration as additions to the chemical chain which has been started.

Explosives are, of course, being produced on a large scale and they are of high grade. Trinitrotoluol is produced at one plant by a process involving crystallization from a medium which results in crystals of great uniformity and unusual purity.

Heavy chemicals are produced in sufficient quantities, the plants being located principally in the Province of Ontario. Sufficient potassium chlorate to meet the requirements, together with a considerable supply of phosphorus are produced, utilizing hydroelectric power. There is the usual by-product recovery from coking plants, including ammonia in its various forms. The electric furnace and electrolytic industries are established in Canada, producing bleach, caustic, cyanamide, abrasives and carbides. Ferro-molybdenum is manufactured in the electric furnace, and in many localities the electric furnace has been brought into play in the production of steels.

Steps have been taken, and a large plant is now under construction, for the electrolytic refining of nickel matte produced in Ontario, where we find nickel deposits valued at \$500,000,000, and supplying over two-thirds the world's requirements for nickel.

PHARMACEUTICAL PRODUCTS AND DYES

In pharmaceutical chemistry a large number of the finer preparations are manufactured in Canada. Phenacetin has been produced since the war started, as has also acetyl salicylic acid, otherwise known as aspirin. There is one plant with a capacity of over a ton a day making acetyl salicylic acid, which is possibly due to the fact that the patent situation is not in the same condition as in the United States. Para-amidophenol, so essential in fur dyeing, is being produced. Bismuth salts, iodine preparations, resublimed iodine, iodides and iodoform, are being made in quantities sufficient for domestic use as well as for export. Hydrogen peroxide by the barium process is manufactured in quantity, and many sodium and potassium salts are purified and recrystallized. Alkaloids are prepared, and salvarsan of a grade equal to the best German product is now being prepared commercially.

Aniline, phenol and salicylic acid may be added to the list.

A few dyes are now being made in Canada, but the economic conditions are such as to make it improbable that any extension of the work can be carried out.

WOOD PRODUCTS

Hardwood distillation was carried on in Canada previous to the war, but since its beginning new articles have been prepared and refinement of crude materials carried to a greater extent.

The very important pulp industry must be mentioned in passing. At the present rate of expansion and development Canada bids fair to lead in the world's production of pulp in the very near future, if she does not do so already.

ORGANIZATIONS FOR RESEARCH

So much for the material accomplishments which show that considerable is being done. The future would seem to offer much. An Advisory Council on Scientific and Industrial Research has been appointed by the Government, and this Council is about to make a complete inventory of the research men and their facilities throughout the Dominion, of the problems which have been solved, of those upon which work is now being done and of those which merit immediate attention. Immediate steps are being taken to assist researchers in the completion of their education and to provide studentships, scholarships and fellowships to encourage the prosecution of scientific research at the educational institutions. The Council, modeled after the Commission in Great Britain, will be generally concerned with research work in Canada and will consider many problems of national importance.

The Forest Products Laboratory is carrying on work similar to that of the Forest Products Laboratory of the United States and has under way work on other problems which are peculiar to Canadian conditions.

The chemists of industrial laboratories are carefully studying the problems pertaining to their particular industry and are endeavoring to plan their work to meet conditions after the war as well as at the present time.

Under the auspices of the Canadian Pacific Railway, Arthur D. Little, Limited, are not only conducting research upon problems, the solution of which would mean much for the Dominion at large, but are also conducting a survey of the natural resources in order that data regarding them may be made quickly available for practical application and for those interested in industrial development work. So far as I am aware the plan of the Canadian Pacific Railway, as put into operation by Lord Shaughnessy, the President and Chairman, is without precedent and indicates, on the part of a public service corporation, a fundamental interest in the country at large, which is not ordinarily ascribed to such an organization.

PLANT UTILIZATION AFTER THE WAR

The question of utilizing plants, which have been erected primarily for war purposes, when peace comes, is receiving the attention of managers and engineers. Some of them strongly advocate the production of nitrates from the air, especially in those locations where plants own their own hydroelectric development works.

CANADIAN RESOURCES

Let us now consider for a moment some of the resources of Canada, which may conservatively form the basis for industries in which chemists and chemical engineers will find their tasks awaiting them.

AGRICULTURE. Agriculture is the greater natural resource of Canada, and while many chemists do not think of agriculture as a natural resource in which they can be interested, it is well known that the products of agriculture frequently claim the chemist's attention. When it is recalled that most of Canada's arable

land lies at a great distance from the present centers of population, it is evident that many problems will present themselves relative to preparing the produce from mixed farming, in order that it may reach the markets in a condition to command a good price. Methods for drying to avoid high freight costs enter in, as well as the establishment of suitable plants in the vicinity of growth to work upon products of agriculture as raw materials. The large corporation farms of the prairies may quite conceivably come to utilize the services which a chemist can render in many departments, from the proper treatment of seed grain and the maintenance of soil fertility and proper rations for stock, to the utilization of the products themselves. The products of agriculture raised in 1913, which is taken as a year not influenced by war prices, were worth nearly \$700,000,000. The production of the Prairie Provinces has increased nearly 600 per cent in the last ten years.

FORESTS—The forests of Canada, while not as extensive as is generally supposed, already form the basis of a great chemical industry in the manufacture of pulp and paper. For the year 1916, nearly \$22,000,000 worth of paper was exported, of which 88 per cent came to the United States. The industry is growing at an enormous rate, the daily production of sulfite pulp approaching 1500 tons daily and that of paper exceeding 2000 tons daily. There is considerable activity in hardwood distillation, and the Forest Products Laboratory is now carrying on softwood distillation experiments hoping to produce oils suitable for use in the oil flotation processes. The west contains some wonderful primitive forests, the Island of Vancouver being a notable example. Here Douglas fir 8 feet in diameter and 300 feet high are to be found, 70 trees to the acre, setting with shallow roots on beds of clay in which glacial boulders are scattered. Timber has been so plentiful there that naturally its values were not appreciated a few years ago, for, in 1876, a lumbering concern refused to pay \$12,500 for 30,000 acres of timber which is still standing and which is now estimated to cut approximately \$300,000,000 worth of timber. There is one timber limit in British Columbia of 72,000 acres of spruce averaging 18 inches in diameter from which about 4,000,000,000 board feet of lumber may be cut, not to mention the pulpwood available.

Reforestation is already receiving careful attention, although the foresters are somewhat divided as to the proper methods. Some believe in planting trees, while others contend that if nature be properly assisted and the young seedlings protected better results are obtained. As in the United States, active measures to prevent and subdue forest fires are receiving consideration. In the Province of Quebec a fire must not be started, excepting for cooking or for warmth, without a government permit, it having been determined that most fires start from bush fires set by settlers when clearing the land. However, 1200 permits were issued last year, and none of the fires got beyond control.

MINERALS The minerals of Canada already yield

an annual income approaching \$200,000,000, and yet vast areas have not been prospected. Many of the deposits are inaccessible at present. There is said to be one deposit of gold-bearing gravel in British Columbia containing 3,000,000,000 cubic yards running 10 cents per yard. Dr. O'Neill, the geologist of the Stefanson expedition, reports an ore body of 6,000,000,000 tons bearing copper distributed through the mass, in a quantity, however, which is not commercially attractive, but the indications are that more careful prospecting will disclose concentrations that may make it feasible in future to commence mining operations on the shores of the Arctic Ocean.

The wonderful mineral resources of Northern Ontario are just being uncovered, while in the vicinity of Cobalt another gold mining camp is already establishing itself.

The nickel deposits in the vicinity of Sudbury, Ontario, are also a part of the great Pre-Cambrian Shield which conforms to Hudson Bay and which continues into practically unexplored portions of the extensive Province of Quebec.

Eighty per cent of the world's supply of asbestos is mined in the Province of Quebec.

Canadian apatite cannot be mined by steam shovel as are the phosphate deposits in Florida, and consequently at present it is not a commercial factor but may be looked upon as a reserve supply of this important substance. Some of the material runs from 83 to 87 per cent phosphate, but it is enclosed in a hard Laurentian rock; that now used for phosphorus compounds of a chemical grade occurs with the mica and may be considered a by-product of this industry.

There are two varieties of soda rock which are interesting as being nearly identical with the German phonolith extensively used in the manufacture of Apollinaris water bottles. It is high in soda, contains very little iron, and approaches a natural fused glass in its composition.

Canadian magnesite has already come to the aid of steel manufacturers in providing a satisfactory refractory and is the source of much of the magnesium now made in the United States as well as all of that made in Canada. I need not emphasize the importance of molybdenum to you, but may say that ferro-molybdenum is being produced from Canadian molybdenum.

A great variety of minerals are to be found in the Dominion, and in the recovery of some of them the chemist and metallurgist, as well as the electrometallurgist, will find much to interest and perplex them.

MISCELLANEOUS—Other resources include fisheries which reach a very large annual business and which may soon become so organized that the chemist will find the problem of waste disposition confronting him. It is interesting to note in passing that thousands of soldiers at the front receive rations of Canadian fish twice a week at the present time, and that in order to encourage the fish industry the Government stands prepared to defray a portion of the expense for transporting fish to the interior of Canada from both the Atlantic and Pacific coasts.

The fur-bearing animals yield an export trade of nearly \$6,000,000, besides furnishing furs to a large domestic market.

WATER POWER

As of especial interest to you, I would emphasize the water powers of Canada, which with other resources may be expected to form the basis of electrochemical and electrometallurgical industries when the population has become sufficiently concentrated and the industries utilizing these products of greater size than at present. The water powers of Canada are more abundant than in any other country. Already nearly a thousand waterfalls are known to be suitable for the generation of electric power, and every expedition into the wilds brings back reports of additional powers which may be developed when the demand comes: 1,712,193 24-hour horse power has been developed, and of the 18,000,000 24-hour horse power which is in sight 8,000,000 is within reach of present markets. In the central portion of Canada 2,000,000 sq. mi. of territory lies at an average elevation of 1500 ft. This area drains into rivers emptying into the St. Lawrence or the sea and affords water power of dimensions difficult to compute. When the potential horse power is considered with respect to area or population, Canada is as favorably situated as other nations, and when horse power per square mile is considered it is well up in the list with other large countries. When it is remembered that 4 lbs. of coal are required on an average to develop one horse power hour under favorable conditions, the amount of coal which would have to be burned to give power equivalent to the Canadian water powers is quite beyond our comprehension. The price at which hydroelectric power is sold varies with the amount of power taken and is ordinarily based on power at the power-house, leaving the cost of transmission to the consumer. Contracts now in force run from some old ones, about to expire, at \$4.50 per horse power year to \$20.00 or more. There are water powers which can be developed at a price per horse power which may make it possible to produce nitrates from the atmosphere in competition with the low prices in Norway where processes have found a home due to cheap power. You may remember that in 1912 Dr. Eyde stated that when the cost of power in Norway reached \$6.00 per horse power year they would be unable successfully to compete with other sources of nitrates.

Transmission would seem to be one of the important problems in connection with hydroelectric power in order to make this energy available in places where economic conditions make it possible to establish electrochemical industries. At present Niagara power is being transmitted 242 miles to Windsor, Ontario. This is the world's record and such a feat enables power to be used over an area of 180,000 sq. mi. We may confidently rely upon the future to provide us with still greater improvements in power transmission.

FUEL

Fuel is always of paramount importance to any sort of industry is under consideration. At present

the domestic fuels in use are principally the coals of eastern and far western Canada, including the anthracite in the vicinity of Bank Head, Alta. The tremendous tonnage of lignite which exists in Alberta, Saskatchewan, and Manitoba has been limited in its use, due to its slacking during drying, but work is now under way which gives promise of making this lignite a satisfactory fuel for power purposes and the prairie provinces thereby more attractive for fields of industry. Research work looking toward the utilization of cereal straws for fuels in certain areas is also under way with considerable promise of ultimate success.

There is also a great quantity of oil shale in New Brunswick and smaller deposits in the western provinces which may be considered reserve supplies of oil.

NEED FOR COÖPERATION OF UNITED STATES WITH CANADA

In closing, I wish to point out the need, the desirability and the advantage of coöperation between Canada and certain forces in the United States. Until Canada can train men to take their places with those now engaged in chemical industries, it is desirable that specialists from the United States seriously consider Canada as a place for their endeavor, in connection with American capital, which will find a favorable field for employment. There is every indication that there will be a preferential duty in favor of Canada of at least 25 per cent so far as the rest of the British Empire is concerned. Therefore, if Americans wish to benefit from this trade arrangement they must manufacture in Canada. The ten years ending with 1913 saw carried out in Canada an industrial program, probably unapproached in other countries of the world, involving an investment of more than \$1,300,000,000 of European capital, for we must remember that, so far as construction is concerned, Canada may be compared with the United States at the close of the Civil War. It is obvious that British, Belgian, Dutch and French capital which formerly found investment in America will not come again for a period of years, while it will be the privilege of the United States to finance new industries the world over. And if America is called upon to aid Canada with specialists and with money she will be doing no more than the "old lion" has done for her, since during the last century nearly \$5,000,000,000 has been loaned to industrial America, principally by Great Britain. Canada will welcome American capital, and her natural resources awaiting economic development offer an attractive and legitimate field for enterprise.

To those of us who are of American ancestry in Canada, it would seem that opportunity is only found at the door of industrial and scientific America but stands with her face averted toward the threshold. Will we keep the key hidden the world goes on down it will we, like a cunning enemy, be invited to look to report on a country whose general policy will stand over a fence, shrank and resistance?

A. E. JAMES, JR.
Chemical Engineer
University of Toronto

ORIGINAL PAPERS

FACTORS CAUSING VARIATION IN THE YIELD OF CAMPHOR IN THE FLORIDA CAMPHOR TREE

By SAMUEL C. HOOD

Received April 10, 1917

The recent increase in the price of camphor gum has renewed the interest in the commercial cultivation of the camphor tree in Florida, and has stimulated the laying down of new plantations as well as the increase of those already under way. Since the methods of production in Florida are widely different from those in Japan and Formosa, and are commercially possible only by the application of special equipment on large areas, it is important that full information be available on the several factors which cause variations in the yield of the gum in the leaves and twigs of the tree.

The present paper is based on observations made on camphor trees growing under various conditions in Florida, during the years 1907 to 1912, at which time the writer was a member of the scientific staff of the Bureau of Plant Industry, United States Department of Agriculture. Samples were taken from nearly 2000 trees over a range of latitude of about 250 miles. This paper presents only the more important results having a direct bearing in the methods of commercial production.

METHODS

The production of camphor in Florida depends upon the planting of the trees in hedges and utilizing either the trimmings, consisting of leaves and small twigs, or by severely pruning the trees each year and distilling the resulting branches and leaves. Such trimming or pruning is done during one of the dormant periods, *i. e.*, during May to June or November to February.

SAMPLES—All tests made during this investigation, unless otherwise stated, were on leaves and twigs of the previous growth taken during the dormant season. Percentages of crude camphor were calculated on the green weight of the material taken at the time of collection.

DISTILLATIONS were made in Remington stills of 5 gal. capacity using about 2 kilos of material in each sample. It was found by repeated tests that with leaves and small twigs of the last growth, no cutting or grinding was needed. In the case of larger wood, the material was cut into small chips crosswise of the grain with a hatchet or power chipping machine constructed for this purpose. The stills were equipped with false bottoms to prevent burning of the charge; about 2 qts. of water were added with each charge, and distillation was carried on over a gas flame. Comparative tests with steam and direct heat distillation showed that better results were secured with the method described, which permitted the more complete recovery of the camphor dissolved in the water.

CONDENSER—The camphor was condensed in a 1-meter Liebig condenser, and was removed to the receiver with the aid of a slender wooden rod and a piece of closely woven cloth moistened with water. It was usually necessary to clean out the condenser

once during the distillation, otherwise so much residue was collected as to make its final removal difficult. The distillate was received in a 200-cc. beaker fitted with a double siphon tube, and the water was returned to the still from time to time.

CRUDE CAMPHOR—After the distillation was complete, and all camphor removed to the receiver, the pasty mass of camphor and oil was moved about with a spatula to gather up separated oil globules and made up into a mass. This was transferred to a folded square of closely woven cotton, moistened with water and placed over the container of a small meat-extract press. The cloth was folded over the mass and the water, with part of the oil, pressed out into the small beaker used for weighing. By means of a capillary pointed pipette the water was drawn out from beneath the oil and the cake of camphor added to it. This mixture of oil and camphor was weighed as crude camphor.

PURE CAMPHOR in the crude was determined as follows: the crude camphor was stored in well-stoppered bottles for at least two weeks until it had recrystallized, forming large crystals about the size of sugar grains. The mass was well mixed with a spatula and about 5 g. weighed into the tubes used for oil extraction.

Spun brass cups about $\frac{3}{4}$ in. in diameter and $2\frac{1}{2}$ in. long were fitted with pressed bags of 100-mesh brass gauze projecting into the cup about one inch. The top of the bag was then trimmed even with the top of the cup and soldered to a $\frac{1}{2}$ -in. band of the same material as the cup. The solder was drawn into a ring forming a shoulder resting on the top of the cup.

The cup and bag were each weighed, and the sample of crude camphor weighed into the bag. The cup was then placed in the pocket of a Babcock milk centrifuge and run at full speed for 5 min. By this process the oil was thrown out into the cup, and from the weight of the cup and oil, the weight of the oil removed could be determined.

CORRECTION—It was found that the amount of camphor dissolved in the oil was nearly uniform for each kind of material distilled. This correction was determined by fractional distillation of considerable samples of crude oil, and the camphor removed from the fraction coming over at 195 to 215° C. by repeated freezing.

DISTRIBUTION OF CAMPHOR IN THE TREE

In order to gain some information on the distribution of camphor in the various parts of the tree, and to determine which portion would provide the most valuable commercial material with the minimum handling costs, distillations were made of the various parts of growing trees 8 to 12 years old.

Leaves and twigs of the two previous growths were collected in May from tree W5. This material consisted of leaves and twigs of the spring growth just matured, and leaves and twigs of the previous summer growth. Of this entire year's growth, 70 per cent

inclined to start first at the top and may develop in a very irregular manner over the tree so that new shoots are continually coming out during the entire summer. It has therefore been found advisable to use only the spring growth for tree-testing purposes.

EFFECT OF PRUNING AND TRIMMING

It has often been recommended that the harvest of commercial plantations be done by pruning the trees severely each year, and at the present time such a method is being used in one instance. Experiments conducted by the writer in 1907 show that this method necessitates the handling of large amounts of wood material of very low camphor yield, and also that even the percentage of camphor in the leaves is reduced in growth of this sort. Tree L1, which was about 10 years old, was cut to the ground in March 1907 and the following May the mature new growth from the stump, consisting of leafy shoots 3 to 5 ft. long, were collected and sorted into several types of material. Tree W225 was very severely headed back in February 1907 and the following May the new growth of a watersprout type was collected and sorted in the same manner as in the case of tree L1. The percentages of camphor in the material from these trees are given in Table 6.

TABLE 6—CAMPHOR PERCENTAGES IN WATERSPROUT GROWTH

	TREE L1		TREE W225		PURE CAMPHOR	
	Crude	Purity	Crude	Purity	L1	W225
LEAVES.....	1.15	75	1.89	74	0.86	1.40
TWIGS: 1 in.....	0.49	85	1.15	80	0.47	0.93
1/4 to 1 in.....	0.06	86	0.31	86	0.05	0.27

In the total growth harvested, the leaves made up about 65 per cent of the weight, and gave a much higher camphor yield than did the twigs and woody material.

Further data on this point were secured from the distillation of material grown in Texas, and consisting of 2-year-old nursery trees. These trees had been cut to the ground at one year old so that the material received consisted of the growth of one year of two growing seasons. The material consisted of 10 entire trees and was sorted into the leaves and twigs of each growing season: 65 per cent of the total was leaves and 53 per cent was leaves of the spring growing season. The tests were made after the spring growth had become dormant. The camphor yields found are presented in Table 7.

TABLE 7—CAMPHOR YIELD (PERCENTAGES) OF TWO YEAR OLD TEXAS TREES

Material	TREES		Crude	Purity	Crude	Pure
	Spring	Summer	Camphor	of	Camphor	Camphor
LEAVES: Spring.....	1.13	76				0.86
Summer.....	1.10	86				0.98
TWIGS: Spring.....	0.69	81				0.56
Summer.....	0.16	81				0.13

In order to gain still further data on the effect of severe pruning on the camphor content of the succeeding growth, one side of each of two trees was severely pruned in January and the following May, after the spring growth was fully dormant, leaves and twigs were collected from the watersprout growth on the pruned sides and also from the normal growth on the unpruned sides of the tree. The results are given in Table 8.

TABLE 8—CAMPHOR YIELD (PERCENTAGES) OF WATERSPROUT AND NORMAL SPRING GROWTH

Tree	Material	NORMAL GROWTH		WATERSPROUT		PURE CAMPHOR	WATER-SPROUT
		Crude	Purity	Crude	Purity	Normal	Normal
W8	Leaves	2.13	76	2.03	71	1.62	1.44
	Twigs	1.60	79	1.69	80	1.26	1.35
W152	Leaves	1.60	73	1.40	71	1.17	0.99
	Twigs	1.40	80	1.18	72	1.12	0.85

These results show that the percentage of camphor is less in the growth of a watersprout nature induced by severe pruning, than in the normal growth of the tree. This is important in connection with commercial operations, since any harvesting method used should supply crude material of a maximum percentage of camphor, and should reduce to a minimum the amount of low-yielding wood material to be handled.

It was found in the earlier hedge trimming experiments that the first cuttings tended to stimulate a heavier growth during the succeeding growing season. In order to determine if this also varied from the normal, the following experiments were carried on with 10-year-old trees which had never been trimmed or pruned. One side of the trees was trimmed with hedge shears to remove the leaves and twigs of the last growth, while the other side was left untrimmed. This trimming was done in January and the following May after the spring growth had become dormant, the leaves and twigs of the spring growth were removed at the last growth scar on both the trimmed and untrimmed sides of the trees. The camphor yields of the different collections are presented in Table 9.

TABLE 9—EFFECT OF TRIMMING ON CAMPHOR YIELD

Tree No.	UNTRIMMED SIDE		TRIMMED SIDE		PURE CAMPHOR	
	Crude	Purity	Crude	Purity	Normal	Trimmed
H852.....	1.38	72	1.90	71	0.99	1.35
S1.....	1.49	80	1.83	75	1.19	1.37
S2.....	1.67	81	1.81	80	1.35	1.45
S3.....	1.60	76	1.63	74	1.22	1.21
S4.....	1.66	81	1.94	76	1.34	1.47
AVERAGE.....	1.56	78	1.82	75	1.22	1.37

These results show that the trimming had caused an increase in the camphor content of the succeeding growth of 14 per cent, but with a slight decrease in the percentage of purity. It is probable that this is due to the more rapid growth caused by the trimming, since it is shown elsewhere in this paper that a very definite relation exists between the rate of growth and the percentage of camphor in the leaves and twigs.

VARIATION DUE TO RATE OF GROWTH

The camphor tree is often planted as a windbreak along the edge of orange groves, and under such conditions, the trees sometimes receive some commercial fertilizer by sending feeding roots into the area fertilized for the orange trees. It also often occurs that a few missing orange trees in a grove are replaced by camphor.

Under these conditions, where the trees receive more or less commercial fertilizer, it has been noted repeatedly that such trees yield a percentage of camphor above the average, and that the growth of the tree was more rapid. In order to find if a relation existed between the rate of growth of the tree and the camphor content, localities were found where a considerable number of trees of uniform age had been planted in a block, and tests were made on trees of different heights

to determine the camphor content. Results obtained from Groves S and H were similar (Table 10).

TABLE 10—VARIATION IN CAMPHOR CONTENT DUE TO RATE OF GROWTH

TREE No.	Height ft.	Purity of Crude		AVERAGE PERCENTAGES	
		Crude Camphor	Purity of Crude	Crude Camphor	Pure Camphor
S3.....	20	1.90	74		
S76.....	20	1.88	78	1.93	75
S5.....	18	2.10	73		1.45
S77.....	8	1.76	69		
S75.....	8	1.76	71	1.75	70
H848.....	14	1.57	71		1.23
H849.....	14	1.63	71		
H845.....	13	1.47	72	1.63	72
H850.....	12	1.85	72		1.17
H847.....	11	1.68	72		
H851.....	10	1.88	70	1.60	71
H844.....	8	1.45	71		1.14
H846.....	8	1.41	70		
H842.....	6	1.57	73	1.52	72
H843.....	6	1.48	72		1.09

These results seem to indicate that the more rapid the growth of the tree, the greater will be the percentage of camphor in the leaves and twigs, as well as the much greater yield of this material. This is important in the handling of commercial plantations, and methods of culture should be used which will force the growth of the tree as much as possible.

VARIATION DUE TO SOIL CONDITIONS

Throughout the entire investigations on Florida camphor, the writer has noted that the character of the soil has much to do with the percentage of camphor in the trees. In order to gain some definite information on this point, a number of trees were tested in selected groves growing in widely different soil conditions. The trees selected were from 8 to 12 years of age, and the total number of trees in the selected groves varied from 50 to 4000 trees. The soil conditions in each grove were as indicated in Table 11.

The highest yield of camphor was secured on the heavy clay soil and the percentages decrease rapidly as the soil becomes more sandy and less retentive of

TABLE 11—CAMPHOR VARIATIONS DUE TO SOIL CONDITIONS
RESULTS IN PERCENTAGES

Grove	No. of Trees Tested	Crude Camphor	Purity of Crude	Pure Camphor
1.....	8	2.14	75	1.61
2.....	5	1.95	74	1.44
3.....	6	1.76	75	1.32
4.....	5	1.62	73	1.18
5.....	8	1.56	76	1.19
6.....	16	1.74	76	1.32
7.....	12	1.58	71	1.12
8.....	16	1.80	76	1.14
9.....	6	1.86	73	1.36
10.....	32	1.88	76	1.41

GROVE 1. A heavy black clay prairie soil of great fertility, and containing a high percentage of vegetable matter.

GROVE 2. A clay loam soil with clay subsoil, and high in vegetable matter. The trees in this grove have also received small amounts of commercial fertilizer.

GROVE 3. A sandy loam with clay subsoil. A much more sandy soil than No. 2.

GROVE 4. Good grade of sandy high pine land with clay about 4 ft. below surface. A soil similar to No. 3 but lower in vegetable matter and with clay deeper down.

GROVE 5. A light sandy soil, low in vegetable matter and with clay about 8 ft. below surface.

GROVE 6. A soil very similar to No. 5, but these trees had received considerable amounts of commercial fertilizer.

GROVE 7. A very light sandy soil with clay 12 ft. below surface.

GROVE 8. Soil formed from old dunes and with almost no vegetable matter. Clay 20 ft. below surface. These trees had received very small amounts of commercial fertilizer.

GROVE 9. White sand similar to No. 8 but no commercial fertilizer had been given to these trees. Trees were badly dwarfed and some yellow in color.

GROVE 10. Same as No. 9 but rather more extreme. Trees very yellow and dwarfed.

moisture. The lowest yields were secured on the soils Nos. 7 and 8, known locally as "sand scrub." No. 6, although located on a light soil, shows a rather high percentage due doubtless to the fact that these trees have been well fertilized with commercial fertilizer and have made good growth. Nos. 9 and 10 seem to be exceptions since although located on an extreme type of sand scrub, they show a high percentage. This is probably due to the very much dwarfed conditions of the trees, and that an abnormal camphor formation has resulted. This same condition has been found frequently on this class of soil where no fertilizer is applied.

From the commercial standpoint, the data presented in Table 11 is very important, and shows that it is essential that a good grade of soil be secured for camphor culture. Taking the yield of hedge trimmings as 10,000 lbs. per acre per year, the difference in yield of crude camphor between Grove 1 and Grove 8 would be 64 lbs. of crude gum, or 48 lbs. of refined camphor per acre. This sum would most certainly pay a good interest on the additional investment in a good grade of land. In fact, however, the difference would be far greater than this, since no account has been taken of the increased growth of the trees under the better conditions.

CONCLUSIONS

From the data presented, the following conclusions can be drawn concerning the factors causing variation in the yield of camphor in commercial plantations under Florida conditions.

I—The maximum yield of camphor is secured from leaves and twigs of the last growth, taken during the dormant season. If allowed to remain on the tree through another growing season, the yield is reduced. The yield from young wood is very small and not to be considered from a commercial standpoint.

II—Severe pruning to induce a watersprout growth gives a low yield in the leaves and small twigs, while the yield of wood so produced is extremely low.

III—The clipping of leaves and twigs, as in hedge trimming, tends to increase the yield of camphor in the next growth.

IV—Any commercial plan of harvesting should provide a material high in yield with a minimum amount of low yielding wood, and with the least injury to the trees.

V—Even slight shade tends to increase the percentage yield of camphor in the leaves, and to reduce the leaf area of the tree.

VI—A considerable yearly variation may be expected under varying climatic conditions and rainfall.

VII—To a considerable extent, the yield of camphor is proportional to the rate of growth, and forcing the growth of the tree will give a large amount of material yielding higher in percentage of gum.

VIII—Higher percentages were secured on the better soils, especially those containing considerable amounts of clay. Under extreme climatic conditions of poverty, the percentage of camphor in the leaves may be rather high.

THE CHEMISTRY OF WOOD

I—METHODS AND RESULTS OF ANALYSIS OF SOME AMERICAN SPECIES

By A. W. SCHÖRGER

Received March 10, 1917

The chemical composition of woods is of considerable importance to many wood-using industries. Of special interest to the pulp and paper industry is the actual yield of cellulose from the different woods as compared with the yield of pulp obtained from them. The various methods of manufacturing chemical pulp destroy from 25 to 35 per cent of the cellulose when based on the cellulose content as found by laboratory analyses. However, knowing the cellulose content of the wood, the manufacturer may strive so to regulate cooking conditions that the yields of pulp will more nearly approach the theoretical.

Spruce wood contains approximately 61.00 per cent cellulose, yet the yield of pulp by the sulfite process rarely exceeds 45 per cent. The remaining 55 per cent of the wood, consisting largely of decomposition products of the lignin, is practically a waste product, and it is believed that a better knowledge of the chemistry of lignocellulose will lead to a much better solution of the problem of its utilization.

The results obtained by the chemical analysis of a wood cannot always be directly correlated with those obtained by processes, such as wood distillation, in which there is a profound decomposition of the wood. The yields of methyl alcohol from softwoods and hardwoods is much smaller than might theoretically be obtained from the percentage of methoxy groups present. This is possibly due to the formation of methyl ethers that remain in the tar. The yield of methyl alcohol from the two classes of woods is not even proportional to the amounts of methoxy groups present, the hardwoods giving decidedly the largest amounts of alcohol. Practically the same condition obtains for the acetic acid.

One of the requirements for the woods used as separators in lead storage batteries is that the amount of organic acids, especially acetic acid formed by the action of the sulfuric acid, be a minimum to prevent destruction of the grids. Analysis has shown that the conifers give the least acid on hydrolysis with sulfuric acid so that the probable value of the various woods may be predicted on this basis. In fact, longleaf pine, giving only 0.76 per cent of acetic acid, has already proved to be very serviceable for separators.

The data available in the literature on the composition of American woods especially are very meagre. Dean and Tower¹ studied the chlorine method of estimating cellulose and determined the cellulose content of several species; and De Chamot² has determined the yields of furfural from a large number of woods. The solution of the wood waste problem appears to lie mainly along chemical lines so that in connection with the industries already utilizing wood by chemical processes a systematic survey of several typical Amer-

ican woods seemed essential. Owing to the highly complex, colloidal nature of wood the results obtained by analysis are not capable of an exact interpretation. A large amount of work will be necessary to secure a correct insight into the true composition of the lignocellulose.

GENERAL COMPOSITION OF WOOD

Wood belongs to the widely distributed class of lignocelluloses of which jute probably represents the purest form. In addition to lignocellulose as the main constituent, hemicelluloses are always present in wood, while resins, gums, tannins, carbohydrates, dyes, ethereal oils, etc., occur as secondary constituents.

Lignocellulose is generally considered to consist of cellulose chemically combined with lignin. Cross and Bevan¹ dissolved jute lignocellulose in zinc chloride-hydrochloric acid solution; on addition of water the greater portion of the lignocellulose was reprecipitated. Since the soluble and insoluble portions showed no difference in their reactions the lignin and cellulose were considered as chemically combined. Several writers have looked upon lignin as an incrusting material,² the combination with the cellulose being purely physical. In support of this view, König and Rump³ have recently published results showing the selective action of certain chemicals. They consider the natural cell membranes to consist of cutin, cellulose and lignin. When thin sections of wood were oxidized with hydrogen peroxide and ammonia only the lignin was removed; further treatment with 72 per cent sulfuric acid removed the cellulose leaving a residue of cutin. Since the residual cellulose plus cutin, and the cutin, still conformed to the cellular structure of the original membrane, it was assumed that the lignin, cellulose and cutin are not chemically but physically combined. Owing to the powerful reagents employed this assumption is scarcely justified.

Lignins are characterized as being carbohydrate derivatives containing methyl, methoxy, formyl and acetyl groups, and consequently have a higher carbon content than cellulose or the hemicelluloses. Lignin is partially soluble in water under pressure,⁴ readily soluble to a greater or lesser extent in dilute acids and alkalies, and is more readily attacked by oxidizing agents than cellulose. The early investigators considered lignin to be a definite compound. Schulze⁵ gave the elementary composition of lignin as 55.55 per cent carbon, 5.83 per cent hydrogen, and 38.62 per cent oxygen. The experiments of Lange⁶ showed that lignin consisted of possibly two substances having a higher carbon content than that previously reported. Isolated lignin has the properties of an acid and the term lignic acid is frequently applied. Lange isolated two lignic acids differing in their solubility toward alcohol. The following analyses were reported:

¹ "Cellulose," p. 114.² This subject is discussed at length in Schwalbe's "Chemie der Cellulose," pp. 451-4.³ "Chemie und Struktur der Pflanzen-Zellmembran," Berlin (1914).⁴ Tausch, *Binder's polytech. J.*, **1890**, 276, 411; König and Sutthof, *Landw. Verst.*, **70** (1900), 402.⁵ *Chem. Zentr.*, **28** (1857), 324.⁶ *Z. physiol. Chem.*, **14** (1890), 15-30, 217-226.¹ *J. Am. Chem. Soc.*, **29** (1907), 1119.² *Am. Chem. J.*, **16** (1894), 224, 611.

		Beech	Oak	Fir
Soluble in Alcohol	C.....	61.47	61.61	61.28
	H.....	5.48	5.47	4.95
Insoluble in Alcohol	C.....	59.04	58.83	60.51
	H.....	5.37	5.15	5.22

It is possible that the two acids may be identical since it was found that by dissolving the material insoluble in alcohol in caustic soda of specific gravity 1.10, precipitating with H_2SO_4 , filtering and washing, the material was then in great part soluble in alcohol.

Streeb¹ isolated from the alkaline liquor of a soda cellulose plant some lignic acids that contained 62.94 to 65.50 per cent C and 5.11 to 5.39 per cent H. The methyl content amounted to 5.78 to 5.08 per cent corresponding to about $\text{C}_{36}\text{H}_{44}\text{O}_{11}$ or $\text{C}_{36}\text{H}_{40}\text{O}_{12}$.

Cross and Bevan,² studying the action of chlorine on lignocellulose, obtained a yellow lignone chloride, $\text{C}_{10}\text{H}_{10}\text{Cl}_2\text{O}_9$, whose properties led them to believe that lignin has a quinone structure. The lignone chloride is readily soluble in a solution of sodium sulfite, a deep reddish purple solution being obtained.

Lignocellulose gives acetic and formic acids on treatment with steam and weak hydrolytic reagents. Oxidation with chromic acid gives about 6 per cent acetic acid. Cross and Tollens³ believe that formyl ($\text{H}.\text{CO}-$) and acetyl ($\text{CH}_3.\text{CO}-$) groups are actually present as such in the wood, while Cross and Bevan believe also in the presence of acetic acid residues ($-\text{CH}_2.\text{CO}-$). Characteristic of lignin is the occurrence of methoxy groups, the estimation of which has been suggested as a means of determining the degree of lignification.⁴

Klason⁵ has assigned to lignin the formula $\text{C}_{10}\text{H}_8\text{O}_{11}$. The reactions of lignin and coniferyl alcohol being analogous in many respects, it is assumed that the lignin is derived from coniferyl alcohol by condensation and oxidation of four molecules of the alcohol.

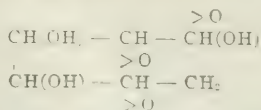
HEMICELLULOSES

Hemicelluloses are defined by Schulze as carbohydrates insoluble in water but soluble in dilute acids and alkalies. They are further characterized by being more easily hydrolyzed by dilute acids than the true celluloses. The principal hemicelluloses in wood are pentosans ($\text{C}_5\text{H}_8\text{O}_4$)_n although small amounts of hexosans ($\text{C}_6\text{H}_{10}\text{O}_5$)_n, such as mannan and galactan, are frequently present. The most widely distributed pentosan is xylan or "wood gum," which, on hydrolysis, gives xylose, usually with small amounts of arabinose. Since on distilling wood with 12 per cent hydrochloric acid, methylfurfural is obtained, in addition to furfural, it is generally assumed that methyl pentosans are also present. The determination of pentosans in wood by means of the furfural reaction is of doubtful accuracy as is pointed out below.

CELLULOSE

Among the various formulae proposed for cellulose that of Green⁶ is widely accepted since it is most in

harmony with the general reactions of the cellulose molecule:



Green's formula may be applied to cotton cellulose but scarcely to wood cellulose. Cotton cellulose gives but a trace of furfural when distilled with 12 per cent hydrochloric acid while from 6 to 17 per cent of furfural may be obtained from wood cellulose, according to the species. This fundamental difference is explained by assigning to wood cellulose an oxy cellulose structure.⁷ König and Huhn⁸ and many other investigators have rejected this explanation as a result of the low yields of furfural obtained from prepared oxy celluloses. Wood cellulose isolated by the chlorine method, in addition to giving furfural, exhibits a strong methoxy reaction.

METHODS FOR THE ANALYSIS OF WOOD

The methods employed in this work were the following:

SAMPLING—A cross-sectional disc about 2 in. thick is taken from the tree about 20 ft.⁹ from the ground



FIG. 1.—SAW WITH GUIDE ARRANGED TO CUT JUST THE WIDTH OF THE SAW SO THAT A PIECE OF WOOD IS CUT ALMOST ENTIRELY INTO SAWDUST

and from this disc two diagonally opposite sectors are split out, the size of the sectors depending upon the diameter of the tree. The material employed for analysis consists of two forms—sawdust and shavings not more than 0.005 in. in thickness. In some cases, especially with very soft woods, a satisfactory sample is best obtained by scraping the wood with a piece of window glass or a cabinetmaker's plane. Some woods work best while wet and others when nearly air dry. The best conditions for a particular species are determined by experiment.

Shavings obtained with a plane should be passed through a grinder having a revolving offset, the resulting fragments being 2 to 3 mm. long and 1 to 2 mm. wide. The material is then screened and all that passes through a No. 20 sieve is discarded. The residual material is thoroughly mixed to secure a uniform sample. The resulting portions of the sample are cut into sections (Fig. 2) and the residual mass

¹ Cross and Bevan, *Cellulose*, 2, 80.

² Bevan and Cross, *Cellulose*, 2, 80.

³ Bevan and Cross, *Cellulose*, 2, 80.

⁴ Bevan and Cross, *Cellulose*, 2, 80.

⁵ Bevan and Cross, *Cellulose*, 2, 80.

⁶ Bevan and Cross, *Cellulose*, 2, 80.

⁷ Bevan and Cross, *Cellulose*, 2, 80.

⁸ Bevan and Cross, *Cellulose*, 2, 80.

⁹ Bevan and Cross, *Cellulose*, 2, 80.

oughly mixed. A portion of the sawdust from coniferous woods is kept in a sealed container (Mason jars are very convenient) for the determination of moisture by the xylol method and the determination of volatile oil, while the remainder, after air-drying, is ground in a mill to pass through a 40-mesh sieve. All the material used for analysis would be in the air-dry form, the moisture content being determined in a separate sample. All results are calculated on the oven-dry basis.

The 40-mesh sawdust is kept in a rubber-stoppered flask so that after the moisture has once been determined the samples taken out for analysis can be easily reduced to the dry weight by calculation.

MOISTURE—Three g. of 40-mesh sawdust are weighed out in a glass-stoppered weighing bottle and dried for 6 hours in an air oven at 105°C . Dry wood is very hygroscopic and should always be weighed in a closed vessel. In the case of coniferous woods the moisture figure also includes most of the volatile oil.

VOLATILE OIL—Twenty-five grams of sawdust from the sealed container are quickly weighed, placed in a 250-cc. Erlenmeyer flask, and 75 cc. of water-saturated xylol added. On distillation the xylol and water distil over together, the distillate being collected in a graduated funnel. The amount of water present can then be read off directly.¹

Ten grams of sawdust are weighed into a tared wide-mouthed, stoppered Erlenmeyer flask. The flask is then provided with a rubber stopper containing a tube extending nearly to the bottom of the flask for the introduction of steam and an outlet tube for connection with a condenser. The flask is heated in an oil bath maintained at 110°C . and steam passed in gently until oil ceases to distil over. This point can be readily ascertained by catching a few cc. of the distillate in a test tube in which case even traces of oil are distinguishable on the surface. When all the oil has been driven over, the stopper is withdrawn and any adhering sawdust is washed down into the flask. Heating the flask in the oil bath is continued until practically all the water is expelled. This operation is greatly facilitated by inserting a tube into the mouth of the flask and applying suction with a water pump. The exterior of the flask is then carefully cleaned and the drying completed in the air oven. The stoppered flask is then weighed after cooling.

In this way the weight of wood substance is obtained, the water and volatile oil having been removed. Since the moisture content of the original sample has been determined by the xylol method, subtracting the combined weight of residual wood substance and moisture from the original weight of the sample gives the amount of volatile oil.

The determination of volatile oil by heating a sample in the oven and subtracting the water found by the xylol method from the resulting total loss in weight usually does not give the true oil content. The "pine oil" of longleaf pine can be quite readily expelled with steam but only partially by heating for a brief period in the oven.

The volatile oil determination may be neglected in the case of only slightly resinous conifers.

WAXES, FATS, RESINS—Three or four grams of 40-mesh sawdust are extracted with ether 4 to 5 hrs. in a Soxhlet extractor, the amount of material extracted being determined by weighing the residue remaining after evaporation of the solvent.

ASH—Five grams of sawdust are incinerated in a shallow platinum dish in the electric muffle at a dull red heat. The contents of the dish are stirred occasionally, if necessary, to insure complete combustion of the carbon. If the combustion is incomplete the carbon will appear as a black suspended material on treatment with dilute hydrochloric acid.

ALKALI-SOLUBLE—Two grams of 40-mesh sawdust are placed in a 250-cc. beaker, 100 cc. of 1 per cent NaOH added, covered with a watch glass, and the beaker placed in a pan of boiling distilled water for exactly one hour, the height of the water in the pan being maintained level with the solution in the beaker by the addition of boiling distilled water. The contents of the beaker are occasionally stirred. The material is then collected in a tared alundum crucible, washed thoroughly with hot distilled water, dilute acetic acid, and water successively, and dried. The difference is the portion soluble in alkali and consists of pentosans, lignin, resin acids, etc.

HOT WATER-SOLUBLE—Two grams of 40-mesh sawdust are digested with 100 cc. of H_2O in a 300-cc. Erlenmeyer flask provided with a reflux condenser. After the water has been boiled gently for 3 hours, the contents are transferred to a tared alundum crucible, washed with hot water, dried and weighed. Duplicate determinations should check within 0.2 per cent.

COLD WATER-SOLUBLE—Two grams of 40-mesh sawdust are placed in a 400-cc. beaker, 300 cc. of water added, and allowed to digest at room temperature with frequent stirring for 48 hours. The sawdust is then transferred to a tared alundum crucible, washed with cold distilled water, dried, and weighed in a weighing bottle.

PENTOSAN AND METHYL PENTOSAN—Two grams of 40-mesh sawdust from coniferous woods (1 g. from hardwoods) are placed in a 250-cc. flask¹ provided with a separatory funnel and attached to a condenser (Fig. II). Add 100 cc. of 12 per cent hydrochloric acid (sp. gr. 1.06) and distil at the rate of 30 cc. in 10 min. The distillate is passed through a small filter before entering the receiver. As soon as 30 cc. of distillate are collected, 30 cc. of HCl are added to the distillation flask and the distillation is continued in this manner until 360 cc. of distillate are collected. To the total distillate, add 40 cc. of filtered phloroglucine solution that has been prepared at least a week previously by heating 11 grams of phloroglucine in a beaker² with 300 cc. of 12 per cent HCl, and after solution has taken place making up to 1500 cc. with 12 per cent HCl. After addition of the phloroglucine, the solution soon turns greenish black. After standing

¹ The flasks are easily made by fusing an outlet tube and funnel to the ordinary all glass wash bottles.

² For details of this method see Forest Service Circular 134.

16 hours¹ the furfural phloroglucide will have settled to the bottom of the beaker. If a drop of the supernatant liquid gives a pink color with aniline acetate paper² the precipitation of the furfural is incomplete. A further amount of phloroglucine solution is then added and the beaker allowed to stand over night as formerly. In no case so far has it been necessary to use more than 40 cc. phloroglucine solution.

The furfural phloroglucide is filtered, using a tared Gooch crucible having a thick asbestos mat and washed with exactly 150 cc. of water. The crucible is then dried for 4 hours in a water oven and weighed in a weighing bottle.

The crucible is placed in a narrow beaker and 20 cc. of 95 per cent alcohol are added to the crucible.

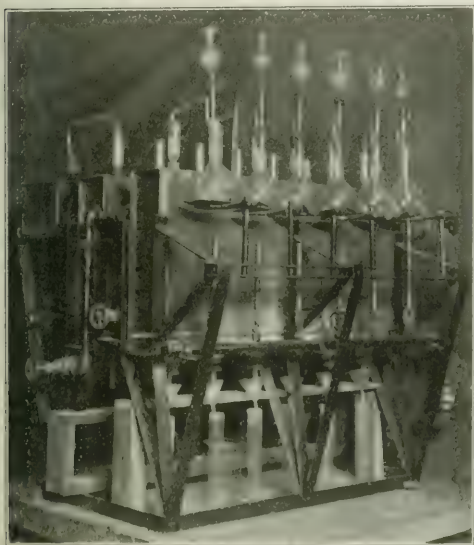


FIG. II.—APPARATUS FOR DETERMINING PENTOSANS AND METHYL PENTOSANS

The beaker is then placed in a water bath maintained at 60° for 10 minutes. The alcohol is removed with a suction pump and the process repeated (usually four or five times) until the alcohol that runs through is practically colorless. The crucible is then dried for 2 hrs. in the water oven and again weighed. The weight of the residual phloroglucide subtracted from the weight of mixed phloroglucides gives the weight of methyl furfural phloroglucide. From the weights of furfural phloroglucide and methyl furfural phloroglucide obtained, the amounts of pentosan and methyl

pentosan present in the wood are calculated from the tables of Kröber and Tollens.¹

CELLULOSE—Two grams of shavings in an alundum crucible are extracted 3 to 4 hrs. with a mixture of equal parts of benzol and alcohol. After evaporation of the solvent the shavings are thoroughly washed with hot water using the suction pump. The moist shavings are then transferred with a pointed glass rod to a 250-cc. beaker, evenly distributed over the bottom, and subjected to a stream (about 40 bubbles per minute for each sample) of washed chlorine gas for half an hour. The end of the tube delivering the chlorine gas should be about 1/2 in. above the shavings. At intervals of 6 to 7 minutes the contents of the beaker are stirred to insure uniformity of chlorination. After the chlorine treatment the shavings are treated with a solution of SO₂ until the chlorine odor disappears, transferred to the alundum crucible, and washed with hot water. The shavings are again returned with the glass rod to the beaker, and 100 cc. of a 2 per cent sodium sulfite solution are added and the beaker, covered with a watch glass, placed in a boiling water bath for 30 minutes. The fibers are then transferred to the crucible and washed with water. The above procedure is seldom sufficient to remove all the lignin, so that the treatment with chlorine and subsequent treatment as outlined above is repeated until the fibers are practically a uniform white. The second and following treatments with chlorine should not be longer than 15 to 30 min. After all the lignin has been removed the fibers are given a final bleaching by adding 20 cc. of a 0.1 per cent solution of potassium permanganate, allowed to stand 10 minutes and rendered colorless with SO₂ solution. The fibers are then thoroughly washed with hot water, dilute acetic acid, then with alcohol and finally with ether, and dried for two hours at 105° in the air oven. When cool, the crucible is weighed in a weighing bottle.

ACID HYDROLYSIS—Approximately 2 g. of 40-mesh sawdust are placed in a 250-cc. Erlenmeyer flask and 100 cc. of 2.5 per cent H₂SO₄ added. The flask is connected with a reflux condenser and the contents are boiled gently 3 hours and then allowed to cool. The interior of the condenser is washed down with a little distilled water and the contents of the flask are transferred to a 250-cc. graduated flask. Distilled water free from carbon dioxide is added to make up to the mark and the solution allowed to stand several hours with frequent shaking, and then filtered.

A wide-mouthed, round-bottomed, 750 cc. flask is provided with a rubber stopper containing (1) a long, pure funnel, (2) a glass tube 1/2 in. in diameter and 12 in. long, closed with a rubber tube, the funnel end extending to the bottom of the flask; and (3) a Soxhlet connecting tube. An 800-cc. condenser is fixed to the end of which is connected a receiver flask containing 100 cc. of water with a beaker to catch and connected with a manometer and pressure pump. A few pieces of porous clay placed in the boiling flask to which is added 100 cc. of the hydrolyzate.

¹ Kröber and Tollens, *J. Prakt. Chem.*, 58, 587. It has been found that if the distillate containing the phloroglucine is heated to 80 to 85° and then allowed to stand for 2 hours, the precipitate of furfural phloroglucide can be filtered off without stirring, for the solution is then very muddy. The latter method, however, is preferable.

² The aniline acetate paper is conveniently prepared by dipping strips of filter paper into aniline acetate. The latter is prepared by adding several drops to a mixture of equal parts of aniline and alcohol until a clear solution is obtained. It is preferable to use two sheets, and a piece of water and once the latter has been used, immerse them again in a red coloration with aniline.

³ *See* *Journal of Industrial and Engineering Chemistry*, Vol. 9, No. 1, 1917, for details of the apparatus and method.

TABLE I—ANALYSIS OF WOODS—RESULTS IN PERCENTAGES ON BASIS OF OVEN-DRY SAMELE

SPECIES	Sample No.	Solubility of Cold Water		Hot Water	Ether	SAMPLE IN 1% NaOH	Hydroxy-acids	Methoxy-groups (CH ₃ O)	Pen-tosan	Methyl Pen-tosan	Cellu-lose	Ash in Cellu-lose	Ash-free Cellu-lose	Pento-san Cellu-lose	Methyl Pento-san Cellu-lose	Volat-ile Oil
		No.	Ash													
Longleaf Pine (<i>Pinus palustris</i>)	11	0.40	7.75	8.20	6.70	24.62	0.70	5.00	7.33	3.48	55.33	0.31	55.02	8.38	1.26	1.60
	12	0.34	5.60	6.03	6.70	21.07	0.93	4.90	7.52	3.29	57.53	0.30	57.23	7.19	1.39	1.12
	13	0.35	5.40	6.78	2.65	18.89	0.62	5.76	7.57	3.87	61.41	0.32	61.09	7.30	1.03	0.87
	20	0.38	6.08	7.57	9.23	24.87	0.79	5.03	7.43	3.67	59.67	0.36	59.31	7.90	0.96	1.16
	Mean,	0.37	6.20	7.15	6.32	22.36	0.76	5.05	7.46	3.60	58.48	0.32	58.16	7.71	1.16	1.30
Douglas Fir (<i>Pseudotsuga taxifolia</i>)	1	0.40	3.79	6.62	0.94	15.82	0.93	4.81	6.03	4.24	61.97	0.21	61.76	5.56	1.26	...
	2	0.37	3.16	6.07	1.00	16.76	1.01	5.17	6.30	4.64	57.00	0.10	56.90
	3	0.35	2.94	6.36	1.11	15.12	1.13	4.88	6.00	4.38	63.08	0.07	63.01
	5	0.38	4.25	6.96	1.02	16.72	1.07	4.92	5.73	4.38	63.82	0.26	63.56	5.12	1.15	...
	Mean,	0.38	3.54	6.50	1.02	16.11	1.04	4.95	6.02	4.41	61.47	0.16	61.31	5.34	1.20	...
Western Larch (<i>Larix occidentalis</i>)	1	0.21	10.45	12.57	0.72	22.07	0.61	5.08	11.15	2.47	58.25	0.24	58.01	9.12	1.40	...
	2	0.32	11.00	12.40	0.74	21.93	0.91	4.91	11.04	2.83	58.71	0.18	58.53	8.41	1.32	...
	3	0.22	8.16	10.08	0.93	19.44	0.76	5.08	10.22	3.14	60.91	0.29	60.62	8.67	1.24	...
	4	0.16	12.83	15.30	0.83	25.11	0.55	5.05	10.78	2.80	53.31	0.49	52.86	9.55	0.90	...
	Mean,	0.23	10.61	12.59	0.81	22.14	0.71	5.03	10.80	2.81	57.80	0.29	57.51	8.94	1.19	...
White Spruce (<i>Picea canadensis</i>)	1	0.33	1.28	1.88	1.95	11.33	1.58	5.31	10.78	3.08	62.61	0.27	62.34	10.26	0.83	...
	2	0.29	0.92	2.28	0.90	11.58	1.57	5.26	10.31	3.52	63.29	0.39	62.90	9.29	0.68	...
	3	0.30	4.5	5.82	0.97	12.75	1.49	5.20	10.04	3.95	60.43	0.25	60.18
	4	0.32	0.82	1.88	1.63	10.63	1.73	5.32	10.42	3.64	61.09	0.30	60.79	9.33	0.66	...
	Mean,	0.31	1.12	2.14	1.36	11.57	1.59	5.30	10.39	3.55	61.85	0.30	61.55	9.63	0.72	...
Basswood (<i>Tilia americana</i>)	1	0.80	2.04	3.84	1.50	23.43	5.78	6.23	19.82	3.72	62.92	0.11	62.81	24.48	1.19	...
	2	0.74	1.63	2.94	1.14	21.61	6.14	6.05	19.54	3.85	62.41	0.14	62.27	23.54	1.46	...
	3	0.96	3.14	5.66	3.39	26.93	5.46	6.11	20.37	3.68	54.66	0.24	54.42	26.61	1.62	...
	4	0.94	1.23	3.22	0.89	21.46	5.41	5.91	19.14	4.16	63.13	0.22	62.91	21.89	1.45	...
	5	0.85	2.55	4.67	2.68	25.38	6.18	5.72	20.79	3.23	63.08	0.22	62.86	24.86	2.00	...
	Mean,	0.86	2.12	4.07	1.96	23.76	5.79	6.00	19.93	3.73	61.24	0.19	61.05	24.28	1.54	...
Yellow Birch (<i>Betula lutea</i>)	1	0.58	2.88	4.21	0.55	20.02	3.99	6.12	24.26	3.18	60.49	0.11	60.38	28.40	1.11	...
	2	0.57	2.58	3.87	0.67	20.20	4.39	6.03	25.40	3.12	61.08	0.12	60.96	29.96	1.32	...
	3	0.54	3.15	4.66	0.54	19.51	3.81	6.19	23.00	2.25	61.82	0.14	61.68	26.55	1.04	...
	4	0.37	2.06	3.15	0.63	19.65	5.02	5.92	25.86	2.21	61.85	0.16	61.69
	Mean,	0.52	2.67	3.97	0.60	19.85	4.30	6.07	24.63	2.69	61.31	0.13	61.18	28.30	1.16	...
Sugar Maple (<i>Acer saccharum</i>)	1	0.46	2.60	4.27	0.29	16.98	4.26	7.22	21.10	2.50	60.78	0.13	60.65	21.08	1.04	...
	2	0.51	2.73	4.22	0.22	17.20	4.25	7.23	21.90	2.14	61.67	0.28	61.39	25.82	1.05	...
	3	0.40	2.94	4.87	0.30	18.04	4.60	7.25	22.21	2.05	60.20	0.33	59.87	25.83	1.00	...
	4	0.38	2.33	4.15	0.20	18.35	4.74	7.28	21.62	2.85	60.48	0.39	60.09	25.20	0.77	...
	Mean,	0.44	2.65	4.36	0.25	17.64	4.46	7.25	21.71	2.39	60.78	0.28	60.50	24.48	0.96	...

above (in the case of hardwoods use 100 cc.). The flask is heated in an oil bath maintained at 85° C., while the pressure is reduced to 40 to 50 mm. When the contents of the flask are reduced to about 20 cc., distilled water is added through the dropping funnel, drop by drop, at the same rate that distillation takes place. When 100 cc. of wash water have been distilled over, the distillate is titrated with $N/100$ NaOH by using phenolphthalein as indicator. If (a) 200 cc., or (b) 100 cc., of solution were taken for distillation, the number of cc. of NaOH used is multiplied by (a) 5/4, or (b) 5/2, respectively, and calculated as acetic acid.

All the distilled water used in this determination should have been recently boiled to expel carbon dioxide.

DETERMINATION OF METHOXY GROUP (CH₃O)—The principle of the methoxy determination depends upon heating the substance to be examined with hydriodic acid, whereby methyl iodide is formed. The methyl iodide is swept from the reaction flask by a current of CO₂ into vessels containing an alcoholic $N/10$ silver nitrate solution, the methyl iodide being decomposed with the formation of silver iodide. When only a few determinations are being made it is preferable to weigh the silver iodide directly.

The silver nitrate solution is prepared by dissolving 17 grams of the salt in 50 cc. of distilled water and making up to a liter with absolute alcohol. The silver nitrate and potassium sulfocyanate solutions are standardized as follows: a known weight (0.5 g.) of pure dry sodium chloride is made up to 250 cc. with distilled water; to 25 cc. portions of the salt solution known volumes (about 15 cc.) of the alcoholic

silver nitrate solution are slowly added with constant stirring. The beakers are placed in the steam bath and heated until all the alcohol is expelled. A few drops of nitric acid are added, the precipitated silver chloride is filtered off, washed, and the filtrate titrated with the solution of potassium sulfocyanate by using 5 cc. of a saturated solution of ferric alum acidified with nitric acid as the indicator. From the weight of sodium chloride employed the strength of the silver nitrate and potassium sulfocyanate solutions can be readily calculated.

Twenty-five cc. of the silver nitrate solution are placed in the absorption bulb. To the heating flask containing 0.30 to 0.35 g. of sawdust are added 15 cc. of hydriodic acid (sp. gr. 1.70). The flask is heated in a glycerin bath kept at 130°. As soon as all the connections are made, a current of washed CO₂ gas is passed through the apparatus at the rate of 45 to 50 bubbles per minute. The heating is continued until the silver nitrate solution, at first milky, has become perfectly clear; this requires about 2 hours. The contents of the absorption bulb are washed into a beaker, made up to 300 cc. and heated on the steam bath until the contents have evaporated to 50 cc. A little nitric acid is added, the AgI filtered off, washed with hot water containing a little nitric acid, and the silver nitrate remaining in the filtrate is titrated with the potassium sulfocyanate solution. One cc. of $N/10$ AgNO₃ is equal to 0.0031 g. of methoxy (CH₃O).

¹ According to Rosanoff and Hill [*J. Am. Chem. Soc.*, **29** (1907), 269] in using the Volhard method no appreciable error is involved in titrating directly solutions containing AgI and AgBr but AgCl must be removed.

RESULTS

The results of the analysis of seven American woods are summarized in the accompanying table. A discussion of the results, as well as a discussion of methods of analysis, is given in the following paper.

FOREST SERVICE
FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN

THE CHEMISTRY OF WOOD

II—DISCUSSION OF METHODS AND RESULTS

By A. W. SCHORGER

Received March 10, 1917

In order to obtain a better understanding of the reasons for adopting the methods given in the previous paper, it is essential to consider both methods and results in detail.

DRYING—The methods of drying wood and other forms of cellulose have received considerable attention. Ost and Westhoff¹ believe that a temperature of 120 to 125° C. is necessary to drive out all hygroscopic moisture, but it is very doubtful if water retained near this temperature should be considered as merely hygroscopic. Winterstein² found that cellulose that had been heated at 105° for 48 hours gave increased amounts of glucose when boiled with dilute sulfuric acid.³ Suringar and Tollens⁴ obtained 2 to 3 per cent less cellulose from jute that had been heated at 97° for 3½ hrs. than from air-dry material. Renker,⁵ however, reached different conclusions. Unbleached sulfite cellulose that had been heated at 105 to 107° for 48 hrs. showed no difference in the yield of cellulose by the chlorine method of Cross and Bevan as compared with the air-dry material. Furthermore, unbleached sulfite cellulose that had been heated several days at 105 to 107° gave no greater yields of glucose than the air-dry cellulose, when hydrolyzed with sulfuric acid. The statement of Hofmann⁶ that unbleached sulfite cellulose lost 8.175 per cent by weight in a vacuum over phosphorus pentoxide and 9.36 per cent by heating at 100° was not confirmed.

Methods of drying should be considered from the standpoint of convenience as well as accuracy. Renker⁷ found that 3 to 4 weeks are required to dehydrate cellulose standing over phosphorus pentoxide, but by employing a vacuum the time could be reduced to about 20 hrs. for air-dry material; if saturated with water a longer time is required. He agrees with Schwalbe⁸ that all hygroscopic moisture can be removed by heating at 105 to 107° C., and in fact this method was employed as the standard of absolute dryness. König and Huhn⁹ also accept this method of drying. Accordingly heating to constant weight at

105 to 107° may be accepted as reliable except in case of special cellulose derivatives, or when it is desired to subject the cellulose to a critical subsequent examination as in the work of Renker.

Some confirmatory experiments were made in the drying of sawdust that showed that the moisture content could be determined in the oven with sufficient accuracy. Samples of sugar maple sawdust were dried in an electric oven at 105 to 107° and in a vacuum desiccator containing fresh concentrated sulfuric acid for three consecutive periods of 7, 6 and 8½ hrs., respectively. The results are given in Table I.

TABLE I—DRYING SUGAR MAPLE SAWDUST BY VARIOUS METHODS

Sample	APPARATUS	Temp. Heating °C	Hours	Sample Grams	LOSS IN WEIGHT Gram Per cent
A	Electric Oven	105-107	7	4.0963	0.2811 6.86
B ₁	Vacuum: Pressure 60 mm.	55	7	3.2229	0.2128 6.60
B ₂	Vacuum: Pressure 30 mm.	57	6	3.2229	0.2181 6.77
B ₃	Vacuum: Pressure 30 mm.	60	8½	3.2229	0.2178 6.76

The sample heated *in vacuo* reached constant weight after 13 hrs. heating; and after 21½ hrs., the total loss in weight is still 0.10 per cent less than that produced by heating for only 7 hrs. in the electric oven. That drying in the oven was more efficient is shown by the following experiment: A sample of spruce sawdust that had been digested with dilute alkali and then thoroughly washed with hot water was placed in the oven for 7 hrs. The sample then weighed 1.6635 g. After remaining in a Hempel vacuum desiccator containing concentrated sulfuric acid for 7 hrs. at 55° C. and 60 mm. pressure the sawdust actually increased in weight 0.0070 g. After an additional heating for 6 hrs. at 57° and 30 mm. pressure the sample weighed 1.6670 g., showing that half of the absorbed moisture was still retained. This is in harmony with previous observations that the various forms of cellulose have a greater affinity for moisture than the reagents ordinarily used for drying.¹

The effect of prolonged heating on the weight of wood in an air oven at 105 to 107° was determined in the case of basswood and longleaf pine sawdust sufficiently fine to pass through a 40-mesh sieve. The weighing bottles used were of about 40 grams weight.

TABLE II—EFFECT OF PROLONGED HEATING ON WEIGHT OF WOOD CORRESPONDING TO 40 MESH

SAMPLE HEATED HEATING HOURS PERIODS	Total	BASSWOOD No. 1		LONGLEAF PINE No. 20	
		Weight Grams	Decrease Per cent	Weight Grams	Decrease Per cent
0	0	3.438		3.11	
3	3	3.481	8.92	3.13	4.54
4	4	3.434	8.89	3.11	4.50
4	11	3.411	8.96	3.11	4.50
10	21	3.403	8.97	3.10	4.50
8	59	3.417	8.93	3.10	4.51
18	144	3.401	8.96	3.08	4.58
18	165	3.406	8.90	3.10	4.50
69	164	3.403	8.97	3.10	4.50
98	289	3.409	8.96	3.10	4.50
194	486	3.406	8.98	3.09	4.54
361	1111	3.404	8.98	3.10	4.50

The results given in Table II illustrate that the weights of both woods remain practically constant during 18 hrs. heating. The trend line for the longleaf pine during the last 108 hrs. heating is 1.25 per cent, while that for the basswood during the same period has only 0.25 per cent. Since the longleaf pine contained only 1 per cent of water the basswood must have been expected.

VOLATILE OIL—Determination of the volatile oil

¹ Journal of Industrial and Engineering Chemistry, 33, 1005 (1917).

¹ Chem. Ztg., 33, 1909, 19.

² Z. physikal. Chem., 17, 1894, 394.

³ Schwalbe, "Chemie der Cellulose," p. 76, and of the opinion that the results observed by Winterstein were due to the presence of considerable amounts of oxycellulose in the material examined.

⁴ Z. anorg. Chem., 9, 1896, 349.

⁵ Bestimmungsmethoden der Cellulose, 1910, p. 16.

⁶ Papier Ztg., 1907, p. 528.

⁷ Bestimmungsmethoden der Cellulose, p. 18.

⁸ Ber., 40, 1907, 144.

⁹ Bestimmung der Cellulose in Holzarten und Compositen, p. 1.

by subtracting from the total loss in weight by drying in the oven at 105 to 107° the amount of moisture found by the xylol method, gives lower results than if the volatile oil is expelled with steam. The "pine oil" in longleaf pine is difficult to expel completely by heating in the oven. Table III presents comparison of the amount of volatile oil obtained from longleaf pine by the two methods.

Longleaf Pine Sample No.	Heating in Oven	Steaming
11	1.20	1.60
12	0.98	1.12
13	0.65	0.87
20	1.47	1.60

WAXES, FATS, RESINS—The portion of the wood soluble in ether, consisting of waxes, fats, resins, etc., was determined in two ways: *viz.*, loss in weight of the wood extracted, and direct weight of the extract after evaporation of the solvent. Only the latter method was found to give reliable results.

ALKALI-SOLUBLE—The action of alkali on wood is not specific. Among the products rendered soluble are lignin, resin acids, pentosans, and other carbohydrates. The action of alkali on hardwoods is much more pronounced than on conifers. This is in part due to the slight solubility of the pentosans of the conifers in alkali as compared with dilute acids.

The action of alkali is determined by Cross and Bevan¹ by boiling the solution containing the material to be examined. This method was not adhered to since the temperature is difficult to regulate and the solution bumps violently. The material should be washed with dilute acetic acid in order to remove the alkali adsorbed.

WATER-SOLUBLE—It is necessary, especially in the case of hot water, to limit the time of extraction as there is no sharp limit to the solubility of wood in boiling water. Klason² found that the wood of the Norway spruce, which had been first extracted with ether to remove resins, etc., lost about 12 per cent of its weight by alternate extraction with alcohol and water.

The chief materials extracted by water are tannins, bitter principles and carbohydrates. The lignin is also partially attacked, methyl alcohol and acetic acid being formed. The method employed would not be applicable to woods containing tannins with phlobaphenes rendered insoluble by boiling.

The water-soluble portion of the western larch was found to consist largely of a galactan, apparently ($C_6H_{10}O_6$)₂₀, that yielded only galactose³ on hydrolysis. Investigation showed that galactans were characteristic of the water-soluble portions of the conifers.

PENTOSAN AND METHYL PENTOSAN—The determination of pentosans and methyl pentosans as worked out by Tollens and his pupils is very accurate so far as duplicating results is concerned. A comparison was made of the two methods of extracting the methyl furfural phloroglucide. Extraction with alcohol in a

beaker¹ at 60°, while more tedious than extraction in a modified Soxhlet as recommended by Ishida and Tollens,² was found to give more accurate results, since by the latter method it is difficult to determine when the extraction is completed.

The weights of wood chosen (2 g. for conifers and 1 g. of hardwoods) give about 0.20 g. mixed phloroglucides. The results of extraction of pure furfural phloroglucide (about 0.20 g.) by Ellett and Tollens³ show that about 0.0014 g. are dissolved during each extraction. A correction cannot be easily applied for this loss since when the table⁴ is examined giving the amounts of arabinose and rhamnose found when known amounts of these sugars were taken, it is seen that the amount of arabinose found is 3 per cent too high and the rhamnose is 1.7 per cent too high. It was also found that 3 to 4 extractions with alcohol as recommended were usually insufficient to give even an approximately colorless extract. In Table IV are given the number of extractions necessary for approximately 0.20 g. of mixed phloroglucides from the various woods and celluloses, using 20 cc. of alcohol:

Douglas Fir	White Spruce	Yellow Birch	Basswood	Sugar Maple	Longleaf Pine	Western Larch
8 to 9	6 to 7	4 to 5	6 to 7	5 to 7	4 to 6	5 to 6

It is evident that appreciable errors will result from a large number of extractions. These errors might be reduced by correcting for the solubility of the furfural phloroglucide were it not for the fact that the amounts of arabinose and rhamnose found by Ellett and Tollens were both too high in spite of the 3 to 4 extractions. In view of these facts it is highly probable that the figures given for methyl pentosans especially are too high.

It would probably be better to give the results as furfural and methyl furfural since wood not only contains true pentosans but apparently "furfuroids." Furthermore the true pentosans are mixtures of at least arabinans and xylans, each giving different amounts of furfural. The source of the methyl furfural is attributed to the presence of methyl pentosans, though no methyl pentose of methyl pentosan has so far been isolated from wood. The various wood celluloses also give considerable amounts of furfural. To account for this behavior Cross and Bevan⁵ have assigned to wood cellulose an oxycellulose structure. König and Hühn⁶ are firmly of the opinion that wood cellulose obtained by the chlorine method contains residual pentosans, and that their method of determining cellulose (digestion with glycerin and sulfuric acid followed by oxidation with hydrogen peroxide and ammonia) is the only one giving true cellulose, *i. e.*, cellulose free from lignin, pentosans, etc. It seems essential, however, to look upon wood cellulose from a broader view-point. Cotton is doubtless the typical cellulose of the ($C_6H_{10}O_6$)_n group, but it is no more reasonable to expect cotton to be the only cellulose in nature than

¹ Ellett and Tollens, *J. Landw.*, **53** (1905), 20.

² *Ibid.*, **59** (1911), 61.

³ *Ibid.*, **53** (1905), 20.

⁴ *Ibid.*, **53** (1905), 22, Table IV.

⁵ "Cellulose," p. 82.

⁶ "Bestimmung der Zellulose, etc.," p. 50.

¹ "Cellulose," p. 117.

² "Beiträge zur Kenntnis der chemischen Zusammensetzung des Fichtenholzes."

³ Schorger and Smith, *This Journal*, **8** (1916), 494-9.

glucose to be the only sugar. It is probable that wood celluloses should be looked upon as definite compounds of hexosans with varying amounts of pentosans. The methoxy reaction may also be due to the presence of small amounts of methyl glucosides or similar derivatives. In this paper *cellulose will be defined as the residue remaining after alternate treatment with chlorine gas and sodium sulfite up to the point where the chlorine-sulfite color reaction, or the Maule reaction, ceases.*

Analysis has shown that the hardwoods can be sharply divided from the conifers by means of the pentosan content of the cellulose. In general, the pentosan content of the hardwood cellulose is greater than that of the original wood, while with the conifers the reverse is true. The pentosan content of the cellulose from the conifers varied from 5 to 10 per cent and that from the hardwoods from 24 to 28 per cent. The methyl pentosan content of the various celluloses is fairly uniform but in the case of the woods there are considerable variations. Douglas fir contains the largest amount of methyl pentosan, the latter amounting to 42 per cent of the total pentosans and methyl pentosans present. In general the conifers contain more methyl pentosan than the hardwoods.

TABLE V—PENTOSAN CONTENT (PERCENTAGES) OF THE CELLULOSES

HARDWOODS		CONIFERS	
Basswood.....	24	Western Larch.....	9
Sugar Maple.....	25	Longleaf Pine.....	8
Yellow Birch.....	28	Douglas Fir.....	5
		White Spruce.....	10
	Mean 26		Mean 8

CELLULOSE—Owing to the work of previous investigators, especially that of Renker,¹ no attempt was made to determine the relative merits of the various methods of determining cellulose, since the chlorine method of Cross and Bevan is the only one that can be applied satisfactorily to woods.

One of the most important points in determining cellulose consists in obtaining the sample in the proper physical condition. Dean and Tower² rasp the wood. This method with dry woods gives mainly dust and even with wet wood the use of the rasp is tedious and unsatisfactory. In the case of such softwoods as basswood very satisfactory material may be obtained from the damp wood with a small sharp plane. However, with most woods the use of the plane is not to be recommended since the resulting material is not of uniform thickness. For the purpose of chlorination the thickness of the material should not exceed 0.005 in. The best method of attaining this result for the harder woods is by the use of a cabinet-maker's scraper which is a thin rectangular steel plate with square edges. Unfortunately, considerable skill is required for the proper use of this tool. Unless the user has had a large amount of experience, dust rather than a fine excelsior is obtained. The wood to be scraped should contain 25 to 30 per cent moisture. Nearly as good results are obtained with broken window glass as with the scraper. Certain soft woods do not scrape well, so that it is necessary in some cases to choose a method by trial. All the material that passes through a 40 mesh sieve should be rejected.

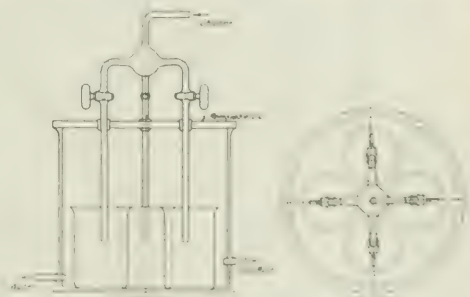
The material placed in beakers was chlorinated in a specially designed apparatus of the type shown in the accompanying figure. This apparatus has several advantages: four samples can be chlorinated at the same time; the material is maintained at a low temperature by means of a constant stream of cold water; the stream of chlorine gas can be regulated by means of the stopcocks; and the excess chlorine is carried off by the water.

At intervals of 6 to 7 minutes the contents of the beakers were stirred with a glass rod and the position of the beakers changed in order to insure uniformity of chlorination. The chlorination was limited to half-hour periods or fractions thereof in the results herewith. A first chlorination of one hour, as usually recommended, is too long in some cases. The number of chlorinations or fractions thereof necessary to obtain the cellulose practically free from lignin were as given in Table VI. The conifers are decidedly more resistant to the action of chlorine than the broad-leaved trees.

TABLE VI—CHLORINATION NECESSARY TO OBTAIN LIGNIN-FREE CELLULOSE

Douglas Fir	White Spruce	Longleaf Pine	Western Larch	Yellow Birch	Basswood	Sugar Maple
4 to 5	4 to 5	4	5	2 to 3	1	1

To determine the freedom of the cellulose from lignin the yellow color produced by chlorine and particularly



APPARATUS FOR CHLORINATING WOOD

the pink to purple-red color which the lignin chloride gives with sodium sulfite were found very sensitive. The latter reaction is considerably more sensitive for broad-leaved woods than for the conifers. Maule's¹ reaction that has been considered a very sensitive test for lignin is the following: the fibers are covered with a dilute solution of potassium permanganate and allowed to stand for several minutes; the permanganate is decolorized and the conjugated diene color, adhering to the fibers, is removed by allowing them to stand in contact with hydrochloric acid of sp. gr. 1.06. After addition of the strong alkali, the fibers are thoroughly washed with water and then a few drops of ammonia are added. In some lignins a pink or deep red coloration is produced. The reaction was found to be sensitive for the hardwoods but not for the conifers in red cedar was very characteristic. When the original wood is green the color produced is a greenish black brown. As the chlorine

¹ "Bestimmungsmethoden der Cellulose," Berlin (1910).

² J. Am. Chem. Soc., 29 (1907), 1125.

³ Beitr. z. chemisch. Botanik, 4 (1900), 168.

tion proceeds, and more and more lignin is removed, the Maule reaction changes from a brown to a dirty brownish gray that is not at all characteristic. Besides being indefinite, this reaction requires considerable time and manipulation. The reaction of the wood fibers with ferric chloride and potassium ferricyanide¹ has a certain qualitative value, but quantitative determinations gave inconsistent results.

The yields of cellulose do not apply to material that is absolutely free from lignin. There are invariably present small fragments of wood that are only partially reduced. However, in obtaining the cellulose absolutely free from lignin the error involved by destruction of the cellulose is out of all proportion to that caused by the presence of the small amount of lignin.

In the original method of Cross and Bevan² the ligneous material was boiled for half an hour with 1 per cent NaOH previous to chlorination. Also the chlorinated fibers were boiled for 5 min. with a solution of sodium sulfite containing 0.2 per cent NaOH. Renker³ states that in both cases the alkali attacks the cellulose and reduces the yield. These statements have been confirmed.

A number of experiments were made to determine the effect of alkali on the yield of cellulose. In the results that follow only the mean results of duplicate determinations are given. As an example of the effect of preliminary digestion with alkali on the yield of cellulose, basswood (Table VII) may be taken as an extreme case.

TABLE VII.—YIELD OF CELLULOSE FROM BASSWOOD

PRELIMINARY TREATMENT:	Chlorinations Hrs.	Yield of Cellulose Per cent
Extracted with Alcohol-Benzol.....	1 1/2, 1 1/2	62.92
Digested with 50 cc. 1% NaOH in water bath for 30 min.....	1 1/2, 1 1/2	59.78
Digested with 100 cc. 1% NaOH in water bath for 60 min.....	1 1/2, 1 1/2	58.25

Renker⁴ working with unbleached sulfite cellulose claims that the chlorination proceeds as smoothly without the preliminary treatment with caustic soda. In the case of basswood that had been digested for 1 hr. with 100 cc. of 1 per cent NaOH, 90 per cent of the fibers showed no lignin reaction (Maule) after the first half hour's chlorination and an additional chlorination of 5 min. was sufficient to remove the lignin entirely. In all cases the preliminary digestion with alkali was found to assist in the removal of the lignin, the time of chlorinating being perceptibly shortened. This is especially true of hardwoods. In the case of the conifers the effect is less evident. As a general rule, however, the treatment results in an appreciable reduction in the yield of cellulose.

YELLOW BIRCH PRELIMINARY TREATMENT:	Chlorina- tions Hrs.	Yield of Cellulose Per cent
Extraction with Alcohol-Benzol for 5 hrs.....	1, 1 1/2, 1 1/2, 1 1/2	61.33
Digested with 100 cc. 1% NaOH in Water Bath for 30 min.....	1, 1 1/2, 1 1/2, 1 1/2	60.69

The effect of the alkali on hardwoods is appreciable even in the case of fairly thick shavings, as is evident in the case of the above experiments in which yellow birch was used.

¹ Cross and Bevan, "Cellulose," p. 134; Sherman, *J. Am. Chem. Soc.*, 19 (1897), 304.

² "Cellulose," p. 95.

³ "Bestimmungsmethoden der Cellulose," p. 44.

⁴ *Loc. cit.*, p. 44.

Douglas Fir was digested both with acids and alkali, the result being that the yield of cellulose was lowered by the acid hydrolysis but not appreciably affected by the alkali in this case.

DOUGLAS FIR PRELIMINARY TREATMENT:	Cellulose Per cent
Extracted with Alcohol-Benzol.....	62.90
Digested with 50 cc. 1% NaOH on Steam Bath for 1 1/2 hour.....	63.10
Boiled with 100 cc. 2.5% H ₂ SO ₄ for 3 hours.....	55.12
Boiled with 100 cc. 2.5% H ₂ SO ₄ for 3 hours (material that would pass through a 40-mesh sieve was used in this case).....	49.00

The effect of addition of alkali to the sodium sulfite solution in the removal of the lignin from Douglas Fir is also illustrated by the following:

DOUGLAS FIR REMARKS:	Chlorinations Hrs.	Cellulose Per cent
All samples were first extracted with Alcohol-Benzol:		
a Sulfite Solution without Alkali.....	1, 1 1/4, 1 1/4	60.53
b Sulfite Solution with 0.2 per cent NaOH.....	1, 1 1/4, 1 1/4	59.35

Since sodium sulfite gives decidedly alkaline solutions owing to hydrolysis it appeared probable that sufficient alkalinity might be developed to attack the cellulose. Bleached sulfite pulp that had been thoroughly washed with hot water and then dried at 60° was employed. In all cases 2 g. of the pulp were heated with 100 cc. of 2 per cent sodium sulfite solution. The moisture in the pulp was determined by heating a separate sample in the air oven at 105° and the samples treated with sodium sulfite were reduced to the dry weight by calculation. After treatment with the sulfite solutions the pulp was washed with dilute acetic acid, hot water, alcohol, and ether in succession and finally dried at 105° for 2 hrs.

BLEACHED SULFITE PULP MANNER OF HEATING:	Period of Heating Hrs.	Loss in Weight Per cent
a Boiling Water Bath.....	1 1/2	1.99
b Steam Bath.....	1	2.03
c Steam Bath.....	2	2.15
d Sample b Second Treatment on Steam Bath.....	2	1.24
e Sample d Third Treatment on Steam Bath.....	2	1.26
f One of samples e given Fourth Treatment on Steam Bath.....	2	1.16
g Second sample e treated with 2% NaHSO ₃ on Steam Bath.....	2	0.57

The loss by the first treatment, approximately 2 per cent, may have been due to the presence of oxycellulose, but the total loss of Sample b (5.69 per cent) by the four treatments can hardly be attributed to this one cause.

Some experiments were made in which the sodium sulfite solution containing the chlorinated wood was boiled for 5 min. In one series the boiling solution was maintained saturated with SO₂ by passing in the gas. In some cases this gave an increased yield of cellulose while in others the yield was slightly lowered.

A marked difference in the rate of removal of the lignin from spruce was noted when a 2 per cent NaHSO₃ solution was used in place of a 2 per cent Na₂SO₃ solution. After each chlorination the fibers were heated with 100 cc. of the sulfite solutions in a water bath for half an hour.

WHITE SPRUCE TREATMENT:	Half hour Chlorinations	Cellulose Per cent
a With Sodium Sulfite.....	3 1/2	63.50
b With Sodium Bisulfite.....	6	62.80

After three chlorinations a did not show the Maule reaction but chlorine colored the fibers a slight yellow. They were accordingly given an additional chlorination of 5 min. In the case of b, after the third chlorination the Maule reaction was brown; after the fifth chlorination the Maule reaction was pale saffron,

and the chlorine reaction decidedly yellow; after the sixth chlorination there was no Maule reaction but chlorine gas gave a pronounced yellow color. The fibers were bleached with potassium permanganate, washed as usual and dried. The cellulose obtained with sodium bisulfite was a dark grayish yellow. The sodium bisulfite solutions were never colored more than a pale yellow. This fact, combined with the large number of chlorinations required, shows that it is essential to have a slightly alkaline reaction in order to render the method efficient.

ACTION OF THE CHLORINE—The rate at which the chlorine is passed into the beaker containing the ligneous material does not appear to have received special attention. Cross and Bevan state that a "slow stream" should be used. It was found that the amount of lignin removed was almost directly proportional to the rate of the introduction of the chlorine as will be seen from the following:

WHITE SPRUCE		YELLOW BIRCH	
Chlorine Bubbles per Min.	Per cent Loss in Weight	Chlorine Bubbles per Min.	Per cent Loss in Weight
52 to 53	12.84	44 to 45	15.31
77 to 78	16.31	72 to 74	21.57
120 to 122	22.58	120 to 122	26.11

According to Cross and Bevan the action of the chlorine is mainly additive and substitutive. It is difficult to conceive of the reaction being other than mainly an oxidation. This is also borne out by the considerable excess of chlorine obtained as hydrochloric acid over the chlorine combined with lignin as found by Heuser and Sieber.¹

The presence of a chlorine carrier such as iodine appears to be without effect. Yellow birch wood was saturated with alcohol containing a few crystals of iodine and after standing a few minutes washed with cold water. After chlorinating at the rate of 64 to 65 bubbles per minute for 30 min. the wood lost 19.83 per cent by weight. When this loss is compared with the losses in the above table it is evident that the iodine did not improve the reaction.

There is an advantage in using a rapid stream of chlorine gas during the first half-hour chlorination, but during succeeding chlorinations, except possibly the second in some cases, the rate should not exceed about 40 bubbles of chlorine per minute. The loss in weight during chlorination was followed by using the regular method for determining cellulose. After heating with sodium sulfite solution the residue was washed with acetic acid, alcohol, and ether. After drying and weighing, the chlorination was repeated. The results obtained appear in Table VIII.

TABLE VIII. ACTION OF CHLORINATION

WESTERN LARCH 40 Chlorine Bubbles per Minute			YELLOW BIRCH 35 to 40 Bubbles per min. after first Chlorination			BIRCH 20 Bubbles per Minute throughout		
Chlori- nation Period	Per cent Loss	Maule Reac- tion	Chlori- nation Period	Per cent Loss	Maule Reac- tion	Chlori- nation Period	Per cent Loss	Maule Reac- tion
1st 1/2 hr.	29.05	Brown	1st 1/2 hr.	8.08	1st 1/2 hr.	71.88		
2nd 1/2 hr.	8.83	Brown	2nd 1/2 hr.	8.08	2nd 1/2 hr.	17.13		
3rd 1/2 hr.	2.65	Saffron	3rd 1/2 hr.	2.73(a)	3rd 1/2 hr.	11.79(a)		
4th 1/2 hr.	1.23	None	4th 1/2 hr.	1.10	4th 1/2 hr.	4.38		
5th 1/2 hr.	0.57	None	5th 1/2 hr.	1.15	5th 1/2 hr.	1.8		
Next hr.	0.94	None	Next hr.	1.48	Next hr.			

(a) Residual cellulose free from lignin

The greatest difficulty of the present method of estimating cellulose lies in judging just how long the

final chlorination should be in order to remove all the lignin and not attack the cellulose. It is probable that the attack of the cellulose consists in the formation of oxycellulose, and possibly hydrocellulose, which are soluble in the sodium sulfite solution. However, Heuser and Sieber¹ by using methylene blue found that practically no oxycellulose was formed up to the point where all the lignin was removed.

For analytical purposes formation of degradation products of the cellulose would be of little consequence providing that they did not pass into solution. All attempts to accomplish this end were negative. The chlorinated fibers, when extracted with 95 per cent alcohol in a Soxhlet extractor to remove the lignin chloride, still lost 1.5 to 2.0 per cent by weight for each half-hour chlorination following the point where the lignin reaction ceased.

The accuracy attainable in determining cellulose is dependent largely on following the same procedure exactly with duplicate determinations. Two half-hour chlorinations followed by treatment with sodium sulfite are by no means equivalent to a one-hour chlorination. Unfortunately check analyses do not necessarily indicate that the correct amount of cellulose has been secured. The results obtained by different chemists, even if following the same directions, may be considered satisfactory if they check within one per cent. The results attainable by experience may be judged from Table IX, the figures being taken at random.

TABLE IX. PER CENT CELLULOSE NOT ASH-FREE

Sample No.	1	2	3	4
Sugar Maple.....	60.75	61.64	60.10	60.58
	60.82	61.70	60.31	60.75
Western Larch.....	57.82	58.66	61.20	53.34
	58.67	58.77	60.82	53.28

The conifers invariably are harder to reduce than the hardwoods and less satisfactory checks may be expected. In spite of the fairly good agreement it is doubtful if the results may be considered as having an accuracy greater than one per cent.

The cellulose content of the various species is quite uniform, especially when the cellulose is calculated on the weight of the wood free from material soluble in hot water and ether. On this basis the figures in Table X were obtained:

TABLE X

SOFTWOODS	Per cent Cellulose	HARDWOODS	Per cent Cellulose
Western Larch	66.40	Sugar Maple	63.43
Longleaf Pine	67.20	Yellow Birch	64.88
Douglas Fir	66.30	Basswood	64.61
White Spruce.....	63.79		

The conifers appear to contain more cellulose than the hardwoods. Occasionally the cellulose content of a tree will be unusually high or low. For example, the cellulose content of basswood No. 2* was only 54.42 per cent; microscopic examination showed no evidence of fungous attack. The analysis was repeated with the same result. On the other hand, the cellulose content of longleaf pine No. 4* is high by several per cent. It was thought that by subtracting the per cent soluble in ether and hot water from a fixed number, say 60, the case of longleaf pine, the cellulose content of the various species could be approximately

¹ *Z. Angew. Chem.*, Unterfeldt, **36** (1913), 805.

with fair accuracy. That marked exceptions may exist is shown by the following:

LOGANAT TEST	Sample No	11	12	13	20
Hot water-soluble.....		8.20	6.03	6.78	7.57
Ether-soluble.....		6.70	6.70	2.65	9.23
Cellulose.....		55.02	57.23	61.09	59.31
Total Percentage.....		69.92	69.96	70.52	76.11

The analysis of Sample No. 20 was checked by several determinations but the cellulose content remained about 5 per cent higher than the average of the remaining three samples, the calculations being based on the wood free from materials soluble in ether and water.

ACID HYDROLYSIS—The method of determining the acids formed by hydrolysis was adopted after considerable experimentation and, while somewhat tedious, very accurate results may be obtained. Duplicate determinations should agree within 0.1 per cent. It is absolutely necessary to use low temperatures and pressures to prevent decomposition of the carbohydrates, etc., by the sulfuric acid before all the volatile acids are removed. The distillate obtained in a blank determination remained pink for 30 seconds, when phenolphthalein was used as the indicator and one drop of $N/10$ NaOH was added, showing that no sulfuric acid had been carried over. The distillate consists mainly of acetic acid. The volatile acids formed from a sample of yellow birch amounted to 4.0 per cent, calculated as acetic acid. After heating on the steam bath with mercuric oxide to destroy formic acid, 3.6 per cent of acid was recovered. It is probable that the formic acid results from decomposition of carbohydrates and not from formyl groups.

It is not yet certain that all the acetic acid is formed by hydrolysis of acetyl (CH_3CO —) groups. A 2-g. sample of yellow birch by digestion with 100 cc. of 2.5 per cent H_2SO_4 lost 31.41 per cent by weight, showing that a decided decomposition is produced. It is accordingly not impossible that a portion of the acetic acid is formed from acetic acid residues ($-\text{CH}_2\text{CO}$ —). The effect of the strength of acid on the yield of volatile acids from yellow birch was the following:

Strength of Sulfuric Acid (Per cent).....	2.5	5.0	10.0
Yield of Acetic Acid (Per cent).....	3.99	4.31	4.53

Small amounts of acetic and formic acids appear to be present in some woods in the free state or at least in very feeble combination. Guijo, a Philippine wood, has a marked corrosive action on metal fastenings. Investigation showed that about 0.2 per cent of acetic and formic acids could be leached from guijo sawdust with cold water. The silver salts in aqueous solution were heated on the steam bath to decompose the silver formate. After filtering off the metallic silver the filtrate deposited beautiful crystals of silver acetate on cooling. The crystals were analyzed as follows:

0.2712 g. silver salt gave 0.1746 g. Ag = 64.38 per cent Ag.

Silver acetate, CH_3COOAg , requires 64.64 per cent Ag.

METHOXY GROUPS—The efficiency of the apparatus and the quality of the acid were tested by using a compound, vanillin, the methoxy content of which is

known: Vanillin, $\text{C}_7\text{H}_7\text{O}_2\text{OCH}_3$, requires 20.40 per cent CH_3O —. Found, 20.26 per cent CH_3O —.

Maple gave the highest yield of methoxy groups. The yields of methyl alcohol obtained by destructive distillation are much lower than would be expected from the methoxy numbers.

YIELD	Birch	Maple	Western Larch
Methyl Alcohol (Per cent).....	1.53(a)	1.94(a)	0.65
Methoxy (Per cent).....	6.07	7.25	4.95

(a) Palmer, *Bull.* 129, U. S. Dept. Agr., Forest Service.

As previously mentioned, the low yields are probably due to the formation of methyl ethers.

FOREST SERVICE
FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN

ON THE TOXICITY TO A WOOD-DESTROYING FUNGUS OF MAPLEWOOD CREOSOTE AND OF SOME OF ITS CONSTITUENTS AND DERIVATIVES, TOGETHER WITH A COMPARISON WITH BEECHWOOD CREOSOTE¹

By ERNEST J. PIEPER, S. F. ACREE AND C. J. HUMPHREY

Received March 7, 1917

Considerable interest has been shown the past few years in the industrial use of wood creosotes. At the present time they are on the market to a certain extent as wood preservatives, but their high antiseptic properties render them most useful in general sanitation work and for special technical purposes as well. For example, they dissolve rosin and linseed oil soaps and thus form disinfectants which with water give emulsions having coefficients three to five times, or more, that of phenol. They also have a great advantage over coal-tar creosotes in that they do not inflame the skin and are not toxic or poisonous to humans or animals. Indeed, hardwood creosote, U. S. P., and guaiacol have long been administered as internal medicines, whereas carbolic acid is a well-known poison.

As toxicity to fungi and bacteria is one of the very important attributes in the utilization of the oils or their several constituents, the present study has been undertaken to throw light upon their behavior in this respect. These creosotes are by-products in the destructive distillation of wood and can be produced at a moderate cost. The main products of the distillation are charcoal, methyl alcohol, and acetic acid.

The toxicity of beechwood creosote, both crude and refined,² has been determined by R. M. Fleming and C. J. Humphrey,³ of this laboratory, and found to be much greater, 2 to 4 times, than that of the coal-tar creosote. The toxicity of maplewood creosote and of its constituents and derivatives has been found in the present investigation to be equally as high.

METHOD

Toxicity studies at the Forest Products Laboratory have largely been confined to the petri-dish method;⁴

¹ The present paper is one of four prepared by the junior author in partial fulfillment of requirements for the degree of Doctor of Philosophy in the University of Wisconsin.

² Data on refined product not yet published.

³ *THIS JOURNAL*, 7 (1915), 652.

⁴ Humphrey and Fleming, U. S. Dept. Agr., *Bull.* 327 (1915), for general method.

that is, the preservative and nutrient culture medium are mixed, poured into a petri-dish and inoculated with a wood-destroying fungus. The rate of growth is compared with a check petri-dish containing only the agar culture medium. This method gives approximate toxicity values in a short period of time and has been followed in the present study with minor variations in the technique.

An electrical stirring device,¹ specially developed for toxicity investigations and other lines of work where uniform and very finely divided emulsions or mixtures are essential, was used in the present experiments (Figs. I and II). The oil-agar emulsion thus prepared was made permanent by quickly cooling it in the petri-dish over ice, by which method the small oil globules were imprisoned in the solidifying agar, thus

preservative bottles were covered with stopcock grease and capped with muslin fastened around the neck of the bottle by rubber bands. The bottles were then sterilized in the autoclave at 100° C. for 30-min. intervals on three successive days. A bottle each of agar and preservative was then transferred to a sterile culture case and the agar culture solution was poured into the preservative bottle, the mouth of which was then covered with a sterile muslin cap in place of the glass stopper. Two slits at right angles were burned into the center of the cloth through which the stirring-rod of the electric mixer was inserted. This was then set in motion and the contents stirred until the agar was about to solidify. The resulting finely divided mixture was poured into a petri-dish which had been previously cooled over ice. It was then returned to the ice until the contents had solidified.

After all the petri-dishes had been prepared in this way they were returned to the culture case and after their temperature had risen to that of the surrounding air they were inoculated at the center with a transfer of mycelium 6 mm. square cut from petri-dish cultures of *Fomes annosus* Fr. two to three weeks old. For each set of tests a check culture on the nutrient agar was prepared at the same time. The dishes were then placed in an incubator and held approximately at 25° C. for 6 weeks, the extent of growth being noted each week.

SUBSTANCES TESTED

The maplewood creosote used in the tests was prepared¹ by distilling crude tar, obtained from a commercial company in Michigan, from an iron retort. After further distillation from a glass apparatus a fraction distilling between 195 and 265° C. was collected.² This was a clear, light lemon-yellow oil whose specific gravity was 1.04 at 21° C.

The toxicity of this oil and the various portions tested is shown in Table I, the duplicate tests being represented by (A) and (B), respectively.

In order to determine if the phenols, or so-called wood tar acids, are the principal toxic constituents, the maplewood creosote was treated two or three times with an equal volume of 15 per cent sodium hydroxide solution in a separatory funnel and the neutral layer separated from the alkali-soluble portion. The neutral oil obtained was washed with water to free it from alkali. It represented 24 per cent of the total creosote. The neutral oil was redistilled and the fraction between 195 and 260° C. collected. This was almost colorless; its specific gravity was 0.97 at 20° C.

The sodium hydroxide solution of the maplewood creosote was then treated with dilute sulfuric acid until no more oil separated on shaking. This oil was separated and washed with water until free of sulfuric acid. It represented 15 per cent of the total creosote, 8 per cent of the creosote being lost in washing. The oil was redistilled and the fraction between 195 and 260° C. collected. This was almost colorless; its specific gravity was 0.97 at 20° C.

The oil was redistilled and the fraction between 195 and 260° C. collected. This was almost colorless; its specific gravity was 0.97 at 20° C.

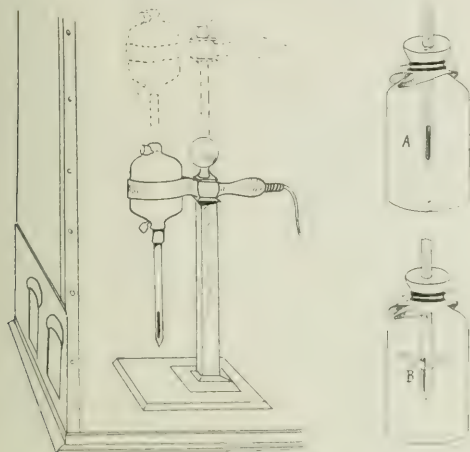


FIG. I—ELECTRICAL STIRRING DEVICE OPERATED IN A STERILIZED GLASS CASE TO AVOID CONTAMINATIONS

FIG. II—BOTTLES WITH SHAFT OF STIRRING DEVICE INSERTED
(A) SHAFT AT REST WITH THE ARMS COLLAPSED
(B) HORIZONTAL POSITION OF THE ARMS WHEN IN MOTION

preventing the oil from separating out as a layer on the surface of the medium.

The culture medium consisted of the following:

Extract of 1 lb. lean beef in distilled water	1000 cc.
1.6 lb. fluid's malt extract	25 g.
Agar-agar	18 g.

The medium was filtered, but the reaction was not adjusted; it was somewhat acid, around +32 Fuller's scale.

Of the above medium 17.5 cc. were measured from a graduated pipette into 25 cc. glass-stoppered bottles; 0.5 cc. of this was extra to compensate for the amount adhering to the bottles after pouring, leaving 17 cc. to be mixed with the preservative.

The preservative was weighed into 50 cc. glass-stoppered bottles and then diluted to 3 cc. with distilled water. The concentration of the preservative was based on the actual weight in grams in 20 cc. of the agar preservative mixture.

Before sterilizing, the stoppers of the bottles and

¹ This apparatus will be described in a forthcoming article by R. S. Tiller and L. P. Acres.

TABLE I—TOXICITY OF MAPLE CREOSOTE AND ITS FRACTIONS: RESULTS GIVEN IN TERMS OF RADIAL GROWTH OF FUNGUS IN MILLIMETERS

PRESERVATIVE USED (Per cent)	CONCENTRATION First Week		Second Week		Third Week		Fourth Week		Fifth Week		Sixth Week		KILLING POINT
	A	B	A	B	A	B	A	B	A	B	A	B	
Maplewood Creosote... 0.05	2-5	0	11-15	1-4	23-29	13-28	36-38	22-28	39-44	32-45	*	*	0.10% Solution. Equivalent to 0.0624 Lb. per cu. ft.
0.10	0	0	0	0	0	0	0	0	0	0	0	0	
0.20	0	0	0	0	0	0	0	0	0	0	0	0	
Check	23-30	25-30	*	*	*	*	*	*	*	*	*	*	0.15-0.20% Solution. Equivalent to 0.0936-0.1248 Lb. per cu. ft.
Neutral Oil..... 0.05	0	1-3	18-22	19-24	38-42	39-44	*	*	*	*	*	*	
0.10	0	0	12-13	11-12	31-32	28-31	*	*	*	*	*	*	
0.15	0	0	0	0	0	0	0	0	0	0	2-3	1-4	
0.20	0	0	0	0	0	0	0	0	0	0	0	0	
Check	24-25	22-26	*	*	*	*	*	*	*	*	*	*	0.05% Solution. Equivalent to 0.0312 Lb. per cu. ft.
NaOH-Soluble Portion 0.025	7-10	5-7	12-14	14-16	24-30	30-35	32-42	38-43	*	*	*	*	
0.05	0	0	0	0	0	0	0	0	0	0	0	0	
0.75	0	0	0	0	0	0	0	0	0	0	0	0	
Check	25-28	21-28	*	*	*	*	*	*	*	*	*	*	
195-230° C. Fraction... 0.05	2-4	0	20-25	12-13	38-39	28-30	0	39-40	*	*	*	*	0.10% Solution. Equivalent to 0.0624 Lb. per cu. ft.
0.10	0	0	0	0	0	0	0	0	0	0	0	0	
Check	24-25	25-27	*	*	*	*	*	*	*	*	*	*	
230-265° C. Fraction... 0.05	0	0	0	0	10-11	9-10	17-22	15-19	22-28	20-23	25-33	24-30	0.10% Solution. Equivalent to 0.0624 Lb. per cu. ft.
0.10	0	0	0	0	0	0	0	0	0	0	0	0	
Check	*	*	*	*	*	*	*	*	*	*	*	*	

* Surface covered.

255° C. collected. A light yellow oil with a specific gravity of 1.052 at 20° C. was obtained.

The results show that a 0.05 per cent emulsion with the alkali-soluble wood tar acid or phenols prevents the growth of the fungus and is three to four times as efficient as the neutral oils and about seven times as efficient as the coal-tar creosote used for comparison. It is because of this high toxic coefficient of the wood tar phenols and the large proportion, 70 to 85 per cent, present in the hardwood creosote that this oil has such an advantage over coal-tar creosote.

In order to determine whether there was any difference in the toxic value of the higher and lower boiling fractions of maplewood creosote, the refined creosote was redistilled and the fractions 195-230° C. and 230-265° C. separated. The specific gravity of the fraction 195-230° C. was 1.022 at 22° C., while that of the 230-265° C. fraction was 1.043.

A concentration of 0.10 per cent of either fraction entirely prevents the growth of the fungus and a 0.05 per cent emulsion of the 230-265° C. fraction seems to be slightly more toxic than a 0.05 per cent emulsion of the 195-230° C. fraction. As the more toxic phenols occur in the 195-230° C. fraction to the extent of only 65 to 70 per cent and in the 230-265° C. fraction to the extent of 80 to 85 per cent, the higher toxicity of the 230-265° C. fraction is to be expected.

In all the previous tests those petri-dishes upon which no growth occurred after six weeks were kept in the incubator for two weeks longer. There was no indication of further growth in any case.

Table II gives a summary of the results secured on all the samples.

TABLE II—TOXICITY OF MAPLEWOOD CREOSOTE AND ITS DERIVATIVES: SUMMARY

PORTION USED	KILLING POINT Per cent Concentration	Pounds per cu. ft.
Total Creosote.....	0.10	0.0624
Neutral Portion.....	0.15-0.20	0.0936-0.1248
Alkali-soluble (Phenol) Portion.....	0.05	0.0312
195-230° C. Fraction.....	0.10	0.0624
230-265° C. Fraction.....	0.10	0.0624

For comparison with the preceding data we give in Table III the results¹ obtained by Ruth M. Fleming and C. J. Humphrey on the toxicity of samples of beechwood creosote.

It is seen from Table II and III that the corre-

¹ Manuscript covering these data has been prepared for publication; an article describing the methods of preparation of the samples will be published later by R. C. Judd, H. K. Smith and S. F. Acree.

sponding fractions of maplewood creosote and beechwood creosote have nearly the same toxicities, those of beechwood being perhaps slightly greater.

TABLE III—TOXICITY OF SAMPLE NO. 3359 BEECHWOOD CREOSOTE AND ITS FRACTIONS

PORTION USED FOR TESTS	KILLING POINT Per cent Concentration
Total Distillate (B. P. 180 to 260° C.).....	0.05-0.10
Phenol Portion of Above.....	0.025-0.05
Phenol Portion of 195 to 200° C. Fraction.....	0.075-0.10
Neutral Portion of 195 to 200° C. Fraction.....	0.20-0.50
180 to 185° C. Fraction.....	0.25-0.30
185 to 190° C. Fraction.....	0.20-0.25
190 to 200° C. Fraction.....	0.15-0.20
200 to 215° C. Fraction.....	0.10-0.15
215 to 225° C. Fraction.....	0.075-0.10
225 to 255° C. Fraction.....	0.05-0.075

The phenolic portions of each of these creosotes are two to four times as toxic as the neutral portions.

In Table IV the toxicities of maplewood and beechwood creosotes are compared with a few of the more important preservatives.¹

TABLE IV—TOXICITY TO *Fomes Annosus* OF MAPLEWOOD CREOSOTE COMPARED WITH COMMERCIAL PRODUCTS

PRESERVATIVE	KILLING POINT Per cent Concentration	Pounds per cu. ft.
Maplewood Creosote.....	0.10	0.0624
Phenol Portion of Above.....	0.05	0.0312
Beechwood Creosote (Commercial Product Containing Pitch), Sample No. 3183.....	0.12-0.24	0.0749-0.1498
Beechwood Creosote, Refined.....	0.05-0.10	0.0312-0.0624
Beechwood Creosote, Phenol Portion.....	0.025-0.05	0.0156-0.0312
Coal-tar Creosote(a).....	0.35	0.2184
Sodium Fluoride.....	0.25	0.156
Zinc Chloride.....	0.50	0.312

(a) Grade C of Amer. Ry. Eng. & Maint. Way Specifications.

CONCLUSIONS

From the preceding data it is evident that the representative American maplewood creosote used has a high toxic coefficient. Its general composition and toxicity are practically identical with those of beechwood creosote. These two American hardwood creosotes can, therefore, be used interchangeably in the mixtures often produced commercially from the mixed woods. The results indicate that the toxicity is due to the presence of carbocyclic compounds containing free hydroxyl groups in some cases and in others the corresponding methoxy groups. The alkali-soluble portion of the maplewood creosote is twice as toxic as the total creosote and four times as toxic as the neutral oil. The introduction of an alkyl radical in place of the hydrogen of the hydroxyl group evidently decreases the toxicity.

The killing points of the fractions 195-230° C. and 230-265° C. are practically the same as for the total

¹ C. J. Humphrey and R. M. Fleming, U. S. Dept. Agr., Bull. 337.

creosote. The toxicity of the higher boiling fraction, however, is slightly greater than that of the lower boiling fraction. This is due to the fact that the higher boiling fraction contains a greater percentage of phenols (80–85 per cent) than does the lower fraction (65–70 per cent). The lower fraction consists principally of the monohydroxy and dihydroxy phenols and their derivatives, the most important being cresol, guaiacol and creosol. The higher fraction consists principally of the trihydroxy phenols and their derivatives, the most important of which are the dimethyl-ether of pyrogallol and its homologues.

INVESTIGATION IN FOREST PATHOLOGY, BUREAU OF PLANT INDUSTRY
IN COÖPERATION WITH THE FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN

THE DETERMINATION OF PHENOL IN CRUDE CARBOLIC ACID AND TAR OILS

By JOHN MORRIS WEISS AND C. R. DOWNS

Received March 27, 1917

INTRODUCTION

The purpose of this paper is to describe a method which is capable of giving accurate results for the determination of phenol in mixture with cresols, higher phenols, and neutral oils.

Many methods for the determination of phenol have been proposed. Most of these, however, are designed to serve as an assay of pharmaceutical phenol, and are of no value for the purposes which this paper is designed to cover.

Leube¹ used a colorimetric method with ferric chloride. Nietsch² converted the phenols into sulfonates, formed the barium and lead salts and made a determination of the metal content of these salts. Carre³ converts the phenol to picric acid and makes a colorimetric determination. None of these methods are applicable for even an approximate assay of the real content of phenol in a crude acid or tar oil.

Warnes⁴ gives three very empirical methods for testing carboic acid. The results give only the melting point of a definite volume percentage fraction of the original acid, and though comparative between different samples, does not give any real indication of the actual amount of true phenol present.

Lunge⁵ gives a table showing the lowering of the fusing points of mixtures of para-cresol and phenol according to tests made by Lunge and Zschokke. This table is patently useless for estimation purposes, as, in ordinary cases, meta- and ortho-cresols are also present in varying proportions, and affect the melting point to a very considerable degree.

Later, Lunge⁶ gives a method of examining crude phenols (carboic acid) for its yield of crystallizable phenol of a melting point from 15.5 to 24° C. This is known as the method of Lowe, and was in use among English tar distillers for some time. The crude acid is fractionally distilled and the melting point taken on a definite per cent by volume of the crude acid.

The test is, however, more a specification for quality of crude acids, than a method of analysis. Lunge further states that for the purpose of "acquiring good practice in this method" mixtures are made of various content of pure crystallized carboic acid and of cresols (preferably tar cresols, *i. e.*, a mixture of the three isomers) and the melting points of these mixtures are previously determined. No account is taken of variation in melting point due to variation in the interproportion of the three cresols. As Lunge himself points out, the relative proportions of the three cresols in coal tar are not constant. No attempt was made to take advantage of the differences in specific gravity between phenol and the cresols. The method is very crude and would give only very approximate results.

Stochmeier and Thurnauer¹ extract tar acids from carboic oil, separate the hydrocarbons from the carbolate by steam distillation, liberate the tar acids and fractionate them. They then use Koppeschaar's bromination method² on the fractions and use special factors for the fractions containing the cresols. The titration of such mixtures is clearly not allowable as shown by Vaubel.³

In 1912 one of the authors⁴ made, perhaps, the first published attempt to develop a rational method for the estimation of phenol in crude carboic acid and tar oils, and it is along the general lines of that method that the method given in the present paper was developed. The method was fairly accurate, giving results within about 10 per cent of the phenol present. The range of the series of mixtures, however, was not close enough and the cresols available at that time were not quite so pure as to-day. Moreover, the recent increase in value of phenol has made a more accurate method necessary, whereas in the past, the close determination of phenol was not of prime importance. In the present method the procedure has been considerably changed and amplified, and a much more complete series of mixtures of known composition has been prepared and studied.

Very recently, while this paper was in course of preparation, René Masse and M. H. Leroux⁵ published a method which is in some respect very similar to the method submitted by the authors of this paper. We have taken the liberty of reproducing the determination curve (see Fig. 1) given by them, in this paper, and plotting on it points as found in the examination of our own series of mixtures. At some points the error can be very great. They use a dilution process alone for their determination, and with estimation of the proportion of the cresols among themselves, there might be an error of 2.6 per cent at the 10 per cent point, of 1.8 per cent at the 15 per cent point and of 4.4 per cent at the 20 per cent point. This will be seen more clearly by a comparison to the curve. Masse and Leroux used a mixture of 10 per cent cresols and 90 per cent of a solution of 20–44 of cresols and 60–56

¹ *Dreger's J. Ind. Eng. Chem.*, **202**, 108.

² *Ann. Chem. Tech.*, **1897**, 1039.

³ *Compt. rend.*, **1891**, 139.

⁴ Warnes' *Coal Tar Distillation*, **1913**, 166.

⁵ Lunge, *Coal Tar and Ammonia*, 5th Ed., **1916**, 273.

⁶ *Ibid.*, 80.

¹ *Ann. Chem.*, **1893**, 100, 101.

² *Ann. Chem.*, **1896**, 133.

³ *Ann. Chem.*, **1896**, 48, 49.

⁴ *Ann. Chem.*, **1912**, 180.

⁵ *Ann. Chem.*, **1916**, 136, 137.

cresols, for the basis of the determination. In our work we used a 50 : 50 meta-para-cresol mixture (as naturally occurring in our oils) and varied the relation of the ortho-cresol to this. In the following table we have shown the variation in percentage between their curves and ours on the mixtures which correspond most closely to their proportions:

TABLE I

Per cent Phenol	Per cent o-Cresol	Per cent m50/p50 Cresol	Per cent Variation
95	2.5	2.5	1.0
90	5.0	5.0	0.8
85	7.5	7.5	0.2
80	10.0	10.0	0.0
75	12.5	12.5	0.3
70	15.0	15.0	0.5
65	17.5	17.5	0.2

This shows their curve to be quite correct if the proportion of ortho-cresol to meta- and para-cresol

have been variously given in the literature (see Table II).

TABLE II

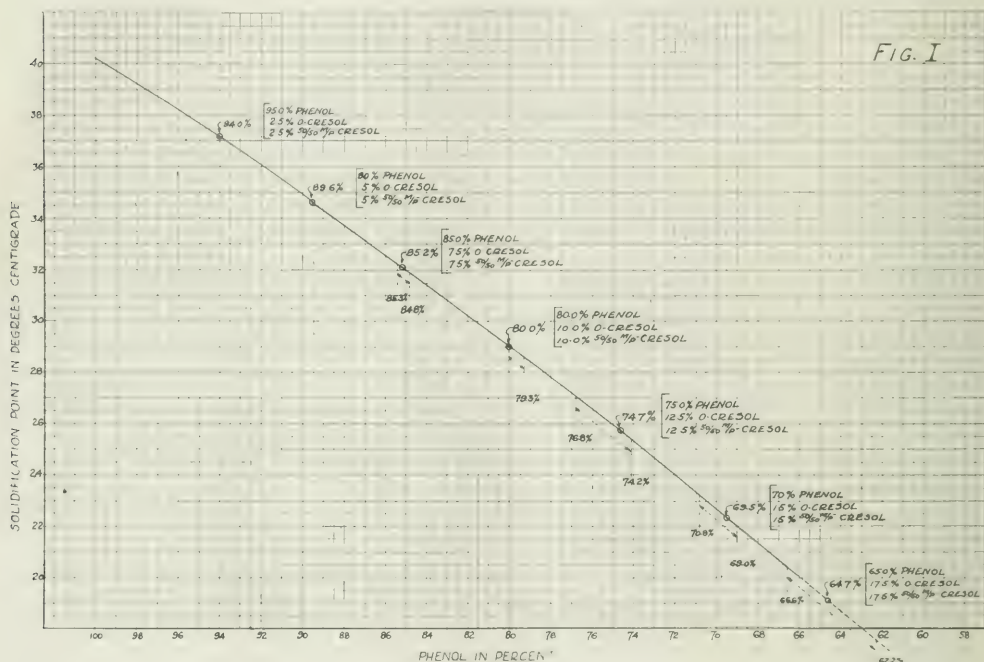
Beilstein(a)	Melting Point	Boiling Point	Specific Gravity
Phenol.....	42.5 to 43° C.	178.5 to 184.1° C.	1.0906 at 0°
o-Cresol.....	30	190.8	1.0578 at 0°
m-Cresol.....	3	202.8	1.0498 at 0°
p-Cresol.....	36	201.8	1.0522 at 0°
Olsen(b)			
Phenol.....	42.5 to 43	182.6	1.0677 at 35°
o-Cresol.....	30	191	1.0511 at 35°
m-Cresol.....	3 to 4	202	1.0390 at 35°
p-Cresol.....	36	202	1.0390 at 35°
Landolt-Börnstein(c)			
Phenol.....	42.5 to 43	181.5	1.0489 at 50°/4°
o-Cresol.....	30	187.5 to 188	1.0427 at 23°/4°
m-Cresol.....	About 4	200.5	1.0347 at 13.6°/4°
p-Cresol.....	36	201.1	1.0344 at 17°/4°

(a) Beilstein, "Hand. d. org. Chem.," 3rd Ed., 1893.

(b) Olsen, "Chem. Annual," 3rd Ed., 1913.

(c) Landolt-Börnstein, "Phys. Chem. Tab.," 4th Ed., 1912.

There are numerous other single references dealing with single properties of these substances but it does



be equal but this is not generally true of tar oils. Therefore, the use of the simple solidification point curve is insufficient.

In general, their directions for the distillation of the liberated acids are fairly complete as is also their description of the method for determination of the solidifying point of the fractions. There are, however, a number of points in the handling of tar acids to remove neutral oils, on which their directions are not explicit, and here there is considerable chance for the introduction of serious errors. These errors may be further increased in the procedure for the determination of the phenol content of a tar oil.

The physical properties of the cresols and of phenol

not seem worth while to collate them here. We have ourselves made a considerable investigation on the true solidifying point of pure phenol and find it to be 40.5° C. In this we are confirmed by Eger.^{1,2} The differences in the literature are probably due to early tests being made on small samples by the capillary tube method which might give higher figures than our solidifying point tests taken on a much larger bulk of material. It is also probable that some of the other melting points given are taken on the same basis although we have not investigated them to the same degree as we have in the case of phenol. A comparison

¹ Pharm.-Zig. 1903, 210.

² Chem.-Zig. Rep., 1903, 86.

of our method for solidifying point (see later) with the ordinary capillary tube melting point will indicate clearly how such differences might arise.

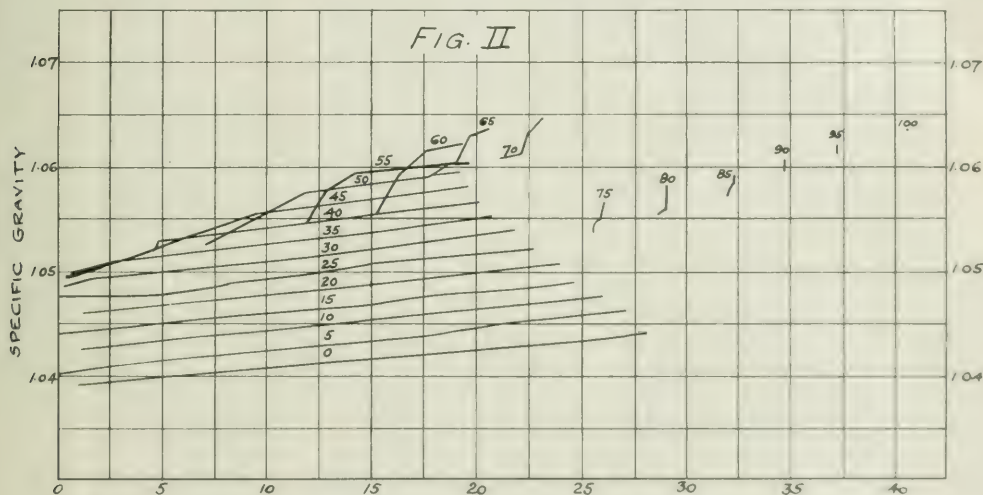
EXPERIMENTAL

The authors have attempted to give the experimental work in chronological order inserting from time to time the conclusions drawn. We have not attempted to give all the details of manipulation in the single experiments, but have collected these together at the end in a description of the method. We wish to express at this point our appreciation of the work of H. E. Lloyd and C. J. Downey who performed most of the laboratory work in connection with the problem.

A—MATERIALS USED FOR STANDARD MIXTURES

(1) *Phenol* was prepared in the plant and represented a close cut middle fraction from the final distillation of synthetic phenol. It did not require further purification by the laboratory.

(2) *Ortho-Cresol*—We selected from a works run



an *o*-cresol fraction of high purity, but containing some neutral oil and naphthalene. It was dissolved in caustic soda solution, the carbolate freed from neutral hydrocarbons by steam distillation and the cresol precipitated again by dilute sulfuric acid. The liberated cresol was separated and fractionated through a 3-bulb LeBel-Henninger column, cutting so as to give a cresol of a boiling point of about 2° C.

(3) *Meta Para Cresol* was prepared in the same way as the *ortho* cresol from another fraction obtained similarly. The final material was shown by the Rastig nitration test to contain 40 per cent *meta* cresol and 60 per cent *para* cresol.

The three materials as finally used in the mixture showed the constants given in Table III.

	Solidification Point	Specific Gravity at 25° C./25° C.	Boiling Point Range
Phenol.....	40.4° C.	1.0636(a)	180–182° C.
<i>o</i> -Cresol.....	29.0° C.	1.0444	189–191° C.
<i>m-p</i> -Cresol.....	Below 0° C.	1.0339	199–201° C.

(a) Taken at 45°/45° C.

B—MIXTURE OF PURE MATERIALS

Twenty-one so-called series were made up using from 0 to 100 per cent of phenol, each series representing a 5 per cent phenol increment. In the series themselves the relative proportions of the *o*-cresol and the *m-p*-cresol were varied for every even 5 per cent. This involved making and testing a total of 231 mixtures.

The mixtures were made up by weight and the accuracy of the weighings was such as to make a maximum possible error in the final percentage of the material in the mixture of not over ± 0.2 per cent. Proper precautions were taken to prevent absorption of water both in making up the mixtures and in subsequent handling of them. The mixtures were then subjected to various physical tests as described below.

(1) *Bulb Distillation*—The first few mixtures were submitted to this test, but it was soon found that sufficiently concordant results could not be obtained. It was necessary to have accurate readings of percentages distilled every even degree in order to differentiate between mixtures made over such a short range as these were. There were so many factors, such as barometric pressure, changes from corrections, thermometer lag, rate of distillation, effect of air currents, etc., any of which could produce as error as great or nearly as great as 1° C., that the authors decided it to be utterly impractical to use boiling point ranges as a method of differentiation. After a number of years had indicated the futility of this method of attack it was finally abandoned.

TABLE IV—TESTS OF PHENOL-CRESOL MIXTURES: PHENOL VARIED FROM 0 TO 100 PER CENT OF MIXTURE

Phenol	m-p- Cresol	Sp. Gr.	Solidification Point, ° C.	Ref. Ind. 50° C.	Phenol	m-p- Cresol	Sp. Gr.	Solidification Point, ° C.	Phenol	m-p- Cresol	Sp. Gr.	Solidification Point, ° C.			
SERIES 1	SERIES 3	SERIES 5	SERIES 7	SERIES 9	SERIES 11	SERIES 13	SERIES 15	SERIES 17	SERIES 19	SERIES 21	SERIES 23	SERIES 25			
0	100	1.0339	Below -7	1.5281	10	0	90	1.0374	Below -7	20	0	80	1.0414	Below -7	
0	5	95	1.0344	Below -7	1.5281	10	5	85	1.0380	Below -7	20	5	75	1.0420	Below -7
0	10	90	1.0349	Below -7	1.5281	10	10	80	1.0388	Below -7	20	10	70	1.0426	Below -7
0	15	85	1.0354	Below -7	1.5290	10	15	75	1.0394	Below -7	20	15	65	1.0433	Below -7
0	20	80	1.0359	Below -7	1.5290	10	20	70	1.0399	Below -7	20	20	60	1.0438	Below -7
0	25	75	1.0364	Below -7	1.5290	10	25	65	1.0405	Below -7	20	25	55	1.0443	Below -7
0	30	70	1.0369	Below -7	1.5291	10	30	60	1.0410	Below -7	20	30	50	1.0448	Below -7
0	35	65	1.0374	Below -7	1.5294	10	35	55	1.0415	Below -7	20	35	45	1.0454	Below -7
0	40	60	1.0379	-5.0	1.5299	10	40	50	1.0421	-2	20	40	40	1.0461	1.2
0	45	55	1.0384	-3.0	1.5299	10	45	45	1.0427	1.2	20	45	35	1.0467	4.6
0	50	50	1.0391	1.0	1.5300	10	50	40	1.0433	3.8	20	50	30	1.0473	7.8
0	55	45	1.0399	4.5	1.5298	10	55	35	1.0438	10.0	20	55	25	1.0479	10.4
0	60	40	1.0404	7.2	1.5303	10	60	30	1.0444	12.8	20	60	20	1.0485	13.4
0	65	35	1.0409	10.1	1.5305	10	65	25	1.0450	15.8	20	65	15	1.0491	16.2
0	70	30	1.0414	12.8	1.5305	10	70	20	1.0456	18.2	20	70	10	1.0498	18.8
0	75	25	1.0419	15.8	1.5310	10	75	15	1.0462	21.0	20	75	5	1.0504	20.2
0	80	20	1.0424	18.5	1.5312	10	80	10	1.0467	23.6	20	80	0	1.0509	23.8
0	85	15	1.0429	21.5	1.5312	10	85	5	1.0473	25.8					
0	90	10	1.0434	23.9	1.5319										
0	95	5	1.0439	26.0	1.5311										
0	100	0	1.0444	29.0	1.5310										
SERIES 2					SERIES 4					SERIES 6					
5	0	95	1.0347	Below -7	15	0	85	1.0393	Below -7	25	0	75	1.0428	Below -7	
5	5	90	1.0352	Below -7	15	5	80	1.0397	Below -7	25	5	70	1.0435	Below -7	
5	10	85	1.0357	Below -7	15	10	75	1.0405	Below -7	25	10	65	1.0442	Below -7	
5	15	80	1.0363	Below -7	15	15	70	1.0411	Below -7	25	15	60	1.0449	Below -7	
5	20	75	1.0370	Below -7	15	20	65	1.0417	Below -7	25	20	55	1.0455	Below -7	
5	25	70	1.0377	Below -7	15	25	60	1.0423	Below -7	25	25	50	1.0462	Below -7	
5	30	65	1.0384	Below -7	15	30	55	1.0429	-6.5	25	30	45	1.0469	-2	
5	35	60	1.0391	Below -7	15	35	50	1.0435	-4	25	35	40	1.0476	0	
5	40	55	1.0397	-4	15	40	45	1.0441	0	25	40	35	1.0480	4.8	
5	45	50	1.0403	0	15	45	40	1.0447	2.9	25	45	30	1.0483	6.6	
5	50	45	1.0410	2.0	15	50	35	1.0453	6.2	25	50	25	1.0490	8.4	
5	55	40	1.0416	5.3	15	55	30	1.0459	9.0	25	55	20	1.0498	12.2	
5	60	35	1.0421	8.3	15	60	25	1.0463	11.7	25	60	15	1.0508	14.9	
5	65	30	1.0427	11.2	15	65	20	1.0469	14.8	25	65	10	1.0512	17.7	
5	70	25	1.0433	14.4	15	70	15	1.0475	17.3	25	70	5	1.0517	20.2	
5	75	20	1.0440	17.4	15	75	10	1.0481	19.9	25	75	0	1.0524	22.6	
5	80	15	1.0447	19.4	15	80	5	1.0487	22.6	25	80				
5	85	10	1.0453	22.4	15	85	0	1.0493	24.4	25	85				
5	90	5	1.0458	24.7											
5	95	0	1.0464	27.0											

(2) *Refractive Indices*—A few preliminary tests on the components of the mixtures showed definitely that their constants were too close to enable us to determine at all accurately the character of a mixture by this means.

(3) *Specific Gravity*—This test proved very useful and was adopted for general use. The details of carrying out this test will be given later in connection with the described testing method. It was found desirable to use two standard temperatures. The mixtures having a solidifying point less than 25° C. were taken at 25° C. compared to water at 25° C. Above this point the specific gravities were taken at 45° C. compared to water at 45° C. Occasionally a mixture test will be found where the solidifying point is 25° C. or a trifle higher and still the specific gravities given as of 25° C.—for all these cases the specific gravity was never taken in the solid state or by correction from a higher temperature, but represents an actual determination in the supercooled liquid.

(4) *Solidifying Point*—The old method used ordinarily for phenol, in which the thermometer is used as the stirring rod in the test tube, was given a thorough trial and proved to be too inaccurate, in so far as checks by different operators were concerned, to be used for the present purposes. Accordingly a modified method was devised, the details of which are given later under the testing method. This modification of the method was used throughout the work presented in this paper.

(5) *Detailed Tests*—These are shown in Table IV. The curves in Figs. II, III and IV bring out graphically important features of these tests.

(6) *Consideration of Results*—In Fig. II there are

plotted curves of all mixtures, where the solidifying point is above 0° C., using the solidifying points as ordinates and the specific gravities as abscissas and plotting a curve for each 5 per cent of phenol. It is evident from an examination of the detailed results in the tables that if a solidifying point of a mixture is indeterminate, that is below 0° C., that the specific gravity alone is not sufficient data for an exact determination. Therefore, for determination of phenol by this method it is first necessary to concentrate the phenol into a fraction containing only phenol and cresols of such a nature that the solidifying point is above 0° C.

It will be further noted in Fig. II that, from 0 to 30 per cent of phenol, the curves are well separated and the constants of a mixture will serve for exact quantitative determination. From 30 to 70 per cent phenol, the curves cross each other irregularly and points in this area are indeterminate and, therefore, not susceptible of exact determination. From 70 to 100 per cent phenol the curves are well separated and this area can be considered as determinate. The two determinate areas are shown on a larger scale in Figs. III and IV. It is, therefore, evident that to determine phenol, it will be necessary to bring it into a fraction containing only phenol and cresols of such composition that its physical constants will plot to a point within one or the other of the determinate areas shown. The first portion of the remaining problem was, therefore, to develop a method of fractional distillation which would separate all the phenol from a crude acid with only cresols as an impurity. It is evident that with such a fraction, if its constants do not throw it into the determinate area, that a mix-

TABLE IV—(Continued)

Phenol	o-Cresol	m-Cresol	Sp. Gr. 25/25° C.	Solidification Point, °C.	Phenol	o-Cresol	m-Cresol	Sp. Gr. 25/25° C.	Solidification Point, °C.	Phenol	o-Cresol	m-Cresol	Sp. Gr. 25/25° C.	Solidification Point, °C.	Phenol	o-Cresol	m-Cresol	Sp. Gr. 25/25° C.	Solidification Point, °C.		
SERIES 7					SERIES 10					SERIES 14					SERIES 15						
30	0	70	1.0448	Below -7	45	0	55	1.0507	3.4	65	0	35	1.0590	17.6	70	0	30	1.0590	17.6		
30	5	65	1.0454	Below -7	45	5	50	1.0514	3.6	65	5	30	1.0595	18.1	70	5	25	1.0604	18.1		
30	10	60	1.0461	Below -7	45	10	45	1.0521	4.7	65	10	25	1.0604	19.1	70	10	20	1.0608	19.1		
30	15	55	1.0467	-4	45	15	40	1.0528	5.6	65	15	20	1.0617	19.2	70	15	15	1.0622	19.2		
30	20	50	1.0473	-3	45	20	35	1.0534	6.2	65	20	15	1.0617	19.2	70	20	10	1.0630	19.4		
30	25	45	1.0479	-1	45	25	30	1.0541	7.4	65	25	10	1.0622	19.6	70	25	5	1.0636	19.6		
30	30	40	1.0486	0.3	45	30	25	1.0548	8.5	65	30	5	1.0630	20.4	70	30	0	1.0636	20.4		
30	35	35	1.0493	1.6	45	35	20	1.0555	9.4	65	35	0	1.0636	20.4	70	35	0	1.0636	20.4		
30	40	30	1.0500	5.0	45	40	15	1.0562	12.2	65	40	0	1.0608	1.0520	22.0	70	40	0	1.0614	1.0525	22.2
30	45	25	1.0506	8.6	45	45	10	1.0569	14.6	65	45	0	1.0614	1.0525	22.2	70	45	0	1.0623	1.0530	22.4
30	50	20	1.0513	11.7	45	50	5	1.0576	17.2	65	50	0	1.0623	1.0530	22.4	70	50	0	1.0632	1.0533	22.6
30	55	15	1.0520	14.2	45	55	0	1.0583	19.6	65	55	0	1.0632	1.0533	22.6	70	55	0	1.0636	1.0540	22.8
30	60	10	1.0527	16.8	45	60	0	1.0590	21.7	65	60	0	1.0636	1.0540	22.8	70	60	0	1.0644	1.0547	23.0
30	65	5	1.0534	19.3	45	65	0	1.0597	23.4	65	65	0	1.0644	1.0547	23.0	70	65	0	1.0650	1.0554	23.2
30	70	0	1.0541	21.7	45	70	0	1.0604	25.1	65	70	0	1.0650	1.0554	23.2	70	70	0	1.0650	1.0554	23.2
SERIES 8					SERIES 11					SERIES 16					SERIES 17						
35	0	65	1.0466	Below -7	50	0	50	1.0527	7.1	70	0	30	1.0608	1.0520	22.0	70	0	30	1.0614	1.0525	22.2
35	5	60	1.0473	-4	50	5	45	1.0534	7.9	70	5	25	1.0614	1.0525	22.2	70	5	25	1.0623	1.0530	22.4
35	10	55	1.0480	-1	50	10	40	1.0541	8.6	70	10	20	1.0623	1.0530	22.4	70	10	20	1.0632	1.0533	22.6
35	15	50	1.0486	0.5	50	15	35	1.0548	9.1	70	15	15	1.0632	1.0533	22.6	70	15	15	1.0636	1.0540	22.8
35	20	45	1.0493	0.2	50	20	30	1.0555	9.8	70	20	10	1.0636	1.0540	22.8	70	20	10	1.0644	1.0547	23.0
35	25	40	1.0500	1.4	50	25	25	1.0562	10.3	70	25	5	1.0644	1.0547	23.0	70	25	5	1.0650	1.0554	23.2
35	30	35	1.0506	3.0	50	30	20	1.0569	11.7	70	30	0	1.0650	1.0554	23.2	70	30	0	1.0650	1.0554	23.2
35	35	30	1.0513	4.2	50	35	15	1.0575	11.7	70	35	0	1.0650	1.0554	23.2	70	35	0	1.0650	1.0554	23.2
35	40	25	1.0520	7.4	50	40	10	1.0583	14.4	70	40	0	1.0650	1.0554	23.2	70	40	0	1.0650	1.0554	23.2
35	45	20	1.0527	10.4	50	45	5	1.0590	17.0	70	45	0	1.0650	1.0554	23.2	70	45	0	1.0650	1.0554	23.2
35	50	15	1.0534	13.2	50	50	0	1.0597	19.2	70	50	0	1.0650	1.0554	23.2	70	50	0	1.0650	1.0554	23.2
35	55	10	1.0541	15.8	50	55	0	1.0604	21.7	70	55	0	1.0650	1.0554	23.2	70	55	0	1.0650	1.0554	23.2
35	60	5	1.0548	18.2	50	60	0	1.0611	23.4	70	60	0	1.0650	1.0554	23.2	70	60	0	1.0650	1.0554	23.2
35	65	0	1.0555	20.6	50	65	0	1.0618	25.1	70	65	0	1.0650	1.0554	23.2	70	65	0	1.0650	1.0554	23.2
35	70	0	1.0562	22.4	50	70	0	1.0625	26.8	70	70	0	1.0650	1.0554	23.2	70	70	0	1.0650	1.0554	23.2
SERIES 9					SERIES 12					SERIES 18					SERIES 19						
40	0	60	1.0487	-1	55	0	45	1.0546	11.5	80	0	20	1.0556	28.6	90	0	10	1.0560	34.6		
40	5	55	1.0493	0	55	5	40	1.0553	11.9	80	5	15	1.0560	29.0	90	5	5	1.0560	34.6		
40	10	50	1.0500	0.8	55	10	35	1.0560	12.2	80	10	10	1.0560	29.0	90	10	0	1.0560	34.6		
40	15	45	1.0507	2.4	55	15	30	1.0567	12.4	80	15	5	1.0560	29.0	90	15	0	1.0560	34.6		
40	20	40	1.0514	3.4	55	20	25	1.0574	12.7	80	20	0	1.0560	29.0	90	20	0	1.0560	34.6		
40	25	35	1.0521	4.6	55	25	20	1.0581	12.9	80	25	0	1.0560	29.0	90	25	0	1.0560	34.6		
40	30	30	1.0528	4.8	55	30	15	1.0588	13.0	80	30	0	1.0560	29.0	90	30	0	1.0560	34.6		
40	35	25	1.0535	6.9	55	35	10	1.0595	13.4	80	35	0	1.0560	29.0	90	35	0	1.0560	34.6		
40	40	20	1.0542	9.8	55	40	5	1.0602	14.0	80	40	0	1.0560	29.0	90	40	0	1.0560	34.6		
40	45	15	1.0549	12.4	55	45	0	1.0609	14.3	80	45	0	1.0560	29.0	90	45	0	1.0560	34.6		
40	50	10	1.0555	15.1	55	50	0	1.0616	14.6	80	50	0	1.0560	29.0	90	50	0	1.0560	34.6		
40	55	5	1.0561	17.5	55	55	0	1.0623	14.9	80	55	0	1.0560	29.0	90	55	0	1.0560	34.6		
40	60	0	1.0567	20.0	55	60	0	1.0630	15.2	80	60	0	1.0560	29.0	90	60	0	1.0560	34.6		

(a) The values for the specific gravity given in this column are plotted on Fig. IV.

(b) These values are plotted on Fig. II because if plotted at 45/45° C. the curve for 70 per cent phenol would interfere with the other curves in this figure.

ture of the fraction with a known amount of pure phenol can be made, which mixtures can be made to fall in one of the determinate areas. The percentage of phenol can be readily determined in the mixture and from the knowledge of the amount of phenol added, the percentage of phenol in the original fraction can be readily deduced. With this then as a basis, work was commenced on known mixtures of phenol, cresols, higher acids and oils to perfect the manipulative details necessary to bring phenol, no matter what its form, quantitatively into a fraction in which it was accompanied by cresols alone.

C—WORK ON KNOWN MIXTURES TO PERFECT THE DETAILS OF THE METHOD

The preliminary tests involved a comparison of the Hempel and the LeBel-Henninger fractionating tubes. The Hempel tube was of the standard Barrett type (A. H. T. Cat. No. 20496) and the LeBel, the 3-bulb variety: 6-bulb LeBels were tried but those obtainable were not of sufficiently good workmanship to withstand the required temperature without cracking. For these preliminary tests it was necessary to prepare some phenol-free acids of a boiling point above cresols. This was done by taking ordinary crude acids, removing the oil and naphthalene, and fractionating, taking for use the fraction distilling above 200° C. It was shown by careful test to be free of phenol. In these preliminary tests the acids (free of oil and naphthalene) were fractionated and cut at 190 and 200. The 190-200° fraction was redistilled and cut at 197° C. The total fraction below 197° C.

was compared with the curves and the phenol content estimated. If necessary a suitable mixture was made with pure phenol so as to bring the mixture into the determinative range. Needless to say, all details of the distillation were gravimetrically quantitative.

Tests 1 to 7 may be tabulated as follows:

Test No.	Mixture Phenol	Mixture o-Cresol	Mixture m-Cresol	Per cent Higher Acids	Per cent Phenol Recovered	Error in Per cent of Phenol Present
1	33.3	0	66.7	66.7	32.2	-34.5
2	20.0	20.0	60.0	40.0	16.0	-24.0
3	20.0	20.0	60.0	40.0	19.2	-4.8
4	10.0	15.0	75.0	60.0	10.4	-4.6
5	50.0	10.0	40.0	30.0	48.0	4.0
6	25.0	25.0	50.0	25.0	24.2	-1.8
7	30.0	5.0	65.0	60.0	29.5	-1.7

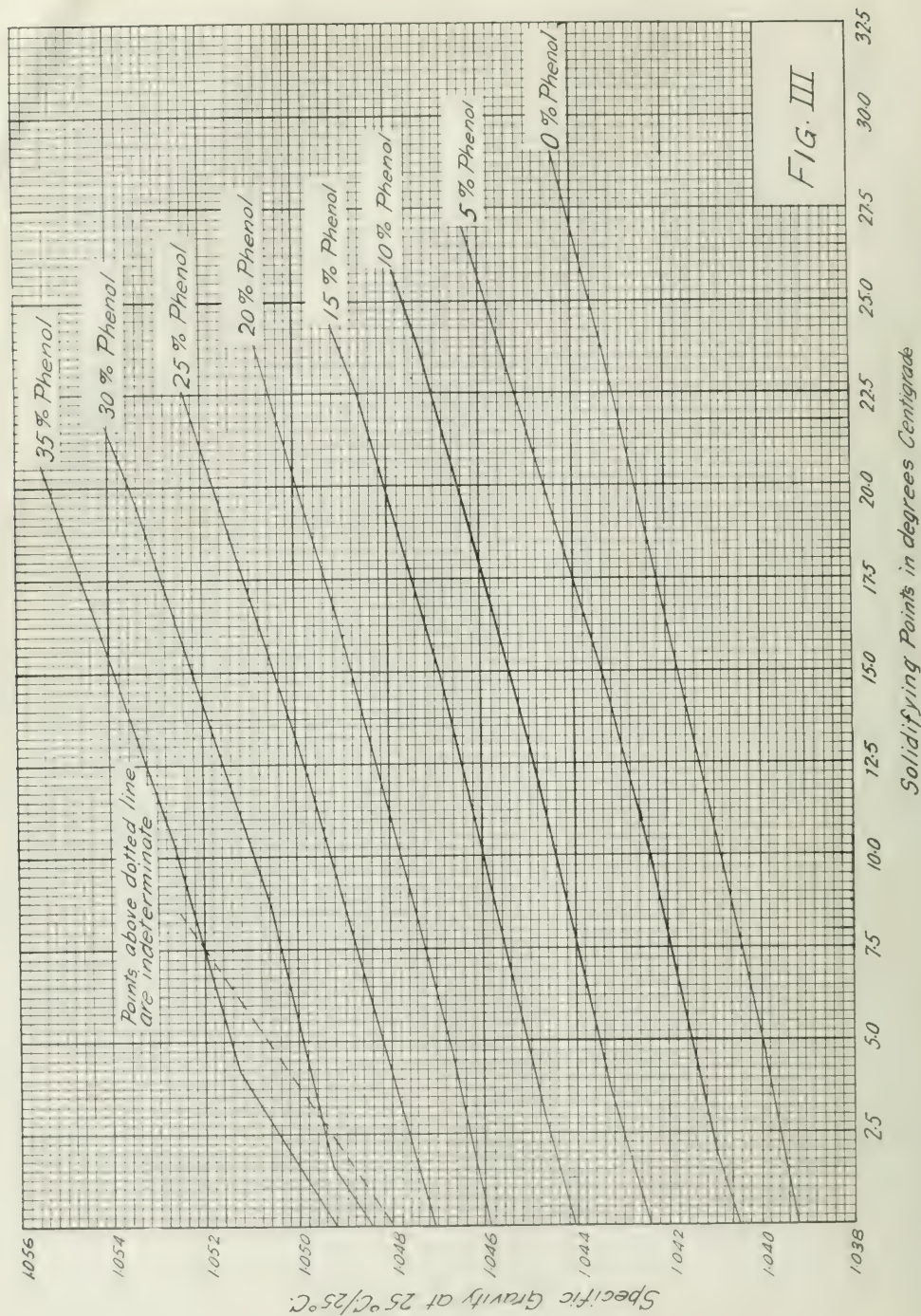
oil in this test the Hempel column was used in all others the LeBel was used.

After these tests we decided to abandon the Hempel distillation for this purpose and until otherwise noted all tests were run using the LeBel 3-bulb column. A comparison of the bulb distillations of the "to 107°" fraction of Tests 2 and 3 shows why Test 2 was so much further off than Test 3.

BULB DISTILLATIONS OF LEBEL (Cont.)

Test	190-200°	197-200°	200-207°	207-210°	210-213°
Test 2	10.4	19.2	24.0	29.6	34.6
Test 3	10.4	19.2	24.0	29.6	34.6

The Hempel had not removed xylenols as well as had the LeBel. The effect of xylene would be to lower the specific gravity without proportionally lowering the solidifying point, thus giving a lower phenol indication than the truth. This is true to a lesser degree in the LeBel test and is doubtless the cause of the somewhat low results obtained in a number of the tests. In fact, as Table 3 shows, the results



ones where bulb distillations were made on the "to 197°" fraction, all showed some residue above 201° C. It has not been thought worth while to record these distillations in detail as all the essential information is given in the two already shown.

At this point of the investigation we decided that the fractioning method was fairly accurate, though not entirely satisfactory. It was considered advisable now to proceed to oil mixtures to determine the points in this phase of the investigation which required our attention.

TEST 8—For this test we prepared a quantity of acid-free oil by completely extracting ordinary creosote oil with caustic soda. A mixture was made by using 85 per cent of this oil and 15 per cent of acids

benzol washings were agitated with 100 cc. of water in two 50 cc. portions. These were added to the carbolate, which was then boiled gently to expel any benzol present. The sulfate liquor, after acidification, was not washed for recovery of acids.

The general method of fractioning, which was adhered to except where otherwise noted, was to distil to 170°, separate acids from water in the distillate and return the former to the distilling flask. Fractions were then taken to 190° C. The second fraction was redistilled collecting to 197° C. and combining all acid distillates up to 197° for test. The recovery of phenol showed a loss of 22.1 per cent of the phenol present.

TEST 10—In this test no change was made in the

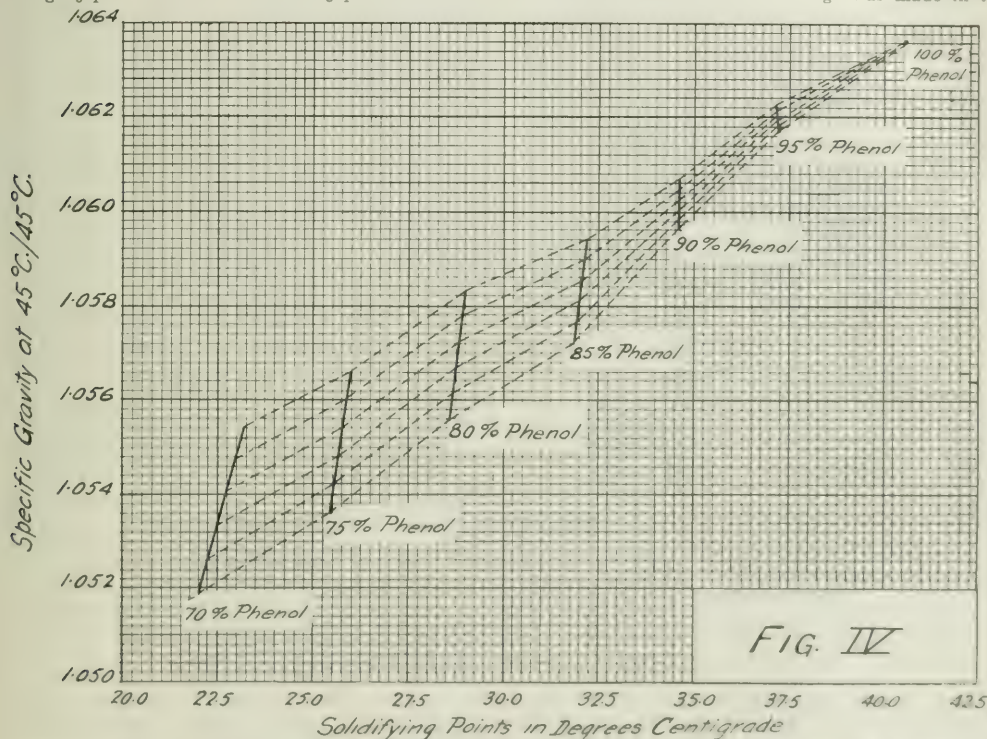


FIG. IV

containing 20 per cent phenol. The acids were extracted by caustic soda solution from a portion of this mixture. The carbolate was steam-distilled to remove neutral oils and naphthalene, the acids liberated by dilute sulfuric acid and carefully separated from the sodium sulfate layer. The test was then carried on in the usual way, taking care to separate all water from the "to 197°" fraction.

The phenol recovered showed an error amounting to —20 per cent of the phenol present.

TEST 9—Here we used 80 per cent of oil and 20 per cent of acids containing 20 per cent of phenol. The carbolate was formed as in Test 8, and washed with 600 cc. of benzol in three 200 cc. portions. The united

relative proportion of the acids and neutral oil. The carbolate was steam-distilled. The NaOH solution was added in three 100 cc. portions. The sulfate liquor was washed with 100 cc. of benzol in three 50-cc. portions and these washings were added to the liberated acids. The sulfate used was the same as in Test 8. The error amounting to a loss of 100 per cent of the phenol.

The practical separation fractionation was continued and tested for phenol. The same was found. In this test the benzol was separated from the acids by fractionation. The benzol recovered had an acid odor, but only a trace of acids could be recovered by solution in NaOH.

The results of Tests 9 and 10 showed that the tar oils and naphthalene in the carbolate may be removed with benzol, instead of steam distillation.

TEST 11—In this test the acid-oil mixture was approximately the same as in the previous tests. The method of procedure was the same as in the previous test, except that the liberated acids were washed with 200 cc. of a saturated NaCl solution for removal of sulfate liquor. The solidifying point of the acid mixture made on fractionation of the acids was so low that no further data were taken.

TEST 12—This test in conjunction with Test 14 was made in order to determine the loss due to solution of acids in the sulfate liquor. In the light of further tests, however, it does not indicate much. This is due to other greater losses which had not been discovered at this time. No neutral oil was used in the mixture.

The carbolate was formed using 125 per cent of the theoretical NaOH necessary. The acids were liberated with 50 per cent H_2SO_4 . The sulfate liquor was washed with 150 cc. benzol in 50-cc. portions and the recovered acids fractionated. An acid containing 20 per cent of the phenol was taken. The error amounted to —8.5 per cent of the phenol present.

TEST 13—In this test the new modifications were the weakening of the H_2SO_4 to 33 $\frac{1}{3}$ per cent and the washing of the extracted oil with an additional 100 cc. of NaOH solution (making a total of 140 per cent). Benzol was used to wash the carbolate. The sulfate liquor was agitated with 125 cc. of benzol and the washings added to the main quantity of acids. The acids were fractionated in the LeBel-Henninger column. The same mixture was used as in Test 12. The error found was —13.2 per cent of the phenol present.

TEST 14 was made in order to compare the loss of phenol with the loss in Test 12, where a carbolate was made and the acids liberated. The mixture contained no oil and was simply fractionated in the LeBel column. Here the error was —8 per cent of the phenol present.

The results of this test would indicate that the loss in recovery from a carbolate was not much.

TEST 15 was made in order to check the curve with a mixture containing 20 per cent of phenol.

Mixture No. 1	{ Pure Phenol.....	30.15 g.
	{ Pure <i>o</i> -Cresol.....	40.05 g.
	{ Pure <i>m-p</i> -Cresol.....	40.05 g.
Mixture No. 2	{ Pure Phenol.....	75.00 g.
	{ Mixture No. 1.....	25.00 g.
Solidification Point of Mixture No. 2.....		28.8° C.
Specific Gravity (45/45° C.) of Mixture No. 2.....		1.057
Phenol in Mixture No. 2.....		80 per cent
Phenol in Mixture No. 1.....		20 per cent

This shows the curves to be correct at this point.

TEST 16—In view of the results of tests to this point it was thought that a considerable part of our losses was due to fractionation and that a change in the temperature at which the fractions were cut might help in the phenol recovery. Accordingly a mixture of acids was made and fractionated using the LeBel-Henninger column as in previous tests. The first fraction collected was to 190° C., the second between 190 and 205° C. This second fraction was redistilled until a temperature of 198° C. was reached. The first and redistilled fractions were collected in the same

flask as in previous test. Using the usual 20 per cent phenol acid, an error of —16.5 per cent of the phenol present was obtained.

TEST 17—In this test the temperature of fractionation was again changed. The first fraction collected was that coming over to 190° C.; the second between 190 and 204° C. This fraction was redistilled up to 195° C. With the same mixture as in Test 16 we showed an error of —10.1 per cent of the phenol present.

Changing the temperature of fractionation did not increase the amount of phenol recovered. We then concluded that the column used in fractionation should be changed.

TEST 18—We then decided to try the 12-pear column. To determine the efficiency of this apparatus as a fractioning device, we made a mixture of pure acids as in previous tests, and fractionated the mixture using the original temperature, *i. e.*, to 190° C. (190–202° C.) and redistillation to 197° C. The error here amounted to only +1.4 per cent of the phenol present.

Results of this test showed that the losses due to faulty fractionation had been overcome. From this point on, our tests were made with a view to overcoming the losses which occur on formation of carbolate and subsequent liberation of the acids. This involved the proper strength and amount of H_2SO_4 , the temperature of acidification, the washing of carbolate and recovery of the acids dissolved in the sulfate liquors.

TEST 19—In this test we attempted to recover all of the phenol in a pure acid mixture after converting the acids to a carbolate. The acids were agitated with 125 per cent of the theoretical amount of NaOH necessary. The acids were then liberated with 25 per cent solution of H_2SO_4 , using a very slight excess of acid (about 10 cc.). The sulfate liquor was washed with 100 cc. of ether in two 50-cc. portions and the washings added to the main quantity of acids. The acids were then fractionated with the 12-pear column. It was impossible to make a clear separation of the ether and acid distillates. The ether and water that came over were agitated with an NaOH solution and the acids recovered. They amounted to about 4 cc. However, they were not added to the acid distillate and so were lost. Better results were obtained here by reducing the strength of the sulfuric acid to 25 per cent. There was a cleaner separation, the acids were lighter colored and there was no gas formation. The error here was —2.1 per cent of the phenol present.

The results of this test indicated that the phenol in a mixture of pure acids could be recovered substantially quantitatively from a carbolate.

TEST 20—In this case 150 per cent of the theoretical quantity of NaOH was used to form the carbolate. The sulfate liquors were washed with benzol. Any acid was recovered from the benzol by washing with caustic soda as described previously. This acid was added to the main bulk of acids. The recovery of phenol showed a very low error, only 0.2 per cent of that present.

TEST 21 was made using a mixture of 20 per cent of pure phenol with crude cresols and higher acids, instead of the purified acids, as in Tests 19 and 20.

125 per cent of the theoretical amount of NaOH was used. The carbolate was washed with 500 cc. benzol in 125-cc. portions. The acids were recovered from the sulfate liquor as in Test 20. The error was —1.3 per cent of the phenol present.

TEST 22 was a check on Test 20, the same procedure being used in each test. The error here was —0.8 per cent of the phenol present.

After running Tests 20, 21 and 22, we concluded that the phenol present in a mixture of acids with small amounts of oil could be recovered with but slight loss. Our next attempt was to recover the phenol from an acid-oil mixture which contained a large amount of neutral oil.

TEST 23—In this test we added enough neutral oil to the acids to make it 80 per cent of the total mixture and attempted to recover the phenol. The acids were extracted from the mixture with 150 per cent of the theoretical amount of a 20 per cent NaOH solution: 800 cc. of the NaOH solution were used in three 200-cc. and two 100-cc. portions. The carbolate was washed with 500 cc. of benzol in 100-cc. portions. The sulfate liquor was washed with ether, and the dissolved acids recovered from ethereal solution with a weak NaOH solution and added, after liberating with H_2SO_4 , to the main quantity; 9.2 grams were recovered. This method of recovery and separation from the solvent is a new and important step in the process. The acids were fractionated as before.

Acid Oil Mixture	Phenol.....	59.85 grams	20%	20 per cent
	o-Cresol.....	59.80 grams	20%	
	m-Cresol.....	59.80 grams	20%	
	Higher Acids.....	119.30 grams	40%	
Neutral Oil.....	1212.50 grams			80 per cent

In the above mixture the acids, with the exception of the phenol, were crude.

The loss of phenol in this test (—16 per cent of the phenol present) was very high (due to imperfect technique, as will be seen later), and it was decided to make tests using smaller quantities of neutral oil.

From this point on, the general method of recovery of the acids was the same, *i. e.*, formation of a carbolate with NaOH (20 per cent strength) washing of the carbolate with pure benzol, washing the benzol solution of carbolate with water, boiling of the carbolate, liberation of the acids with 25 per cent H_2SO_4 , washing the sulfate liquors with benzol and recovery of the dissolved acid with weak (10 per cent) solution of NaOH. All fractionations were made with the pear column.

The essential results of Tests 24 to 35 inclusive are shown in the following table:

Test	Grams a	Grams b	Grams m p	Grams Crude Oil	Grams Higher Acids	Grams Oil	Grams Phenol Recovered	Error in Percent
24	59.78	60.00	60.88	119.30	101.8	14.84	66.6	—0.6
25	59.20	59.78	59.88	119.30	101.0	14.08	66.8	—0.8
26	60.00	60.10	60.00	119.60	101.50	14.10	67.1	+0.1
27	60.00	59.61	59.70	119.10	101.00	14.08	66.8	+0.13
28	58.55	60.00	59.60	119.70	120.00	13.10	66.8	—0.8
29	59.68	70.00	70.00	119.30	111.30	14.30	67.1	+0.2
30	59.40	60.00	60.00	119.30	111.30	14.30	67.1	+0.2
31	14.68	15.00	15.00	134.30	134.30	14.08	66.8	—0.8
32	15.08	15.00	15.00	134.30	134.30	14.08	66.8	—0.8
33	68.55	44.00	45.10	119.70	82.30	67.0	—7.0
34	149.90	30.08	29.60	90.10	149.30	66.8	—0.2
35	15.08	14.85	15.00	134.80	134.80	14.30	67.1	+0.1

In Test 33, a known loss occurred in manipulation, so that the result is natural. The test seemed to us to be accurate enough for all practical purposes, and

checks should be obtained to 0.8 gram of phenol if the work is carried on carefully and conscientiously.

Up to this point we had succeeded in the recovery of the phenol from its mixtures with other pure acids, with unpurified acids in varying portions, and with neutral oil in varying proportions.

To determine the reliability of the test, when applied to crude carboic acid, we first determined the percentage of phenol in a sample of ordinary crude acids, and next in these acids to which we had added a known amount of pure phenol.

TEST 36—*Determination of the phenol in ordinary crude carboic acid:* The acids contained 5.32 per cent (by weight) of water and had a specific gravity at 15.5° C. of 1.072.

We first tried to wash a carbolate made with the crude acids as obtained, but there was not a clean separation of the benzol and carbolate layers. We found it necessary to distil the acids first. The crude acids were distilled, after weighing, directly into a 2000 cc. separatory funnel.

Weight of acids distilled.....	301.5 grams
Weight of distillate (by difference).....	271.3 grams—90 per cent
Black pitch residue.....	30.2 grams

The carbolate was now formed as in previous tests, and washed with benzol. The recovery of the acids and the fractionation were carried out as in the previous tests. We found the phenol content by weight to be 16 per cent on the dry acids or 15.14 per cent on the wet acids.

TEST 37—In this test we added a known amount of pure phenol to the crude acids tested above.

Crude acids.....	301.15 grams
Pure phenol added.....	15.85 grams

On determination of the phenol we found that of the phenol added we had recovered 99.2 per cent.

The better results in the later tests were due to constant improvements in the technique with experience. In the following description, we believe, we have given that technique with sufficient wealth of detail to enable any operator following directions carefully, to obtain consistent, accurate results.

STANDARD METHOD FOR DETERMINATION OF PHENOL IN CRUDE CARBOIC ACID AND TAR OILS

I. PRELIMINARY. In this test extreme care and closest attention to detail are necessary to secure accurate results. All instructions given are the epitomized result of considerable experience and are not given arbitrarily, but with a purpose. The test has been a difficult one to develop and needs greater care and skill than do the ordinary tar tests methods. Some loss of distillation from the water (10%) between acid and base, and some loss of phenol in the washings, are common discrepancies.

II. PREPARATION OF THE OIL. If the oil is of oil duty, as that the subsequent separation of the carbolate will not be exact, it must be washed. This can be accomplished by weighing a known quantity of oil into a clean copper beaker and taking the oil from the stillage from the start of distillation to ending. The amount of wash stillage by weight shall be added so that results may be figured back to the original oil, if desirable. If any more wash oil is added, the

distillation, the run must be rejected and a new one undertaken.

III. EXTRACTION OF THE ACIDS FROM THE OIL—The approximate percentage of tar acids in the oil should be determined by a rough test. A weight of oil which contains between 300 and 350 g. of acids shall be placed in a separatory funnel and treated with 300 cc. (approximate) of 20 per cent caustic soda solution; this caustic soda solution may be made from commercial caustic soda. The oil and caustic soda shall be given a thorough mixing by shaking, care being taken to prevent mechanical loss. The mass shall now be allowed to stand until the carbolate settles completely and a sharp line of division appears between the oil and the carbolate. With a properly distilled oil, from 15 to 30 minutes should suffice. If the oil contains solids, it shall be warmed before extraction to a temperature sufficient to keep solids in solution, and while settling be suspended in a bath of like temperature.

After settling is complete, the carbolate shall be separated and brought into another separatory funnel. The oil shall be washed successively with three more portions of 200 cc. each of the same caustic soda solution, observing the same precautions as to agitation, settling and separation. These separated soda solutions are to be added to the first carbolate. On the last separation it is better to run a few drops of oil along with the carbolate, rather than leave a few drops of carbolate in the oil. After this treatment the oil shall be tested to determine if it is free from tar acids and if so, it may be discarded.

NOTE—If crude acids, not oil, are to be tested, 300 to 350 g. of the crude acid shall be taken in a separatory funnel and dissolved in 800 cc. of 20 per cent caustic soda solution. The treatment from this point on is the same as with carbolate extracted from oil. If the crude acids are tarry it is advisable to distil them quantitatively before dissolving them in caustic soda.

IV. PURIFICATION OF THE CARBOLATE—The carbolate in a separatory funnel shall be extracted five times successively with 100-cc. portions of pure benzol. The manipulation shall be: Add the benzol to the carbolate, mix thoroughly by shaking and allow to settle. Draw the carbolate into another separatory funnel and draw the benzol into a third separatory funnel. Repeat the agitation with fresh benzol four times more, using the two original separatory funnels for this purpose. Finally, after running the washed carbolate into a beaker, rinse each of the funnels which contained carbolate, twice, with 25 cc. each of water, and add the water to the carbolate in the beaker. Take the third separatory funnel, which contains the combined benzol, and wash twice with 50 cc. of water, adding this water also to the carbolate in the beaker. Bring the carbolate in the beaker to a gentle boil until the odor of benzol disappears. No odor of creosote shall be evident in the carbolate at this point. If such odor appears, the washing has not been properly carried out and must be repeated. The carbolate purified of oil is ready for acidification after cooling. The benzol used for extraction may be discarded.

V. ACIDIFICATION—The purified carbolate shall be

placed in a separatory funnel and acidified with sulfuric acid of 25 per cent strength (sp. gr. 1.21 at 15.5° C.). The beaker containing the carbolate shall be rinsed with water and the rinsings added to the carbolate in the funnel. During acidification the mass *must* be kept below 40° C. by immersion in a bath of cold water. Test for acidity should be made from time to time with litmus paper. *More than a very slight excess* of acid (5 to 10 cc.) *must* not be added after litmus shows a red color. When acidification is complete, the funnel shall be allowed to stand until complete separation has taken place and the lower layer of sodium sulfate solution is perfectly clear or at most shows a slight opalescence. This settling requires from 3 to 4 hours. After settling is complete the sulfate layer shall be drawn off and kept for further treatment. The carefully separated acid layer shall be drawn down into a weighed 500 cc. round-bottomed short ring neck flask and kept there until further treatment.

VI. TREATMENT OF THE SULFATE SOLUTION—This shall be returned to the separatory funnel which contained the separated tar acids, which still has a thin film of tar acids adhering to the walls. The sulfate liquor shall be extracted three times with successive portions of 100 cc. each of pure benzol and the benzol extracts combined in a separatory funnel of about 500 cc. capacity. The benzol extract shall now be extracted with two successive portions of 25 cc. each of 20 per cent caustic soda solution, or until the soda solution separates nearly colorless. The benzol can then be discarded. The caustic soda solution shall then be warmed until all odor of benzol disappears and acidified with enough 25 per cent sulfuric acid to make slightly acid. This shall be allowed to settle completely, the lower layer of sulfate drawn off and discarded, and the upper layer of acids added to the flask containing the main amount of the separated acid. This flask shall now be weighed and the weight of *wet* crude acids recorded.

VII. FRACTIONAL DISTILLATION—A. *Column*—This shall be the standard 12-pear still head (Eimer & Amend catalogue No. 7156).

B. *Flask*—This shall be a short neck flask as described under V.

C. *Condenser*—This shall be the regular Barrett trough type with a 24-in. tube (A. H. T. catalogue No. 20432).

D. *Thermometer*¹—This shall conform to the following specifications: (1) It shall be graduated from 170 to 225° C. in 1/5° C. and shall be accurate at total immersion to 1/4° C. (2) It shall be well annealed and shall conform to the following dimensions:

Total length—less than 380 mm.

Bulb length—20–25 mm.

170° mark to bottom of bulb—70–80 mm.

Scale length 170–225°—270–280 mm.

Stem diameter—5–7 mm.

Bulb diameter—4–5.5 mm.

E. *Setting up Apparatus*—The flask shall be supported over a burner on a 6 in. square of 1/4 in. asbestos

¹ This thermometer can be obtained from the Taylor Instrument Co

board with an opening in the center 3.5 in. in diameter. It shall be surrounded by a circular asbestos shield about 3½ in. high and of such diameter as to enclose the flask. A piece of asbestos with a hole cut for the neck of the flask forms the top of the shield. The pear column shall be connected to the flask by a tight-fitting cork, and the condenser to the side tube of the pear column. The thermometer shall be inserted into the top of the pear column by means of a well-fitting cork in such manner that the top of the thermometer bulb is opposite the middle of the off-take of the column. The condenser trough shall be kept full of cold water.

F. Method of Conducting the Distillation—The apparatus shall be set up as described and the distillation started and continued at the rate of one drop per second. The distillate shall be first caught in a 100-cc. separatory funnel until the temperature has reached 170° C. The distillation shall then be interrupted and sufficient salt added to the contents of the separatory funnel to cause any acids coming over with the water to rise to the surface. The aqueous layer is removed and the acids returned to the distillation flask, and the flask with contents weighed. Thereby the weight of dry acids is recorded. The distillation shall be again started and the first few drops of acid and water coming over collected in a small, dry separatory funnel. When the last drop of water is over, a fraction to 190° C. is collected in a weighed flask, which shall be closed by a cork as soon as the distillation is completed. The few drops of acid and water which have been collected in the small funnel shall be separated and the acid layer added to the distillate to 190° C. A second fraction from 190 to 202° shall be collected in a 250-cc. round-bottom, short ring-neck flask, which need not be weighed. The distillation shall be discontinued at 202° C. and the flask containing the 190–202° fraction shall be substituted for the first flask, which contained the crude acids. This fraction is now redistilled after drying the condenser tube, using the weighed flask containing the —190° fraction from the first distillate as a receiver. The distillation shall be carried to 197° C. The receiver which now contains the combined fraction up to 197° shall be weighed, the weight of the fraction recorded, and the receiver kept tightly stoppered.

G. Testing the Fraction—The fraction shall be tested for specific gravity and solidifying point as follows:

(1) **Solidifying Point:** A test tube 1 in. inside diameter (this dimension bears no deviation) and 5 in. to 6 in. long is held by a clamp in a vertical position with 3 in. of its lower end immersed in a 500–600-cc. beaker full of water. A standard 0–80° melting point thermometer (A. H. T. Cat. No. 20476), calibrated to an accuracy of at least 0.1° C., is held rigidly by another clamp in the center of the test tube with the bottom of the bulb 0.5 in. from the bottom of the test tube. An agitator, composed of an iron washer attached to a wire and arranged to work freely up and down the test tube around the thermometer, completes the outfit.

The fraction to be tested for solidifying point shall be poured into the tube to a depth of 2 in. and an

approximate solidifying point taken. The contents of the tube shall be again liquefied and the outside bath adjusted to a temperature 4.5 to 5.5° C. below the approximate solidifying point. The temperature relation is very important. The sample is now allowed to cool with constant stirring. The temperature of the sample falls, but when crystals begin to separate a rise is noted which soon reaches a maximum where it remains constant for a varying period of time. This maximum temperature shall be taken as the solidifying point. Two successive tests must give identical results and care must be taken to keep the relation between solidifying point and bath temperature within the 4.5 to 5.5° C. range.

(2) **Specific Gravity**—If the solidifying point is 25° C. or less, this shall be taken at 25/25° C.; if greater than 25° C., the specific gravity shall be taken at 45/45° C. The specific gravities shall be taken with a Westphal balance. Most of the instruments supplied in the United States are standardized for 15.5° C. The balance is set up and the plummet should exactly counterpoise the arm when swinging freely in air. It must be first adjusted to this condition by means of the leveling screw on the base of the column of the balance. The plummet is then immersed in freshly boiled distilled water at 15.5° C. and if the balance and weights are properly made a reading of 1,000 should be obtained. Next, a reading is taken in boiled distilled water at either 25 or 45° C., depending on the temperature desired. After the first adjustment of the balance, the reading in water at 15.5° C. may be dispensed with, but care should be taken to see that the balance in air is correct before readings are made. After the water standard at 25 or 45° C. is established, a reading is taken in the acid fraction at the same temperature. A simple division gives the specific gravity. Precautions to be observed are: keep the balance clean and dry; see that the plummet is properly cleaned and dried when changing from one liquid to another; keep the point to which the wire holding the plummet is immersed constant; control the temperature carefully; and see that the plummet swings freely and does not touch the sides of the vessel containing the liquid.

(3) **Comparison with Curves**—After the solidifying point and specific gravity of the fraction are determined, compare them with the phenol determination curves and see whether the point plotted by the constants falls well within a determination area. If it does not or if it is very close to the limit, it is best to proceed to make a measure of the constant with pure phenol.

(4) **Mixing with Phenol**—Based on the previous method, make a solidifying point of a mixture containing 10% of the sample and 90% of pure phenol. A little more time is required in making the mixture as well as the heat necessary to place the mixture well above the solidifying point. After the mixture well above the solidifying point is determined, proceed to mix the sample with pure phenol in the usual manner. The mixture must be thoroughly equilibrated, and must be made in perfectly dry conditions. The method of mixing must be such that no atmospheric interference is possible.

The specific gravities and solidifying points are taken exactly as described previously.

H. Interpretation of Results—After the tests show the point to be within the determinative areas the method of interpolation is as follows: If the plotted point occurs in the lower set of curves a line is drawn through the point normal to the curves between which it lies. The distance from curve to curve is measured accurately along this line and the fractional distance of the point is interpolated into per cent phenol. If the point occurs in the upper set of curves, the line is drawn through the point parallel to the nearest of the dotted converging lines, the linear distance measured and the percentage interpolated as before.

If mixtures are made, the calculations are somewhat complicated and the following formula may be used:

$$\begin{aligned} \text{Let } A &= \text{per cent phenol found in mixture} \\ B &= \text{Grams "to 197"} \text{ fraction taken} \\ C &= \text{Grams pure phenol taken} \\ X &= \text{per cent phenol in "to 197"} \text{ fraction} \\ X &= \frac{A(B + C) - 100C}{B} \end{aligned}$$

The per cent phenol in the "to 197" fraction multiplied by the weight of the fraction gives the weight of total phenol in the oil or crude acid taken.

A specimen test on acid with the recorded data may be shown as follows:

TAKEN: Crude Acid, 300 g.	
Distilled 170–190°	60.65 g.
190–202°	178.05 g.
190–202° redistilled	
to 197°	78.05 g.
Total under 197°	138.7 g. = 46.2 per cent
Sp. gr. at 25/25° C.	1.0602
Solidifying point.	20.4°
These constants are indeterminate.	
MIXTURE { to 197° fraction	25 g.
Pure phenol	25 g.
Sp. gr. at 45/45° C.	1.0576
Solidifying point.	31.7° C.
Phenol in fraction mixture (from curve)	84.75 per cent
PHENOL IN ORIGINAL ACIDS (calculated)	32.2 per cent

The method requires about two days to complete a test but several can be run simultaneously. The keynote of success in this work is extremely careful and accurate attention to the details of manipulation. This test has been in use in our laboratories since the early part of 1916, and has given very satisfactory results.

RESEARCH DEPARTMENT, THE HARRITY COMPANY
17 BATTERY PLACE, NEW YORK CITY

A NOTE ON SILICON-COATED METAL

By W. E. VAWTER

Received February 10, 1917

The resistance of silicon to the corrosive action of acids and alkalis is taken advantage of in chemical industry by using apparatus constructed of iron which contains a large percentage of silicon. However, the high silicon castings have small tensile or compressive strength and breakage is high. It was therefore thought that, if iron could be satisfactorily coated with silicon, a great saving could be effected. Coating iron by dipping into molten silicon is unsatisfactory, since the melting points of the metals are similar and iron is soluble in fused silicon.

The object of a study made by the author was to investigate a process for coating a metal, preferably iron, with silicon, so that the non-resisting metal would be amply protected from any corrosive chemical, and at the same time stand up under severe handling, without injury to the object or the protective coating. Samples of iron were heated to temperatures of 400 to 600° C. in an atmosphere of silicon hydride,¹ in order to ascertain whether the gas would decompose and form a coating of silicon upon the surface of the iron.

EXPERIMENTAL

1—Iron wire was heated to 550° C. in a current of dry silicon hydride for one hour. Small patches of silicon formed over the surface of the wire, but when the sample was placed in a normal solution of sodium chloride, corrosion immediately started where no silicon was present, totally undermining the silicon coating after two weeks' immersion.

2—A repetition of Experiment 1. In this experiment the silicon did not appear to be undermined; the coating of silicon remained after two weeks' immersion, although corrosion had taken place rapidly at all other places.

3—This sample was heated to 500° C. for two hours. A thin film of silicon was deposited on the wire and the wire became badly pitted where there was no coating of silicon. The silicon coat was intact after two weeks' immersion.

4—This sample was heated for 3½ hrs. at 550° C. Very little silicon adhered to the wire, and that which deposited was in scales and could easily be removed.

5—This sample was first pickled in acid and then heated in a current of silicon hydride at 550° C. for 2 hrs. The resulting coating was smooth and uniform in color, and the treated iron remained in salt solution four days before any corrosion was noticed; this was at the end where the wire had been cut and had no silicon protection.

6—The sample was first heated to 700° C. and then allowed to cool to 550° C. before exposing to the gas. While an excellent coat was obtained, which stood up well in the salt solution, no advantage in preheating could be observed.

7—This sample, after running two hours at 550° C., was further heated for 5 minutes at 700° C. Ten days' immersion in salt solution completely removed the coat. It was expected that the silicon would attach itself more firmly to the iron by the heat treatment, but the after-heating probably broke the coat at some place and allowed corrosion to set in.

8—An exact duplicate of Experiment 5 with similar results.

9—A piece of wire, which had been pickled, washed, dried and exposed to the air for several hours, until

¹ The silicon hydride used in these experiments was prepared by treating an alloy of magnesium and silicon with a dilute solution of hydrochloric acid. The evolved gas consisted of about 5 per cent of silicon hydride and 95 per cent of hydrogen. The alloy was prepared by intimately mixing one part of powdered silicon with two parts of powdered magnesium and heating the mixture for two hours at 600° C. in an atmosphere of hydrogen. This alloy has the composition approximately represented by the formula SiMg_2 .

a film of oxide had formed, was treated as in Experiment 5, but no silicon adhered to the wire.

10—A sample was heated at 550°C . for 10 min. and the temperature was then changed to 700°C . for the same period. This alternation was prolonged $1\frac{1}{2}$ hrs. Little silicon deposited upon the wire and that which did had a tendency to scale off.

11—A sample treated by the method used in Experiment 5 was replaced in the tube and heated to 700°C ., but the coat scaled.

12—This sample was heated 5 hours at 750°C . Silicon deposited upon the wire, but a slight bending would break the coat and it could be peeled off with the fingers. The wire did not heat uniformly and that portion which was maintained at a lower temperature did not give this fracture effect. The iron under the scale was unchanged, which would indicate that the silicon merely forms a shell over the iron.

Other metals, copper, nickel and aluminum, were also subjected to treatment, but no coating of any description was obtained.

It is interesting to observe that silicon will coat iron when applied by this method, under proper conditions; but no practical use can be looked for along this line. What was desired was an adherent, homogeneous deposit of silicon on iron; but the above experiments showed that only a thin and fragile shell formed over the iron.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH
UNIVERSITY OF PITTSBURGH

THE COMPOSITION OF MENHADEN OIL FATTY ACIDS¹

By E. TWITCHELL

The object of this analysis was as much to test the use of my melting-point method of determining fatty acid mixtures as to investigate the true composition of the fatty acids found in menhaden oil.

In a previous paper² I described a method of determining the composition of mixtures of solid fatty acids, which consisted in adding a certain proportion of the mixture to be analyzed to a solvent consisting of a pure fatty acid of the kind to be determined, then finding the melting point and noting how much the original melting point of the solvent had been depressed. This depression was caused by all the acids in the mixture except the one sought, which, being identical with the solvent, would have no effect on it. Assuming that the other acids, singly or in mixture, produced a lowering of the melting point of the solvent proportional to their total concentration and independent of the kind of acid, it was a simple calculation to find the amount of these other acids and, by difference, that of the one sought.

The assumption that the lowering of the melting point of the solvent acid is proportional to the percentage of foreign acids is very nearly true in most cases up to 20 per cent, though, if the solvent is an acid of unusually low melting point as compared with the dissolved acid, as for instance, behenic dissolved

in myristic acid, the melting-point curve beyond 10 per cent of the dissolved acid is no longer a straight line and the depression caused by 20 per cent of this acid is abnormally great. In such cases only 10 per cent of the acid of higher melting point was used in the mixture.

The assumption that all acids produce the same lowering of melting point is for this purpose near enough to the truth where the more common fats and oils are concerned, the fatty acids of which do not differ greatly in molecular weight. I have generally taken 4° as the lowering of melting point caused by adding 20 parts of one fatty acid to 80 parts of another considered as the solvent. However, where the acids are to some extent known it will be more accurate to take values determined for each fatty acid. A number of these values I shall give below.

This as an analytical method is limited to fatty acids solid at ordinary temperatures, but can be extended by applying it to the solid fatty acids obtained from liquid acids either by the hydrogenation process or by fusion with caustic potash. The hydrogenation process, by the addition of hydrogen, converts unsaturated fatty acids into saturated ones having the same number of carbon atoms; oleic, linolic, linolenic and clupanodonic acids are all converted into stearic acid. Fusion with caustic potash produces a decomposition of members of the oleic series by which the principal product is a saturated fatty acid having two less atoms of carbon; oleic acid is converted into palmitic acid, erucic into arachidic, etc. Linolic acid, with two double linkages, is converted into myristic acid and it may be assumed that all acids of the linolic series on fusion with caustic potash yield a saturated acid with four less carbon atoms. As to the action of caustic potash on the still more unsaturated acids, so far as I know, no experiments have been made, though it has been assumed that acids with three double linkages (linolenic acid) would yield a saturated acid of six less carbon atoms and those having four double linkages (clupanodonic acid) would yield a saturated acid having eight less carbon atoms.

It is easily seen what an aid this power of converting liquid acids into solid acids according to definite laws can be toward arriving at the composition of a fatty acid mixture; and in my previous paper I made use of the hydrogenation process. In that paper I gave results of my analysis of menhaden oil fatty acids as follows:

Palmitic acid	100.0
Other solid saturated acids	1.8
Unsaturated acids with 16 carbon atoms	1.8
Unsaturated acids with 18 carbon atoms	1.8
Unsaturated acids with 20 carbon atoms	1.8
Other unsaturated acids	1.8
	100.0

The vacancies in this analysis were due to my not having the pure standard acids corresponding with all of the fatty acids in the mixture. I had at the time only palmitic, stearic and behenic acids. I have since prepared myristic and arachidic acids, making the paper of several unsaturated fatty acids with each main

¹ Read at the 211th regular meeting of the Commercial Section, American Chemical Society, March 28, 1917.

² This Journal, 6 (1914), 564.

ber of carbon atoms complete between myristic and behenic acids inclusive.

PREPARATION OF MYRISTIC ACID

The fatty acids of nutmeg butter were repeatedly crystallized, first from petroleum ether and then from 76 per cent alcohol. In all there were thirteen crystallizations, the last few of which scarcely made any change in melting point or combining weight. The combining weight by titration with alkali was 228.5 (theory 228). The melting point was 53.76°.

PREPARATION OF ARACHIDIC ACID

No fat could be found that contained any considerable quantity of this acid; but rape oil contains erucic acid, which on fusion with caustic potash, should yield arachidic acid.

The fatty acids of rape oil were fused for 6 hrs. with caustic potash at 300° C. At the end of this time the liberation of hydrogen had ceased. The fatty acids were separated from the other products of the fusion, and, as arachidic acid seemed to be the acid of highest melting point in the mixture, it was a simple matter to separate it from the rest and to purify it by simple crystallization from petroleum ether and 90 per cent alcohol. Eight crystallizations gave an acid having a combining weight of 312 (the theoretical) and a melting point of 74.78°.

The following table gives the melting points of mixtures in pairs of all the series of five acids before mentioned, 80 parts being taken of one, considered the solvent, and mixed with 20 parts of each of the others. The method of determining the melting point was about as described in my previous paper. Correction was always made for the stem of the thermometer which extended above the bath.

	Melting point	M. p. of Mixture containing 20% Behenic acid	Lowering of m. p. of Solvent	M. p. of Mixture containing 20% Arachidic Acid	Lowering of m. p. of Solvent	M. p. of Mixture containing 20% Stearic Acid	Lowering of m. p. of Solvent	M. p. of Mixture containing 20% Palmitic Acid	Lowering of m. p. of Solvent	M. p. of Mixture containing 20% Myristic Acid	Lowering of m. p. of Solvent
Behenic acid.....	79.99			76.42	3.57	75.81	4.18	75.45	4.54	75.31	4.68
Arachidic acid.....	74.78	71.17	3.61			71.05	3.73	70.79	3.99	70.49	4.29
Stearic acid.....	69.30		4.02*	65.34	3.96			65.08	4.22	64.91	4.39
Palmitic acid.....	62.37		3.68*		3.88*	58.16	4.21			57.77	4.60
Myristic acid.....	53.76				3.62*		4.42*	49.23	4.52		

*On account of the relatively high melting point of the dissolved acid the mixture was made with 90 parts solvent plus 10 parts dissolved acids. The lowering of melting point multiplied by 2 gives an imaginary value for the 80 + 20 mixture.

The figures given in this table are not quite to be considered as final, as I am not yet satisfied with the accuracy of my method of determining melting points and hope to improve it.

MYRISTIC ACID IN HYDROGENATED MENHADEN OIL

In the course of my previous work on menhaden oil a fractional distillation had been made of the fatty acids separated from the hydrogenated oil. There were twenty-one fractions in all.

In this distillate were found behenic, stearic and palmitic acids. The presence of arachidic and myristic acid seemed probable, but having neither of these acids in the pure state I could not at that time establish their presence in any of the fractions.

If any myristic acid were present it would very

likely be found in the first fraction. To further concentrate it, a portion of this fraction was dissolved in alcohol, partially precipitated with lead acetate and filtered. The fatty acids were separated from the filtrate and melted in the proportion of 20 parts with 80 parts of myristic acid:

The m. p. of this mixture was.....	51.60°
That of pure myristic acid is.....	53.76°
The lowering of the m. p. was therefore.....	2.16°
The lowering of the m. p. of myristic acid by 20 per cent of palmitic acid is.....	4.53°
The percentage of myristic acid in the fatty acids under examination is therefore: $100 \times \frac{2.16}{4.53}$	52.3 Per cent.

which clearly establishes the presence of myristic acid in the hydrogenated oil. Whether it was present in the original oil or was formed from an unsaturated acid by hydrogenation will be determined later.

The value 4.53° (the depression caused by palmitic acid as given in the table) was used in this calculation because it was practically certain that the acids other than myristic in the substance were chiefly palmitic.

For more accurate quantitative results, another mixture should be made as described in my previous paper; that is, using so much of the substance to be examined that the lowering of melting point is about 4°.

ARACHIDIC ACID IN HYDROGENATED MENHADEN OIL

Fractions 15 and 16 of this same distillate had an average combining weight of 308.5 and were the most likely to contain arachidic acid. They were united and crystallized twice from 90 per cent alcohol at 15° C. The mean combining weight of the crystals was 324. In my previous work it had been shown that behenic acid (molecular weight 340) was present in the hydrogenated oil. It would almost certainly be in this fraction. It remained to determine whether the

reduction in combining weight was due to arachidic acid,

20 parts of the crystals melted with 80 parts of arachidic acid had a m. p. of.....	72.95
Arachidic acid has a m. p. of.....	74.78
The lowering of the m. p. was therefore.....	1.83
The lowering of the m. p. of arachidic acid by 20 per cent of behenic acid is.....	3.61
The percentage of arachidic acid in the crystals is therefore: $100 \times \frac{1.83}{3.61}$	49.3 Per cent.

which establishes the presence of arachidic acid in the hydrogenated oil.

As a matter of interest a test was made for behenic acid in the same fraction.

20 parts melted with 80 parts of behenic acid caused a lowering of m. p. of the latter of.....	1.96°
The percentage of behenic acid in the substance is therefore: $100 \times \frac{3.57 - 1.96}{3.57}$	45.1 Per cent

The percentage of arachidic acid in the total fatty

acids of the hydrogenated oil, not distilled, was determined as follows:

20 parts were melted with 80 parts of arachidic acid. The mixture had a m. p. of.....	71.67
The m. p. of arachidic acid is.....	74.78
The lowering of m. p. is therefore.....	3.11
The lowering of the m. p. of arachidic acid by the other acids in the mixture is taken as.....	4.00
The percentage of arachidic acid is therefore $100 \times (4.00 - 3.11) / 4.00 =$	22.2

which is either in the original oil or has been produced by hydrogenation.

THE SOLID FATTY ACIDS OF MENHADEN OIL

These were separated from the liquid acids by the method described in my previous paper. About 31 per cent were obtained, having, however, an iodine value of 9.44, equivalent to 10.5 per cent of oleic acid, which, for the purposes of this calculation, I shall assume it to be.

The menhaden oil which I used for this work was unfortunately not the same as that I had used in my former work. It was not so fresh and contained more free fatty acids than I could have wished. This may account for the rather high iodine value of the separated solid acids.

20 parts of these solid fatty acids melted with 80 parts of myristic acid, had a m. p. of.....	50.57
Myristic acid has a m. p. of.....	53.76
The lowering of m. p. is therefore.....	3.19
The lowering of the melting point of myristic acid by 20 per cent of palmitic acid is.....	4.53
The percentage of myristic acid in the solid fatty acids is therefore $100 \times (4.53 - 3.19) / 4.53 =$	29.6

As a confirmation of this result and to leave no doubt that myristic acid was really present, the above solid fatty acids were dissolved in alcohol and enough lead acetate added to precipitate about one-half. The fatty acids separated from the filtrate, tested as above, gave 45.9 per cent of myristic acid.

20 parts of the same solid fatty acids melted with 80 parts of arachidic acid had a m. p. of.....	70.87
Arachidic acid has a m. p. of.....	74.78
The lowering of m. p. is therefore.....	4.21
The lowering of the m. p. of arachidic acid by 20 per cent of palmitic acid is.....	3.99
The percentage of arachidic acid is therefore $100 \times (3.99 - 4.21) / 3.99 =$	None

In the same way the percentage of palmitic acid in the solid fatty acids was found to be 52.9 per cent, and of stearic acid 5.7 per cent, and as the oleic acid, from the iodine value, was 10.5 per cent, the composition of the solid acids as separated, is:

	Per cent
Myristic acid	29.6
Palmitic acid	52.9
Stearic acid	5.7
Arachidic acid	None
Oleic acid	10.5
	99.7

As the menhaden oil fatty acids contained 31 per cent of acids of the above composition, the amount of myristic acid in the menhaden oil fatty acids is $29.6 \times 0.31 = 9.2$ per cent and of stearic acid $5.7 \times 0.31 = 1.8$ per cent.

In my previous paper I expressed a doubt as to whether there was any stearic acid in the mixture, though the tests gave small positive figures. The doubt might still exist, and to decide this point a fractional precipitation was made of the fatty acids of menhaden oil dissolved in alcohol, using only enough

lead acetate to precipitate about 2 per cent of fatty acids. This precipitate, on decomposing, yielded fatty acids testing 26.5 per cent of stearic acid. There can be no doubt of the presence of stearic acid in the original oil.

GENERAL RESULTS

Having found myristic acid in both the original and the hydrogenated fatty acids in equal amounts, it was not produced by hydrogenation. On the other hand arachidic acid was found only in the hydrogenated and not in the original fatty acids. It was therefore produced by the addition of hydrogen to an unsaturated acid with 20 atoms of carbon.

The composition of menhaden oil fatty acids given in my paper of July 1914, can now be filled out as follows:

	Per cent
Palmitic acid.....	22.7
Myristic acid.....	9.2
Stearic acid.....	5.7
Unsaturated acids with 16 carbon atoms.....	None
Unsaturated acids with 18 carbon atoms = 26.7 less 1.8 per cent stearic acid =.....	24.9
Unsaturated acids with 20 carbon atoms.....	22.2
Unsaturated acids with 22 carbon atoms.....	20.5

As to the series to which the unsaturated fatty acids with the different numbers of carbon atoms belong, the method of fusion with caustic potash above mentioned will give some information. On fusing the menhaden oil fatty acids with caustic potash and separating the higher fatty acids from the product, a mixture was obtained which would not crystallize from 90 per cent alcohol except at very low temperatures, and this already indicated that it contained no arachidic acid. It was crystallized from 76 per cent alcohol.

20 parts of the crystals melted with 80 parts of arachidic acid had a m. p. of.....	70.87
The m. p. of arachidic acid is.....	74.78
The lowering of m. p. was therefore.....	3.74
The lowering of the m. p. of arachidic acid by 20 per cent of stearic and palmitic acids is.....	3.86
The percentage of arachidic acid is therefore $100 \times (3.86 - 3.74) / 3.86 =$	3.1

As this was in a small fraction which should contain all of the arachidic acid present, the amount in the total product of the fusion would be very small if, indeed, it can be inferred from the above low figure that its presence has been proved at all. From this it can be concluded that the unsaturated acid with 22 carbon atoms found in menhaden oil and which, like erucic acid, is converted by hydrogenation into behenic acid, is nevertheless not erucic acid, since on fusion with caustic potash it is not converted into arachidic acid. It is probably a more unsaturated acid which is converted into stearic or palmitic acid by the fusion.

The above fraction was also used for palmitic and stearic acid and found to contain Palmitic acid 13.6 per cent, and stearic acid 1.8 per cent.

The fraction for the fusion of with caustic potash, was soluble although still somewhat in suspension, except for enough from the fusion to affect the results very seriously. From 2 the average value 4.7 for the product found by fusion in pure alcohol and with 80 of arachidic acid have been used in my calculations. The

general conclusions as to the composition of menhaden oil would not have been changed.

As to the usefulness of this method, I know of no other way of determining the composition of a mixture of solid fatty acids of more than two constituents, especially where only a small quantity is available. Even with large quantities, though it might be possible by means of numerous fractional precipitations or distillations to separate some of each of the constituents in a pure state, a quantitative result can never be obtained in this way.

WYOMING, OHIO

NOTE ON THE DETERMINATION OF STRONTIUM AND LITHIUM IN WATER

By S. D. AVERITT

Received December 13, 1916

There are probably no determinations in water analysis which on the whole require more time and work than those of strontium and lithium.

Several years ago while coöperating with the Referee on Water Analysis for the Association of Official Agricultural Chemists, the methods which are now official for strontium and lithium were tested. The great amount of time and work required for these determinations led the writer somewhat later to investigate the accuracy of indirect methods which were sound in theory and which, with careful work, must prove accurate provided there was a really determinable amount of strontium or lithium present; that is, an amount that would not be too seriously affected by the experimental error unavoidable in the most careful work. This investigation led to the conclusion that the indirect methods employed were as accurate as the official methods and the time and labor saved was a matter of considerable importance.

It is self-evident that pure precipitates and careful work are necessary for indirect methods, the lack of which has undoubtedly had much to do with the unfavorable opinion many chemists entertain relative to them.

It is believed that a brief statement of the methods will be of general interest to water analysts and others who have occasion to determine strontium and lithium, as they differ materially from other indirect methods that have been proposed, at least in their application to the separation of calcium and strontium and the extent to which they are carried in the separation of the alkalis. In the brief statement which follows, no details of procedure will be given as they should be perfectly familiar to any analyst of reasonable experience.

The official method (Stromeyer-Rose) for the determination of strontium begins with the weighed oxides of calcium and strontium (CaO and SrO). These are dissolved in nitric acid and brought to dryness, the separation of strontium depending upon the insolubility of strontium nitrate in alcohol-ether mixture.

The writer's method is as follows: Dissolve the weighed oxides in hydrochloric acid and precipitate again as oxalates as in the first case; filter, wash, dis-

solve in sulfuric acid and titrate with standard KMnO_4 , noting the exact volume of KMnO_4 required.

If W = weight of CaO and SrO.

O = total oxygen in CaO and SrO (found by the titration with KMnO_4).

X = O in CaO.

Y = O in SrO.

Then $X + Y = O$ (1)

and $3.5044X + 6.4769Y = W$ (2)

Solving for Y , determine SrO (6.4769 Y) then W — SrO = CaO. When the value of Y is found, in order to get

SrO a constant factor occurs which is $\frac{6.4769}{6.4769 - 3.5044}$ or 2.179. Consequently it is not necessary to solve these equations in order to get the weight of SrO, which is obtained as follows:

(W — CaO equivalent of KMnO_4 titration) 2.179 = SrO. (3)

In order to test the accuracy of the above method, pure CaCO_3 equivalent to 0.9954 g. CaO and SrCO_3 equivalent to 0.1000 SrO were dissolved in hydrochloric acid and made up to 500 cc.; 50 cc. aliquots equivalent to 0.09954 g. CaO and 0.0100 g. SrO were used, giving the results shown in Table I.

Expt. No.	CaO + SrO		CaO Equivalent of KMnO_4	SrO	
	Present	Found		Present	Found
1.....	0.1095	0.1095	0.1048	0.0100	0.0102
2.....	0.1095	0.1096	0.1052	0.0100	0.0096
3.....	0.1095	0.1096	0.1049	0.0100	0.0102
4.....	0.1095	0.1096	0.1051	0.0100	0.0098
5(a).....	0.1095	0.1097	0.1052	0.0100	0.0099

(a) Precipitated in presence of magnesium chloride.

The oxalates were washed with a $\frac{1}{2}$ per cent solution of ammonium oxalate in all cases. Those which were to be titrated were finally washed with 15 cc. of cold water in 5-cc. portions dropped from a pipette around the top of the filter fast enough to cover the precipitate, letting the filter run dry between each washing. This amount of washing with water is sufficient for aliquots containing approximately 0.0300 g. of oxides and it is not advisable to have much larger aliquots for titration nor to use more water in washing, otherwise strontium oxalate will be dissolved.

If the double oxides weigh more than 0.0500 g., aliquots should be taken for the KMnO_4 titration. The KMnO_4 should not be stronger than $N/10$.

The Official Method for the determination of lithium (Gooch) begins with the weighed chlorides (NaCl , KCl and LiCl) and depends upon the insolubility of sodium and potassium chloride in absolute amyl alcohol.

The writer's method is to make the solution in water of the weighed chlorides of sodium, potassium and lithium up to convenient volume. Take an aliquot for the determination of K from which KCl and the Cl in the same becomes known. Another aliquot is titrated with standard AgNO_3 from which the total Cl is obtained.

If W = weight of $\text{NaCl} + \text{KCl} + \text{LiCl}$.

C = weight of total chlorine (as found by titration with AgNO_3).

Cl in $\text{NaCl} + \text{LiCl} = C - \text{Cl}$ in KCl .

$X = \text{Cl}$ in NaCl and $Y = \text{Cl}$ in LiCl .

Then, $X + Y = C - Cl$ in KCl (1).
 and $1.6486X + 1.1957Y = W - KCl$ (2).
 Solving for Y find weight of $LiCl$ (1.1957 Y) in getting the weight of $LiCl$ from Y a constant factor occurs, viz.,
 $\frac{1.1957}{1.6486 - 1.1957}$ or 2.64, and as in the case of strontium it is not necessary to solve the equations.

The weight of $LiCl$ is obtained as follows:

The $NaCl$ equivalent of $C - Cl$ in $KCl - (W - KCl)$ multiplied by 2.64 = $LiCl$ (3).

In order to test the accuracy of the method, 0.5000 g. $NaCl$, 0.1000 KCl and 0.0100 $LiCl$ were dissolved in water and diluted to 100 cc. Spectroscopic tests showed a small quantity of potassium in the sodium chloride and a trace of sodium in the potassium chloride. This was immaterial since no lithium was shown in either the sodium chloride or potassium chloride nor was there any lithium in the calcium and magnesium chlorides used, but a small quantity of sodium and a trace of potassium were indicated in both. The results appear in Table II.

TABLE II—DETERMINATION OF LITHIUM (RESULTS IN GRAMS)

Expt. No.	$KCl + NaCl + LiCl$		LITHIUM $LiCl$	
	Present	Found	Present	Found
1.....	0.6100	0.6098	0.0100	0.0106
2(a).....	0.1525	0.1569	0.0025	0.0025

(a) Determination in a solution containing calcium and magnesium chlorides.

The determination of lithium by this method is based upon two other definite determinations, potassium and chlorine, than which, in the hands of a skilful analyst and under the conditions of this method, no determinations are more accurate.

The only other factor affecting the accuracy of the method is an impurity in the weighed chlorides and under ordinary conditions this can result only from careless work or inexperience.

KENTUCKY AGRICULTURAL EXPERIMENT STATION
 LEXINGTON, KENTUCKY

NITRATE DETERMINATIONS IN THE PRESENCE OF CHLORIDES

By W. F. GERICKE

Received February 2, 1917

The presence of chlorides in solutions on which nitrate determinations are to be made by the colorimetric method has long been a source of trouble to the analytical chemist. When nitrates are present in large amounts in solutions containing chlorides, determinations can very easily be made by the use of some of the reduction methods. Since, however, determinations for nitrates are often called for in solutions in which the amounts present are small, the quantity of ammonia produced by the reduction of the nitrates is of such magnitude as to often introduce a considerable error due to manipulation. It is under such conditions that the phenoldisulfonic acid method for nitrate determination is often employed, and in the absence of chlorides has been found to be sufficiently accurate and expeditious.

The effect of chlorides on nitrate determinations has been the subject of some study and has been duly reported in chemical papers. It is not deemed necessary to review here the literature on the subject. Suffice

it to mention some of the results of the more important investigations.

(1) Chlorides cause losses of nitrates in determinations made by the phenoldisulfonic acid method.

(2) The loss of nitrates is not occasioned by the evaporation of the aqueous solution to dryness prior to the addition of the phenoldisulfonic acid.

(3) The loss of nitrates occurs when the phenoldisulfonic acid is added to the residue from the evaporated solution.

(4) The use of precipitants to remove the chlorides prior to the evaporation of the aqueous extract is recommended for accurate determinations.

(5) The use of calcium oxide and also calcium carbonate for the clarification of aqueous extracts, especially from soils, is recommended as a precipitant that is both efficient and non-interfering in the nitrate determinations.

The result of investigations, the conclusions of which have been briefly stated above, indicates that the presence of chlorides interferes with the reactions at a certain point in the process of the determinations—namely, when the acid and dry salt containing the nitrates and chlorides come into contact. This results in the production of heat with the liberation of both chlorine and nitric acid, and thus interferes with the proper reaction of the latter with the phenoldisulfonic acid. Working on the principles enunciated by the investigators studying the colorimetric method of nitrate determinations, it occurred to me to try a method by which total evaporation of the nitrate-bearing solution to dryness could be obviated together with the necessity of adding the acid to the dry residue. Since the phenoldisulfonic acid reagent is a mixture of sulfuric acid and phenoldisulfonic acid it seems that the proper condition for the reaction of the phenoldisulfonic acid and the nitrates is in a sulfuric acid solution. By the addition of sulfuric acid to the nitrate-containing solution, a condition is brought about by which the complete evaporation to dryness of the aqueous solution may be obviated. When the phenoldisulfonic acid is then added to the acid-treated nitrate solutions some nitrophenoldisulfonic acid is formed. The complete reaction, however, will take place when the proper concentration of the solution has been attained. To attain this concentration and to employ temperature to accelerate the reaction of the nitrates and the phenoldisulfonic acid is the purpose of the partial evaporation to which the samples are subjected.

In making nitrate determinations one must remember that the theoretical reaction that elucidates the principle of the method goes to completion for quantitative determination only when an excess of phenoldisulfonic acid is used. Therefore, proper care should be taken in the preparation of the sample that the amount of nitrate present in the sample be neither too large nor too small to introduce measurable error due to the excessive or insufficient use of a given measure of the reagent acid reagents. Too much acid may seriously affect the accuracy of the determinations of samples in which the nitrate content is small.

because of the action of the acid on the salts, and the increase in temperature involved.

The phenoldisulfonic acid reagent, as used in the laboratory, was prepared according to the Chamot method, *i. e.*, an addition of fuming sulfuric acid is employed to insure pure phenoldisulfonic acid, free from all traces of phenolmonosulfonic acid.

The quantity of the sample used for analysis must be determined by the amount of nitrates in the aqueous solution. If the nitrate content is from 1 to 5 parts per million, a sample of at least 50 cc. should be used. To the sample, placed in a casserole or beaker, 1.5 cc. of concentrated sulfuric acid are added with constant stirring, then 2 cc. of phenoldisulfonic acid reagent. The casserole is then placed on a water bath, and most of the solution evaporated at the ordinary temperature of the steam bath. The last part of the evaporation, however, should be performed at a temperature preferably not over 70° C.

The evaporation should proceed until the original solution is concentrated to a quantity varying from 6 or 7 to 12 or 14 cc. The point to which evaporation must be continued is determined by the amount of nitrates in the original solution; for a low nitrate content a greater concentration of the original solution will be necessary. The proper concentration is determined by the color of the solution, which resembles that of phenoldisulfonic acid, slightly tinged with yellow. This condition will come, and final evaporation be attained at about the time that acid, due to the presence of chlorine, can be detected in the evaporating vapors. The important thing to observe in this modification is to bring about the final evaporation at a relatively low temperature. In no case should the solution be materially colored and turbid, although it may be somewhat darkened. A colored solution will result in an off tint when the alkali is added and will necessarily interfere with the accuracy of the determination. When the evaporation of the solution to its proper concentration has been accomplished, about 50 cc. or more of water are added; the solution is then neutralized with an alkali, care being taken to avoid the formation of excessive temperature when the acid is neutralized. The solution is then placed in the colorimeter and compared with a standard previously prepared, which may be made up according to the old method of total evaporation to dryness before adding the reagents, or according to the modification here reported, either of which will give the proper tint.

RESULTS OBTAINED

Table I indicates the feasibility of adding the phenoldisulfonic acid reagent before evaporation to dryness. Table II indicates the practicability of the method even if relatively large amounts of sodium chloride are present. If the nitrate content is very low and the salt very high, for instance, 1 part per million of nitrate and 1 per cent NaCl, determinations were subject to serious errors, due to loss of nitrates and discoloration of the solution. In cases of very low nitrate and high salt content, evaporation of the solution to its proper concentration should be performed at a much reduced

TABLE I
50 cc. Solution in Sample
1.5 cc. Sulfuric Acid Added
2 cc. Phenoldisulfonic Acid Added

NITRIC NITROGEN P. p. m.	Theoretical Amount in cc. of Standard	ACTUAL READING in cc. of Standard	CHANGE IN TINT
1	50	49	None
1	50	50	None
2	100	100	None
2	100	98	None
5	500	500	None
5	500	500	None
20	1000	1000	None
20	1000	1020	None

TABLE II
50 cc. Solution in Sample
Theoret-
ical Amount

NITRIC NITRO- GEN P. p. m.	NaCl Added mg.	Per cent NaCl Present	Amount in Cc. of Standard	Amount covered (Cc. of Stan.)	CHANGE IN TINT
1	100	0.1	50	50	None
1	100	0.1	50	50	None
1	250	0.25	50	50	None
1	250	0.25	50	48	None
1	500	0.50	50	49	None
1	500	0.50	50	50	None
1	750	0.75	50	50	Slightly colored
1	750	0.75	50	46	Colored
1	1000	1.00	50	35	Badly colored
1	1000	1.00	50	30	Badly colored
5	500	0.50	250	250	None
5	500	0.50	250	250	None
10	1000	1.00	500	500	None
10	1000	1.00	500	500	None

temperature and preferably under partial vacuum, in order to reduce the action of acids on the salts.

SUMMARY

I—A satisfactory modification of the phenoldisulfonic acid method of nitrate determination in presence of chloride salts has been found.

II—Total evaporation of the solution to dryness can be obviated by the use of concentrated sulfuric acid, which is added to the aqueous extract.

III—The addition of sulfuric acid and phenoldisulfonic acid to the aqueous solution prevents the loss of nitrates, which in the old method was due to the action of acid added to the dry salt after evaporation to dryness had been accomplished.

IV—The temperature at which the final evaporation and concentration of the aqueous solution is performed should not exceed 70° C.

SOL. CHEMISTRY LABORATORY
UNIVERSITY OF CALIFORNIA, BERKELEY

A NOTE ON THE PHENOLSULFONIC ACID METHOD FOR NITRATES IN WATERS HIGH IN MAGNESIUM SALTS

By M. STARR NICHOLS

Received February 28, 1917

In the phenolsulfonic acid method for the determination of nitrates in water supplies, as given in the "Standard Methods of Water Analysis of the American Public Health Association," no provision is made for the removal of the hydroxides of magnesium and iron which may form on the addition of the alkali hydroxide used to neutralize the excess phenolsulfonic acid. In this laboratory, until recently, the colored solution containing the nitrated sulfonic acid has been filtered to remove these hydroxides and the filter paper subsequently washed.

In the absence of the hydroxide of iron, the filtration may be dispensed with and the color read immediately if a quantity of an ammonium salt is added to hold the magnesium in solution. There are two

advantages to this procedure. In the process of filtering a deeply colored solution there always remains a small quantity of the color in the filter paper; and in the second place if a large number of samples are being handled each day, the time factor is worthy of consideration.

The quantity of ammonium salt required is dependent upon what alkali is used for the neutralization of the excess acid. If ammonium hydroxide is used, 5 cc. of a saturated solution of ammonium chloride will be found sufficient to hold in solution the magnesium which will be present in from 20 to 50 cc. of most waters. If sodium or potassium hydroxide is used there will be required a larger quantity of the ammonium salt, owing to the result of mass action between the alkali hydroxide and the ammonium salt, and the amount required will be in proportion to the amount of alkali added in excess. The addition of the ammonium salt is made after the neutralization and before the final dilution.

The writer has found this slight change in procedure quite serviceable in routine water analysis.

WISCONSIN STATE LABORATORY OF HYGIENE
UNIVERSITY OF WISCONSIN, MADISON

LEVULOSE THE PREPONDERANT SUGAR OF APPLE JUICES¹

By JOHN R. EOFF, JR.

Received February 19, 1917

Thompson and Whittier² state that levulose is the predominant sugar of apple juice and give the percentages of sugars found in the juice of one variety of apple at different stages of ripeness. Browne³ states that apples contain levulose in excess of dextrose, but gives no figures. Worcollier⁴ says that dextrose and levulose compose 60 per cent to 95 per

sugars present in such juices. The object of this paper is to give the results of some work done on various varieties of apple juices, and is the first of what the author hopes to make a series of several papers treating of the amounts of the different sugars in apple juices.

Twenty varieties of apples were secured through the courtesy of the Virginia Agricultural Experiment Station, at Blacksburg, Va. The fruit had been grown in the orchards of the station, carefully selected as representative and true to name, and picked and immediately shipped when market-ripe. Fifteen of the varieties were native and were the commercial apples best adapted to the section where grown. Five varieties were French cider apples, and had been gathered from trees 14 years old. The juice was thoroughly expressed from the fruit after grinding in a small meat grinder, a very efficient hand press being used for the purpose. The analysis was undertaken immediately after pressing.

The method followed in the examination of the juices was substantially that detailed by Thompson and Whittier: 26 g. of juice were weighed into a 100 cc. flask, clarified with a slight excess of lead acetate, the lead being removed with a slight excess of potassium oxalate after completing the volume. In some instances alumina cream was used in conjunction with lead acetate. The solution was polarized in a 200 mm. tube at 20 and 87° C. before and after inversion with invertase, the instrument used being one of Schmidt and Haensch's make, Ventzke scale. The calculations were made by the following formulas:

$$L = \frac{d - d'}{0.624} \quad D = \frac{b'}{0.794} \quad L \quad S = \frac{a - b}{1.317}$$

ANALYSES OF APPLE JUICES

Variety of Apple NATIVE	Sample Analyzed 1916	Acidity Gravity of Juice of Juice		Temp. C.	PER CENT OF SUGARS AS DETERMINED										PER CENT OF SUGARS OCCURRING AS				
		°Bé	Brin.		SUCROSE					LEVULOSE					Dextrose	TOTAL	SUCROSE	LEVULOSE	Dextrose
					at	at	at	at	at	at	at	at	at	at					
Mother	10 16	47.0	11.8	25	2.2	2.3	8.8	6.4	1.7	2.7	9.7	2.7	9.7	2.7	9.7	2.7	9.7	2.7	9.7
Grimes (Golden)		63.5	12.3	23	3.6	3.9	8.8	6.4	0.3	1.7	9.9	1.7	9.9	1.7	9.9	1.7	9.9	1.7	9.9
Arkansas		69.0	11.9	23	1.5	1.5	8.8	6.2	2.6	3.0	9.9	3.0	9.9	3.0	9.9	3.0	9.9	3.0	9.9
Lambertwig		66.0	11.1	23	0.8	0.7	8.0	3.4	3.8	3.3	9.3	3.3	9.3	3.3	9.3	3.3	9.3	3.3	9.3
York Imperial		67.5	11.8	23	1.1	1.3	6.3	6.6	2.8	2.7	9.9	2.7	9.9	2.7	9.9	2.7	9.9	2.7	9.9
Lankford	10 24	59.0	12.6	24	2.4	2.6		6.8											
Gano		63.0	11.2	23	1.3	1.8	8.9	6.0	3.2	2.6	10.4	2.6	10.4	2.6	10.4	2.6	10.4	2.6	10.4
Peck		67.5	12.0	23	2.4		6.3	6.2	3.3		12.0	3.0	9.9	3.0	9.9	3.0	9.9	3.0	9.9
Northern Spy		56.0	12.0	23	2.8	3.7	6.2	7.1	1.7		10.4	1.6	9.9	1.6	9.9	1.6	9.9	1.6	9.9
White Pippin		50.5	11.9	23	2.4	2.7	8.9	6.8		1.8	10.8	1.8	10.8	1.8	10.8	1.8	10.8	1.8	10.8
Plum Cider	10 27	73.5	10.5	23	0.6	0.6	8.9	6.9	1.4	1.6	9.9	1.6	9.9	1.6	9.9	1.6	9.9	1.6	9.9
Rome (Beauty)		44.5	11.8	22	2.2	1.9	6.1	6.8	1.4	1.9	9.9	1.9	9.9	1.9	9.9	1.9	9.9	1.9	9.9
Yellow Newton		84.0	13.1	22	3.8	3.1	8.9	6.8	1.8	1.1	11.1	1.1	11.1	1.1	11.1	1.1	11.1	1.1	11.1
Stayman Winesap		77.0	13.8	22	3.2	3.1	6.3	6.8	1.1	1.4	11.6	1.4	11.6	1.4	11.6	1.4	11.6	1.4	11.6
Ben Davis		52.0	11.2	22	1.2	1.0	8.9	6.8	2.8		9.9	2.8	9.9	2.8	9.9	2.8	9.9	2.8	9.9
French																			
Honne de Frieulles	11 2	29.0	16.3	22	2.6	2.9	8.8	8.9	2.7	2.0	11.8	2.0	11.8	2.0	11.8	2.0	11.8	2.0	11.8
Amer de Berthecourt		16.0	11.1	22	1.0	1.0	6.6	3.1	1.8	1.8	9.9	1.8	9.9	1.8	9.9	1.8	9.9	1.8	9.9
Gordard		40.0	15.4	22	3.6	3.6	3.1	1.1	1.8	0.0	11.0	0.0	11.0	0.0	11.0	0.0	11.0	0.0	11.0
D'Ardes		118.0	14.3	21	2.2	2.1	6.8				11.0		11.0		11.0		11.0		11.0
Amerodu Surville		41.8	11.1	21	0.7	0.4		6.3			9.9		9.9		9.9		9.9		9.9

at C.

N 10. alkali per 100 cc. of juice

°Bé

Chermet

Acid inversion

on reduction

°B

Optical

rotation

at Cc. N. 10 alkali per 100 cc. of juice.

do Clerget.

do Acid inversion, Cu reduction.

do Optical.

do Brown.

cent of the sugars present in apple juices and in the proportion of 2.8 to 10 times as much of levulose as of dextrose. As far as the author is able to find out, no systematic investigation of any large number of apple juices from various varieties of apples grown in different localities has been made to prove or disprove that levulose is always in greater quantity than the other

Where

d = Direct reading at 20° C.

d' = Direct reading at 87° C.

b' = Direct reading at 87° C.

S = Percent sucrose. L = Levulose. D = Dextrose.

The different sugars were also determined by Browne's method using Mather and Walker's method for the reducing sugars and the following formulae for the calculations:

L = Levulose. D = Dextrose.

S = Percent sucrose. L = Levulose. D = Dextrose.

¹ Published by permission of the Commissioner of Internal Revenue.

² Delaware College Agricultural Experiment Station, *Bull.* 102, 1913.

³ *J. Am. Chem. Soc.* 23, 8.

⁴ *Ann. N.Y.S.* 1, 175.

$$0.793R + S - P = y \quad R - 0.915y = x$$

2.08

where

x = Per cent dextrose. y = Per cent levulose

R = Reducing sugars as dextrose.

P = Polarization of a sucrose normal weight on a saccharimeter, 20° C.

S = Sucrose

The data obtained from the investigation will be found in the accompanying table. It will be noticed that in every instance the amount of levulose exceeds the combined amounts of the other sugars present, and though this work is by no means exhaustive, it by so much substantiates the statements previously made that levulose is the sugar predominating in apple juices.

U. S. INTERNAL REVENUE LABORATORY
WASHINGTON, D. C.

THE INFLUENCE OF CALCITE INCLUSIONS ON THE DETERMINATION OF ORGANIC CARBON IN SOILS

By EDMUND C. SHOREY AND WM. H. FRY

Received February 28, 1917

It has been pointed out by McCaughey and Fry¹ and by Robinson² that soils derived from limestones, especially those of the Limestone and Uplands Province, are peculiar in containing inclusions of calcite and iron oxide in quartz. In a recent mineralogical examination³ of a number of samples of Hagerstown silt loam, one of the important soil types of the Limestone and Uplands Province, the almost universal presence of calcite inclusions in quartz was again brought to our attention and some consideration has been given their significance.

Quartz is among the most resistant soil minerals and it is evident that crystals of calcite inclosed in quartz, so long as such quartz particles were intact, could have no agricultural significance. In fact, such calcite

¹ Bureau of Soils, *Bull.* 91, 1913.

² Department of Agriculture, *Bull.* 123, 1914.

³ The identification of calcite inclosed in quartz in the soils examined was carried out in the manner usual in work with the petrographic microscope. The soil was mounted in an oil having a known refractive index, preferably very close to the index of quartz as this mineral is thereby rendered practically invisible when the analyzing Nicol is removed from the microscope tube.

When the nicols are crossed the calcite grains are readily "spotted" by their high interference colors. The work from that point on is simply confirmatory. Rarely the calcite grains show crystallographic outlines and in these cases the index of the grain can be determined by rotating the stage until the grain disappears and comparing the actual index thus noted with the index calculated for a calcite grain having the same orientation as the grain under consideration. The two indices thus obtained should of course be identical.

The chief difficulty in this procedure is that often the interference figures of the quartz and calcite mutually clash, but with patience grains can be found showing the figures with sufficient clearness to enable the grain to be roughly oriented. When all the conditions are favorable as outlined above, there is no doubt as to the identity of the grains under observation. In other cases the extremely high interference colors practically settle the question, the only probable source of error being the confusion of calcite with dolomite, but so far as any analytical error introduced by the inclusions in quartz are concerned it makes no difference whether they are calcite or dolomite.

So far as is known at present there is no other method of determining roughly the quantity of a given mineral on a slide except actual count of sized material, or measurement of heterogeneous material, and in this latter case, as in rock sections, the material must be of uniform thickness. In the case of inclusions such as those under consideration it is obviously out of the question to apply either of the methods mentioned above, and consequently the quantity of the inclusion present cannot be stated in quantitative terms.

probably would be a less likely source of soluble calcium in a soil than the calcium-bearing silicates.

The analytical significance of such calcite inclusions cannot, however, be ignored, for there are several determinations commonly made by agricultural chemists where their presence would introduce an error.

In carbonate or carbon dioxide determination, where the carbon dioxide is set free from carbonates by a stronger acid, it is evident that any carbonate completely protected by inclusion in quartz would not be determined by any of the methods now in use. Since, however, such calcite or carbonate has no immediate agricultural significance, this error may be ignored where the determination is made for the purpose of indicating proper agricultural practice.

Among the methods used to determine approximately the organic matter in a soil is one that depends on determining the total carbon and calculating this to organic matter by the use of an empirical factor. Two methods are in use for determination of total carbon: combustion in a current of oxygen with or without copper oxide; or, oxidation of the organic matter to carbon dioxide by some moist oxidizing reagent and determination of the carbon dioxide evolved by one of the usual methods. In both cases determination of carbon dioxide evolved from any carbonate present is made on a separate sample and the quantity so obtained deducted from that total obtained on combustion, the difference being stated as organic carbon.

The first method, usually designated the cupric oxide method, is not subject to much modification and is considered an absolute method by which others are to be judged. On account of its tedious character, however, other methods, usually designated moist combustion methods, have been devised. These usually depend on the oxidizing effect of boiling concentrated sulfuric acid to which potassium dichromate has been added; and proposed modifications of this method relate chiefly to the method of determining the carbon dioxide and the design of the apparatus used.

In determining the organic carbon in a soil containing inclusions of calcite in quartz by either of these methods, it would seem from theoretical considerations that in the case of the moist combustion method the carbon dioxide of included calcite would not be set free, while in the case of combustion with cupric oxide the high temperature would decompose the calcite, rupture the quartz grains and the carbon dioxide set free would be calculated as organic carbon, since it would not appear in the ordinary carbonate determination.

Examination of 28 samples of Hagerstown silt loam for calcite inclusions disclosed their presence in all samples but one. One of these, a sample from Chattooga County, Georgia, was selected as suitable for determining whether or not these theoretical considerations would be borne out in practice.

A sub-sample ground to pass a sieve 80 meshes to the inch, well mixed and dried at 105° C., was used throughout, all results being stated as per cent of the dried soil. The following determinations were made: (1) Combustion with cupric oxide in a current of oxygen;

(2) combustion with concentrated sulfuric acid to which potassium dichromate had been added; and (3) combustion of the residue after moist combustion with cupric oxide in a current of oxygen. Determination of the carbonate in the soil gave results less than 0.01 per cent carbon and this has been ignored as a negligible quantity. It was originally proposed to subject the residue from the treatment with sulfuric acid and dichromate after washing and drying to combustion with cupric oxide, but it was found that this material had absorbed a considerable quantity of chromium compounds and gave so much sulfur trioxide on heating that it was not possible to obtain concordant results for carbon when treated in this way, and in place another portion of soil was treated with sulfuric acid and potassium sulfate as in a Kjeldahl digestion, heated until all organic matter was destroyed and the residue perfectly white, washed, dried and weighed.

The following results were obtained, all figures being the mean of three closely agreeing results. The figures obtained on combustion of the residue after treatment with sulfuric acid and potassium sulfate were calculated to original soil.

TOTAL CARBON	Per cent
Moist combustion.....	0.71
Cupric oxide combustion of residue from moist combustion.....	0.12
In soil.....	0.83
Cupric oxide combustion.....	0.80

It is seen from these figures that there is a reasonably close agreement between the total carbon obtained by direct cupric oxide combustion of the soil, and that obtained by adding together that obtained on moist combustion and cupric oxide combustion of the residue.

It has been frequently noted that moist combustion methods have given lower figures for total carbon in soils than those obtained with cupric oxide, and with the idea that the latter was an absolute method, it has been held that the moist combustion method frequently gives figures lower than the actual amount. The results obtained indicate that if this discrepancy is found in the case of soils containing calcite included in quartz, the facts are quite the contrary so far as total organic carbon is concerned.

In other words, in the case of soils containing calcite inclusions, the carbon dioxide of such calcite will not appear in the ordinary carbon dioxide determination but will appear in the cupric oxide combustion and be calculated to organic carbon. This is not the case with the moist combustion method and it would seem fair to assume that in case of soils containing calcite inclusions the figures obtained for organic carbon by this method are more nearly the true value than those by the cupric oxide method.

It should be stated in this connection that in order to obtain all the carbon dioxide in combustion of such soils by the cupric oxide method the heating must be prolonged much beyond the time ordinarily taken for the oxidation of the organic matter. It would seem that the decomposition of the included calcite and the escape of the carbon dioxide by the rupture of the

quartz grains proceeds slowly, and if the combustion is stopped at the end of the period usually adopted, calcite inclusions can still be found under the microscope and the material will give more carbon dioxide on further heating.

Theoretically if the soil were ground so fine that all calcite inclusions were exposed the carbon dioxide of such calcite would appear in the preliminary carbon dioxide determination and no error would be introduced in the subsequent combustion by the cupric oxide method, but it does seem possible to accomplish this in practice. It is evident that the inclusions are exceedingly minute, for the carbon dioxide calculated to carbon in the preliminary carbon dioxide determination was less than 0.01 per cent, while that obtained from the calcite inclusions by cupric oxide combustion was 0.12 per cent, working with a soil ground to pass a sieve of 80 meshes to the inch. The residue from a moist combustion after washing and drying was ground to pass a sieve 130 meshes to the inch and then leached with hydrochloric acid, and after this treatment calcite inclusions were still abundant when examined under the microscope.

It is, of course, apparent that in any comparison of methods all determinations should be made on samples ground to the same degree of fineness.

U. S. DEPARTMENT OF AGRICULTURE
BUREAU OF SOILS, WASHINGTON

THE ACTION OF SOLUTIONS OF AMMONIUM SULFATE ON MUSCOVITE

By R. E. GARDINER and EDMUND C. SHOREY

Received February 16, 1917

Muscovite, one of the micas, is a mineral frequently found in the rocks from which soils are formed and is a commonly occurring mineral in soils. In some soil series it is one of the characteristic or predominating minerals, for instance in a sample of Gloucester stony loam after mechanical separation the sands were found to contain 5 per cent of muscovite and the silt 30 per cent. In the same way a sample of Penn silt loam was found to contain 6 per cent of muscovite in the sand and 9 per cent in the silt.¹

Muscovite is usually considered one of the most stable of soil minerals. Clark says,² "Muscovite, under ordinary circumstances, is one of the least alterable of minerals. The feldspar of a granite may be completely kaolinized while the embedded plates of mica retain their brilliancy unchanged."

McCaughey and Fry say,³ "The micas are potent minerals in soils and show but little evidence of alteration, a fraying of the edges at times being quite characteristic. If alteration of the micas has taken place it has not influenced their optical properties. It would appear that micas are the most stable of the potash minerals found in soils except montmorillonite."

Johnstone reports that after immersion of mica for a year in water charged with carbon dioxide no visible alteration could be discerned.⁴

¹ U. S. Dept. of Agriculture, *Soils*, 122 (1916).

² The Nature of the Elements, p. 116 (1915).

³ *Journal of Soil Sci. Soc. of Amer.*, 10, 91 (1916).

⁴ *Transactions of the Royal Society*, 65 (1905).

On the other hand, Steiger found "that by a very superficial treatment with hydrochloric acid approximately one-third of the potassium may be extracted."

In the study of the alteration of soil minerals in this Bureau one of the procedures adopted has been the subjection of the finely ground mineral to the action of solutions of salts, either those known to be present in soils or commonly added to soils in fertilizers. In the course of this work the behavior of finely ground muscovite when treated with a solution of ammonium sulfate was such that while preliminary work only has as yet been done the results seem worthy of record.

Selected laminae of muscovite from a large sample of this mineral were ground in an agate mortar to pass a sieve 130 meshes to the inch. This material in varying quantities was subjected to the action of 10 cc. of a solution of ammonium sulfate varying in concentration from 0.5 to 1.5 per cent. The insoluble material was removed by filtration and the total potassium in the solution was determined by the official method for potash in mixed fertilizers. The total potassium in the original muscovite was determined by the J. Lawrence Smith method.

The results are shown in the accompanying table. The length of time of contact of the solution with the muscovite was in all cases 24 hours; 10 cc. of the ammonium sulfate solution were used in each experiment. The results obtained with orthoclase by the same treatment are also shown.

In additions to these tests, two portions of 0.5 g. of muscovite were heated in an autoclave for 1 hr. at 160° C. in one case with water only, and in the other with 25 cc. of a 4 per cent solution of ammonium sulfate. In the case of water 4.32 per cent of the total potassium as K₂O was rendered soluble, and in the case of the ammonium sulfate treatment 47.3 per cent.

In the first three tests, where the concentration of the

MINERAL Muscovite No.	(NH ₄) ₂ SO ₄ Solution Wt. used, G.		Per cent	Approx. Temp. 0° C.	Per K ₂ O in Mineral	PER CENT K ₂ O EXTRACTED On Basis of—	
						Mineral	Total K ₂ O
1	0.15	0.5	20	8.40	1.68	20.00	
2	0.15	1.0	20	8.40	1.67	19.98	
3	0.15	1.5	20	8.40	1.87	22.26	
4	0.15	1.0	40	6.47	2.20	34.00	
5	0.15	1.0	40	6.47	2.20	34.00	
6	0.15	1.0	40	6.47	3.73	57.63	
7	0.20	1.0	40	6.47	1.55	23.96	
8	0.40	1.0	40	6.47	1.75	27.05	
9	0.60	1.0	40	6.47	1.65	25.50	
10	0.15	1.5	40	6.47	1.87	28.90	
11	0.15	1.5	65	6.47	2.07	21.98	
12	0.15	1.5	80	6.47	2.33	36.01	
13	0.20	1.5	80	6.47	2.95	45.60	
14	0.40	1.5	80	6.47	2.80	43.28	
15	0.60	1.5	80	6.47	2.33	36.01	
Orthoclase:							
1	0.20	1.5	65	7.78	0.25	3.23	
2	0.40	1.5	65	7.78	0.13	1.68	
3	0.60	1.5	65	7.78	0.08	1.03	

ammonium sulfate was increased while the quantity of muscovite and temperature remained constant, the differences in K₂O extracted were slight with no straight increase with increase of concentration of ammonium sulfate. In Nos. 4, 5, and 6, where the conditions were approximately the same, there was absolute agreement between Nos. 4 and 5, with No. 6 very much higher. In the case of Nos. 7, 8, 9 and 10, with the quantity of muscovite variable and other conditions constant, the differences in quantity of K₂O extracted are not significant in view of the variation noted where the quantity of muscovite was constant.

The remaining tests, while suggestive of increased extraction at higher temperatures, are suggestive only. Throughout this work the temperature control was approximate only and it would appear from the results that other factors are operative and not sufficiently controlled. The only conclusion that stands out clearly is that at temperatures above 20° C. (room temperature) more K₂O is extracted by this treatment.

So far no results have been obtained throwing any light on the chemical changes involved or the process by which the potassium is rendered soluble.

DIVISION OF CHEMICAL INVESTIGATIONS
BUREAU OF SOILS, WASHINGTON, D. C.

LABORATORY AND PLANT

NEW ALLOYS TO REPLACE PLATINUM

By F. A. FAHRENWALD

Received May 11, 1917

The development of materials to take the place of platinum in many of its applications has become not so much a matter of economic desire, as one of actual necessity.

The present phenomenal activities in chemical research and manufacturing enterprises have resulted in a continually increasing consumption of this material, while statistics show that the world's production has been on the decline. At the present time an actual scarcity of metal is a matter of greater importance than its consequent high cost.

PRODUCTION—The following figures taken from a report by the United States Geological Survey, "Platinum and Allied Metals in 1915," give estimates of production in troy ounces during the period from 1912 to 1915, for the principal mining countries of the world.

COUNTRY	1912	1913	1914	1915
Borneo and Sumatra.....	200	2,000		
Canada	30	50	30	100
Colombia.....	12,000	15,000	17,500	18,000
New South Wales and Tasmania...	778	1,275	1,248	303
Russia.....	300,000	250,000	241,200	12,400
United States.....	721	483	570	742

During 1914, the United States imported platinum to the extent of about 75,000 troy ounces, and in 1915 about 65,000 ounces. An additional 65,000 ounces of new metal were recovered by refiners of gold bullion and blister copper, while about 40,000 ounces of metal were derived from refining of various forms of scrap, chiefly from jewelry and dental work.

MARKET—The price of platinum throughout a period of years has shown a steady increase, and there seems small likelihood of a near future return to greatly lowered quotations.

The following figures give average prices per troy ounce for platinum ingots at various times since 1874.

1874	\$ 6.12	1898	\$17.88	1906	\$27.00	1913	\$ 44.88
1888	\$ 8.19	1900	\$19.41	1907	\$28.00	1914	\$ 45.06
1890	\$ 8.67	1901	\$19.93	1910	\$32.70	1915	\$ 49.63
1893	\$ 9.19	1902	\$20.94	1911	\$43.12		\$ 85.50
1895	\$10.22	1905	\$21.45	1912	\$45.55	1916	\$ 85.50
						1917	\$110.00

USES—Platinum is employed chiefly in four general fields, *viz.*, Chemical, Electrical, Dental and Jewelry.

A relatively large amount of this metal is actually consumed in chemical applications, as in electrolytic processes, but a large part of it, as in the form of crucibles, dishes, and other apparatus, is not destroyed, and with care may be used indefinitely.

In the electrical field platinum finds a variety of uses, chiefly, however, in the form of contact points on ignition and lighting systems, and in a similar form on numerous types of automatic electric apparatus from automatic telephones and signalling devices to the ordinary every-day temperature-controlled electric iron or heating pad. Most of the metal used in this manner is destroyed. Large quantities of platinum are also used in the construction of electric resistance furnaces for high-temperature work, as in experimental laboratories. The material in this application is not, however, destroyed and may be refined and used again.

Perhaps the greatest actual consumption of platinum occurs in dentistry. It is employed here as pins in artificial teeth, and as foil, plate and sheet in other forms of dental construction. It is estimated that about one-third of the entire consumption of platinum may be accounted for in this manner. As yet no means have been devised to prevent this noble metal from being lost forever. Perhaps actual necessity may yet become sufficiently pressing to overcome false sentiment, which no doubt at this time would greet with horror a suggestion that all teeth or other devices containing platinum be removed from the remains of those for whom it had completed its time of service, and so be made available for further duty.

The jewelry industry is without doubt the greatest offender, and proper steps should be taken at once to prevent the use of platinum in this field. It is not economically sound to permit mere foibles of fancy or dictates of fashion to remove from service a material which is absolutely necessary in the sciences and industries. It is estimated that the jewelry industry consumes nearly one-third of the entire production of platinum, and while some of this is recoverable, most of it, when once in private ownership, is practically lost.

In many instances where formerly it was thought that only platinum could be used, alloys have been developed which, for a given well defined purpose, are quite as satisfactory: in chemistry, laboratory ware of fused quartz, larger apparatus of the various high-silicon iron alloys, nickel chromium alloys and other materials have been adapted to specific phases of the industry, where hitherto only platinum had been found satisfactory.

In the electrical field, platinum for resistance heating elements has been largely replaced by alloys of nickel and chromium. For electrical contact material

as in many forms of ignition and automatic electric devices, platinum has been, to a certain extent, replaced by tungsten. Most of the manufacturers, however, of high-grade magnetos and other apparatus demanding high-duty service, still think it necessary to use platinum as the material of contact terminals, although in the majority of cases the alloys described herein are satisfactory. Platinum is no longer used extensively in the manufacture of incandescent lamps, having been replaced by a copper coated, nickel-iron alloy which has the same coefficient of expansion as platinum.

Many forms of substitution are practiced in dentistry to avoid the use of platinum. Various forms of German silver, gold alloys, and others, are used with varying degrees of satisfaction, but there are many applications in which no other heretofore available material will serve. The writer has developed a method of coating tungsten or molybdenum with precious metals which gives a material of even greater strength and permanence.

For the manufacture of jewelry no other metal or alloy combining the qualifications of workability, appearance, permanence and intrinsic value, has been available.

It is thus evident that while other materials have been developed to successfully replace platinum in a few specific instances, researches have not heretofore produced a material which in all of its characteristics and properties can serve as a general purpose substitute.

In considering a material to replace platinum it is necessary to regard as criteria those properties which make it valuable in applications where no other metal will serve. Its value industrially is chiefly due to a high melting point, and chemical inactivity under those conditions which exist in its application. It is also very malleable and ductile, and may readily be worked into the great variety of intricate forms so often required.

It is apparent, then, that a proper substitute must satisfy the following conditions:

SPECIFICATIONS FOR A SUBSTITUTE

1.—Its melting point must be high. For chemical purposes a material that would fuse at the temperature of the ordinary gas flame would find limited application. In electrical uses high fusing point is one of the chief requirements, while in dental manufacture, platinum is subjected to temperatures which are seldom below 1200°C., so that about 1500°C. would be a fair minimum temperature that a satisfactory substitute must withstand.

2.—It must not be affected by strong acids or alkalis, either fused or in solution, and must not oxidize at any temperature up to and including that at its melting point.

3.—It must be malleable and ductile, and sufficiently strong to withstand stresses tending to change its form while in use.

4.—The chief requirements for jewelry purposes would seem to be color and high cost, although the above factors are a positive essential factor in this

field also. It is doubtful whether color or appearance are of greater importance than intrinsic value but in order to substitute for platinum in a strict sense, a platinum-white color is desired.

One phase of researches conducted in the writer's laboratories during the past several years has dealt with the development of alloys¹ to replace platinum, and aside from the treatment of special applications, attention has been given to a consideration of the possibilities of producing a material which should practically duplicate platinum in its general characteristics and behavior when judged according to the above set of requirements.

This work has resulted in a material which in most of its general chemical and physical properties is almost indistinguishable from platinum itself, as may be seen from the hereinafter described results.

DISCUSSION OF POSSIBILITIES

It is theoretically indicated, and has been experimentally proved to the satisfaction of the writer, that *no other possible combination of elements can result in alloys of equally enhanced properties, when judged with platinum as the criterion.*

In order to develop this thesis, and in so doing eliminate fruitless fields for further research, it will be necessary before describing these resulting alloys, to consider briefly a few factors involved in their development.

The production of alloys of special properties is no longer a matter of "discovery." In the days of the alchemist men put forth every effort in vain attempts to produce gold artificially, and sought by the use of a philosopher's stone to transmute base metals into a more noble form. At the present time, however, when molecules, atoms, and electrons are a matter of fruitful study, the hope of actually changing one element into another is not so fanciful. But in the meantime, advances can be made only by properly combining the simple elements to form alloys having properties superior to those of the component metals.

The study of metals, as an exact science, is of comparatively recent origin, although some of the devices of metallurgy have been unconsciously employed by men for ages.

The first advances in the art of treating metals to improve certain of their properties were no doubt a matter of accidental discovery, as when some warrior discovered that the metal of his spear and arrowheads could be hardened by hammering between two stones. Even though accidental, an invention of this nature advanced his tribe, more, perhaps, than did the discovery of the metal itself. The forger of the Damascus blade did not know the inner nature of his secret process, but this did not detract from the prowess of its wielder.

So, to the present day, man's advance has been suggestively paralleled by his increasing knowledge of the properties of the metals. With knowledge of the elements came the discovery that certain combinations of metals possessed properties far more valuable

than those of any single one, and the continued pursuit of this study has produced materials which have revolutionized industry and warfare. It has produced tools for mining and agriculture; it has made possible steam vessels and railroads, and has permitted the present great diffusion of thought and knowledge by means of the printing press, photographic appliance, telegraph, cable and telephone.

As the results of these early researches radically changed many phases of industry, so in turn, the present changing industrial and economic conditions demand further applications of science in order that new conditions may be properly met as they develop.

In alloys of iron a great number of special steels have been developed which meet any reasonable specifications in that field. In a like manner the alloys of copper, zinc, tin, nickel and other metals have provided a series of brasses and bronzes of remarkable perfection.

Similar successes have not attended efforts to replace the precious metals, and especially is this true of platinum. In undertaking the solution of this problem, it was found, after the entire list of metals had been considered with the above imposed conditions as criteria, that no element, aside from platinum, would satisfactorily meet the above outlined specifications. In view of the fact that no single metal was available for this purpose, it was evident that any search for the desired material must be among alloys, for experience has shown that the properties of a metal may be radically changed by the addition to it of varying amounts of another element, or of several elements, as in the case of steels, brasses, and bronzes.

A review of the literature reveals nothing of direct bearing on this question. The same underlying principles, however, are involved in all investigations of this nature, so advantage may be taken of the broad generalizations which have resulted from the numerous researches on other alloys. Considerable work in the line of thermal analysis has been reported which covers many of the metals under consideration, and in these resulting diagrams of thermal equilibrium the proportion and type of the different constituents of a series of alloys may be easily detected.

It is known that the relation between the constitution of an alloy and its various properties is rather well defined, so, to a certain extent, it is possible, from a study of a given equilibrium diagram, to interpret in terms of characteristic properties, the terms given as constituents.

In view of the fact, then, that the general properties of an alloy are dependent upon the type of its constituents, and that these in turn are dependent upon the nature of their components (the elements) it is desirable that certain applicable laws be briefly pointed out, and that the inter-relationship of the elements themselves be taken into consideration, for without this information it would not be possible to select, from the entire list of the elements, those which might properly be included in an investigation of this nature.

The relationship of the elements is best revealed by some form of the periodic table, as conceived first

¹ See Bull. A. I. M. E. Jan., 1916. Descriptions of these alloys are also subject-matter of professional reports made in 1913.

by Newlands and later improved and enlarged by Lothar Meyer and Mendeléeff. Werner's rearrangement of this table is, perhaps, the most satisfactory for purposes of alloy comparison.

The accompanying table was constructed in this manner, omitting, however, the rare elements not of interest in this connection, and so allowing a better comparison of the metallic elements than does the complete chemical table.

If one begins at the upper left-hand corner and reads bookwise, it is found¹ that the atomic weights show an almost uniform increase from Hydrogen 1 to Thorium 232.5. The horizontal rows represent groups, each containing seventeen elements arranged in two series of seven, each, with a "transition" series of three elements; that is, 1 to 7 constituting one series, 1a to 7a the second series, and 8 the intermediate or transition series. In the ordinary chemical table the elements are arranged according to valencies,

with markedly acid-forming elements; *e. g.*, zinc, in 1a, and bromine, in 7a, of the same group. The elements (8) connecting these series are intermediate in their behavior between the elements on either side, those of the first vertical column (iron, ruthenium, osmium) forming both bases and acids; the others only acids.

In passing, with consecutive readings, from one horizontal group to the next lower, however, one notes a sudden change in the chemical properties of elements of consecutive atomic weights. Thus, the last element of Group II, fluorine, with an atomic weight of 19, is in complete contrast, in its chemical nature, to the next element sodium, with an atomic weight of 23.5, and which belongs in Group III. Iodine, the last member of Group III, forms powerful acids while cesium, the first member of Group IV, is one of the most powerful base-forming elements known.

If the elements in a vertical column are considered

	1	2	3	4	5	6	7	8	1a	2a	3a	4a	5a	6a	7a			
	(ELEMENT)															I		
I	H	(ATOMIC WEIGHT)																
	1.008	-258? (MELTING POINT)																
II	Li	Be	B	C									N	O	Fl	II		
	7.03	9.1	11.0	12.0									14.04	16.0	19.0			
	186.0	900?	2200?	?									-2.10	-235?	-22.3			
III	Na	Mg	Al	Si									P	S	Cl	III		
	23.5	24.36	21.1	28.4									31.0	32.06	35.45			
	97.0	651.0	658.0	1400									44	(112)	-102			
IV	K	Ca	Sc	Ti	X	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	IV
	39.15	40.7	44.1	48.1	51.2	52.1	55.0	55.9	59	58.7	63.6	65.4	70	72.5	75.0	79.1	79.96	
	62.0	805	1400?	1850?	1750?	1505	1225	1520	1490	1450	1083	419	30	900	800?	217.0	-7.0	
V	Rb	Sr	Y	Zr	Nb	Mo	?	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	V
	85.4	87.6	89.0	90.7	94.0	96.0		109.17	103	106	107.93	112.4	114	118.5	120	127.6	126.5	
	380	830		1600	2100?	2500?		2000?	1900?	1550	96.1	321.0	155	232	630	451	+114	
VI	Cs	Ba	La	Ce	Ta	W	?	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi			VI
	133.0	137.4	138	140	183	184		191.0	193.0	194	197.2	200.3	204.1	207.1	208			
	28.0	850		645?	2900?	3200		2700?	2300?	1755	106.3	-39	302	327.0	270			
VII		Ra		Th														VII
		225		232.5														
		?		1700?														

PERIODIC ARRANGEMENT OF COMMON ELEMENTS

which brings the elements of Column 1 and 1a, 2 and 2a, etc., together, with considerable confusion as to their physical and chemical properties. In the present table the common elements are shown arranged in accordance with their atomic weights, the group designations 1, 1a, 2, 2a, etc., being retained merely as an assistance to those familiar with the usual chemical table.

Within any one group there is no sudden change in properties when passing from one element to the next in order. Considering the two series forming one group, the first begins with elements which are strongly base-forming, and ends with strongly acid-forming elements; *e. g.*, potassium, of Column 1, and manganese, of Column 7. The second series begins with elements which are only moderately base-forming and ends

it is found that they are, on the whole, such as would naturally fall together in a classification of the elements according to their general chemical and physical properties. Thus, in the first column are lithium, sodium, potassium, and cesium—the metals of the alkalis; in the second column are calcium, barium, and strontium—metals of the alkaline earths, and so on.

Space is not available for a detailed discussion of many other relationships which have been found to exist, but it is apparent that the elements of a vertical column are very similar, and that there is no radical difference in the general properties of horizontally adjacent elements. If it is evident, however, that a similarity of properties exists among the elements occurring in any one part of the table, and that the general properties of an element can be forecast from its position in the periodic table, the melting points, for instance, which have been included for comparison in the table, range from low to high as does high to

¹ These simple relationships are, of course, well known. It is thought well, however, briefly to review them in order to draw more clearly a parallelism in the case of alloying characteristics, which is not so commonly recognized.

low, in any given column, and in reading through any one group the successive figures do not represent very great contrasts. This same relationship governs all other properties as, for instance, malleability and ductility. Considering Column 1a, as an example, copper is very easily rolled, drawn, or otherwise manipulated; silver, the next lower, is more so, while gold, at the bottom, is the most malleable of known metals.

If one metal, therefore, possesses special properties which make it valuable for given industrial purposes, it is reasonable to suppose that those metals which occupy adjacent positions on the periodic table may possess these same properties to some extent at least, and would, therefore, bear investigation—especially if they come within the same vertical column.

There is no difference between reactions which take place at very high temperatures, resulting in the formation of alloys, and those which take place under ordinary conditions. All reactions and conditions of equilibrium are governed by the same rules, and corresponding constituents result in all cases. It is evident, then, that the general laws and relationships governing the alloying behavior of the metals are the same as those which have been found to exist in the case of ordinary chemical reactions.

When two or more metals are brought together in the liquid state, the conditions existing are similar to those found if two or more ordinary liquids are mixed. When the temperature is sufficiently lowered the solidified mass may contain any one of the four following constituents: pure components, solid solutions, compounds, or eutectics, or some combination of these.

A comparison of the properties of different alloys containing these constituents has shown that they impart their characteristic properties to the alloy of which they form a part; in fact, the relation between the constitution of an alloy and its properties is so clearly defined that the possibilities of industrial application may be predicted for a given alloy, if its constituents are definitely known. Conversely, if a certain application is desired, as in the problem under consideration, a definite limit may be placed upon the number and amount of constituents permissible.

Fortunately, the number of constituents is limited to four as given above. Pure metals impart their own characteristics; solid solutions are, in general, the ductile constituents (if formed from ductile metals, or of a preponderance of one ductile metal); compounds are hard and brittle; while eutectics are usually brittle and hard, and even when present in very small amounts, tend to solidify between the grains of the alloy and destroy its ductility.

Thus another requirement may be added; a substitute for platinum must be a homogeneous solid-solution alloy.

This brief discussion has, in a very general manner, outlined the inter-relationship of the elements when arranged in the periodic order of their properties, and has pointed out the similarity of properties of elements grouped in any part of the table. The general properties of an alloy have been shown to depend upon its constituents, and these constituents in turn have been

briefly discussed with reference to their characteristic physical properties and with reference to the probability of the occurrence of similar constituents in alloys of closely related elements.

It is not safe, however, to generalize in too broad a manner upon any assumed relationship between certain elements, but it would be impossible to make a logical search for any special alloy, in a field containing all of the elements, without first having definitely outlined the mutual relationship and behavior of the component elements.

With the elements arranged in this manner it becomes at once evident that characteristic chemical or physical properties are confined to definite limited areas of the periodic table. The properties characteristic of silver, for instance, are more or less common also to those eight elements contained in squares surrounding it; this is especially true in the case of those of the same vertical column. In this manner any element on this chart may be analyzed and all other elements contained in non-adjacent spaces will be found markedly dissimilar to it in chemical behavior and in general physical properties.

Considering platinum in this manner, it is at once evident that its general properties will be found in no metal other than those adjacent to it. These surrounding elements are iridium, rhodium, palladium, silver and gold. All metals outside of this block are affected by common reagents and gases, and, without exception, are not stable at elevated temperatures in normal atmospheres.

Considering each of these in turn, however, it is found that not one is suited as a general substitute for platinum. Iridium and rhodium are very refractory; they cannot be readily worked, and are so rare and expensive as not to be economically permissible. Palladium, while meeting most physical requirements, is readily oxidized or carbonized, and is quite soluble in several of the common acids, especially nitric. Silver is readily attacked by acids, and is of too low melting point to serve, except in special cases. Gold resembles platinum in more respects than does any other metal. It is, however, not sufficiently refractory and is too soft to find wide application industrially. A metal falling below platinum in the same vertical column would be possessed of properties still more enhanced, for the "nobility" of the elements of this column becomes greater with increasing atomic weight.

The above consideration is not merely theoretical, for experimental work involving most of the promising metals outside of the above list has supported this view.

Having limited the possibilities to the rather confined area indicated, it was necessary to combine these included metals in such manner as to eliminate or neutralize undesirable features, and to develop those properties which were necessary.

The material of chemical ware must not contain silver because of its affinity for many of the reagents commonly employed. The use of rhodium and iridium in large proportions is obviously not practical, so that

TABLE I—TESTS ON SAMPLES OF RHOTANIUM (Submitted by F. A. Fahrenwald)

Each test piece was about 0.1 mm. thick and presented 10 square centimeters of surface. The palladium was electrolytic metal from Baker and Company. The gold was U. S. mint gold, 0.999 fine. The platinum was the pure foil of commerce.

ACTION OF HYDROCHLORIC ACID

The pieces were boiled in the concentrated acid for 3 hours and showed losses in weight as follows:

S	0.05 mg.	CONCLUSION: Hydrochloric acid is practically without action.
A	0.05	
A5	0.05	
B	0.0	
C	0.0	
D	0.0	
Pd	2.5	
Au	0.05	
Pt	0.0	

ACTION OF HYDROFLUORIC ACID

The pieces were boiled in the concentrated acid for 3 hours and showed the following losses in weight:

S	0.0	CONCLUSION: Hydrofluoric acid is entirely without action.
A	0.0	
A5	0.0	
B	0.0	
C	0.05	
D	0.0	
Pd	0.11	
Au	0.05	
Pt	0.0	

ACTION OF CONCENTRATED NITRIC ACID

The pieces were boiled with the concentrated acid for 3 hours and showed the following losses in weight:

S	2.85 mg.	CONCLUSION: Hot, concentrated nitric acid attacks all the alloys very appreciably, especially those very high in gold.
A	2.15	
A5	2.25	
B	2.15	
C	2.15	
D	2.30	
Au	3.25	
Pd	Much attacked	
Pt	0.05	

ACTION OF DILUTE NITRIC ACID

The pieces were boiled with the dilute acid, one part of nitric to two of water, for 5 1/2 hours; the solution concentrating to a ratio of one acid to one water. The following losses in weight occurred:

S	0.1 mg.	CONCLUSION: Hot, dilute nitric acid is practically without action in all cases.
A	0.05	
A5	0.05	
B	0.05	
C	0.05	
D	0.05	
Au	0.05	
Pt	0.0	

ACTION OF CONCENTRATED SULFURIC ACID

The pieces were boiled with the concentrated acid for 5 1/2 hours and showed the following losses in weight:

S	0.05 mg.	CONCLUSION: Hot, concentrated sulfuric acid attacks the alloys high in gold very slightly, the rate of solution increasing with the proportion of palladium. All the alloys are superior to platinum in this test.
A	0.05	
A5	0.15, . . . 0.10 mg.*	
B	0.20	
C	0.50	
D	1.60?	
Au	0.05, . . . 0.45 mg.*	
Pd	Rapidly attacked	
Pt	2.00	

* After 14 hrs. at 300°C.

ACTION OF FUSED POTASSIUM BICARBONATE

The pieces were all immersed together in potassium bicarbonate kept at a very low red heat in a porcelain crucible for two hours and showed the following losses:

S	0.65 mg. gain	Had a silvery appearance showing probable deposition of Pd on its surface.
A	0.25 mg. loss	
A5	0.40	
B	8.00	
C	16.85	
D	49.4	
Au	0.60 mg. gain	
Pd	Very rapidly attacked	
Pt	0.25	

CONCLUSIONS: The action is similar to that of concentrated sulfuric acid but more intense. It is probable that alloy S and Au were slightly attacked, but the Pd taken up more than compensated for the loss. Alloys high in gold are equal to or better than platinum.

ACTION OF SODIUM HYDROXIDE IN SOLUTION

The pieces were boiled with 10 per cent. sodium hydroxide solution for 4 hours and showed the following losses:

S	0.0	CONCLUSION: Hot concentrated sodium hydroxide solution is entirely without action.
A	0.0	
A5	0.0	
B	0.0	
C	0.0	
D	0.05	
Au	0.10	
Pt	0.0	

ACTION OF FUSED SODIUM HYDROXIDE

The pieces were immersed in the fused hydroxide in a nickel crucible and kept for 2 hours at a low red heat. They showed the following losses:

S	4.45 mg.	CONCLUSION: Alloys high in gold are more resistant, but all are somewhat attacked. It is well known that platinum is badly attacked.
A	4.95	
B	4.00	
D	9.25	
Pd	18.45	
Au	7.95	

ACTION OF FUSED SODIUM CARBONATE

The pieces were immersed in the fused carbonate in a nickel crucible and kept for 2 hours at a bright red heat. They all showed slight gains, when there was any change. They were bright and showed no evidence of corrosion. It is difficult to explain the gain in weight, except in the case of Pd, which was undoubtedly somewhat oxidized.

S	Too soft, tended to stick to crucible	CONCLUSION: The alloys are not appreciably attacked by fused Na ₂ CO ₃ and are equal to platinum in this respect.
A5	0.0 mg.	
B	0.55 mg. gain	
C	0.25	
D	0.257	
Pd	0.25	
Au	Stuck to the crucible	
Pt	3.05	
Pt	0.80	

ACTION OF SODIUM SULFIDE SOLUTION

The pieces were boiled for 3 hours in a solution of sodium sulfide containing a little polysulfide, and saturated at room temperature.

S	0.0 mg.	CONCLUSION: The alloys were somewhat tarnished; the others were perfectly bright. The alloys are not all attacked by concentrated hot sodium sulfide solution.
A	0.05 mg. gain	
A5	0.0	
B	0.1	
C	0.1	
D	0.05	

ACTION OF AMMONIA

The pieces were boiled 5 hours in a concentrated ammonia solution.

S	0.0 mg.	CONCLUSION: The alloys are not in the least attacked by hot concentrated ammonia solution.
A	0.0	
A5	0.05	
B	0.05	
C	0.0	
D	0.10	
Au	0.0	
Pt	0.0	

ACTION AS CATHODE IN ELECTROLYTIC SOLUTION

The pieces were plated with copper in a solution containing sulfuric acid and sulfuric acid, and the deposit was dissolved off for a final treatment with warm dilute nitric acid and one boiling. The losses were:

S	0.0 mg.	CONCLUSION: The alloys are not in the least attacked by the electrolytic deposition of metals.
A	0.1	
A5	0.05	
B	0.1	
C	0.1	
D	0.0	
Au	0.05	
Pt	0.0	

finally only gold and palladium remain as the permissible *chief* components of an alloy which should more nearly duplicate the general properties of platinum than could any other metal or combination of metals.

A detailed investigation of alloys of these metals has resulted in materials¹ which for many practical purposes cannot be distinguished from platinum.

EXPERIMENTAL

The following results of final tests made to determine the behavior of these alloys under practical conditions of operation were carried out on specimens 0.10 mm. thick and of such size as to present exactly 10 sq. cm. of surface. Earlier work revealed the fact that in order to produce the desired results, it was necessary to make use of small percentages of rhodium; this is not necessary in the case of material for chemical ware; for certain electrical and other uses, however, it is quite essential. It is also permissible to use limited percentages of silver in some of these non-chemical applications.

It is necessary to observe every precaution in the preparation of these alloys, because of the affinity of palladium for many gases and solids ordinarily en-

than that of platinum. This is especially true in the case of concentrated boiling sulfuric acid.

VOLATILITY AT HIGH TEMPERATURES

In determining losses by volatilization at high temperatures, test specimens taken from the same ingot and duplicating those described above were employed. These were heated in a gas muffle furnace using natural gas and compressed air. These experiments were run in triplicate in two series: first in the muffle with free access to air, but with the products of combustion excluded; and second, heated directly in the gases of combustion with free air excluded. No difference in results was observed under these two sets of conditions. The comparative test pieces of palladium were of vacuum-fused electrolytic metal, while the test-specimens of platinum were cut from a new Baker crucible.

In these experiments the muffle was brought to the desired temperature and the test samples allowed to remain therein for one hour before cooling and weighing preliminary to the test run. An assay balance, reading directly to the fifth place, was used in determining the weight of each specimen before and after treating.

Each experiment consisted in a continuous 10-hour

TABLE II. LOSS IN MILLIGRAMS PER HOUR PER 100 SQUARE CENTIMETERS (SUMMARY OF TABLE I)

Alloy No.	Boiling Conc. HCl	Boiling Conc. HF	Boiling Conc. HNO ₃	Boiling Dil. 1 to 2 HNO ₃	Boiling Conc. H ₂ SO ₄	Fused (Red heat) KHSO ₄	Boiling 40% Sol. NaOH	Fused (Red heat) NaOH	Fused 1000° C. Na ₂ CO ₃	Boiling Sat. Sol. Na ₂ S + S	Boiling Conc. NH ₄ OH
5.....	0.166	0.0	9.5	0.2	0.1	0.0	0.0	22.2	0.0	0.0	0.0
A.....	0.166	0.0	7.5	0.0	0.1	1.2	0.0	24.7	0.0	0.0	0.0
A ₅	0.166	0.0	7.0	0.0	0.3	2.6	0.0	+2.7	0.0	0.0
B.....	0.0	0.0	7.0	0.0	0.4	25.0	0.0	20.0	+1.2	0.0	0.0
C.....	0.0	0.0	7.0	0.0	1.0	84.0	0.0	+6.2 ²	0.0	0.0
D.....	0.0	0.0	7.0	0.0	3.0	297.0	0.0	196.7	+1.2	0.0	0.0
Pure Au.....	0.166	0.166	10.8	0.0	0.1	0.0	0.3	39.7	+1.5	0.0
Pure Pd.....	8.0	0.33	Rapidly Attacked	Rapidly Attacked	Rapidly Attacked	Very Rapidly Attacked	0.0	92.0 Rapidly Attacked	+15.2	+2.5	0.0
Pure Pt.....	0.0	0.0	0.166	0.0	4.0	1.45	0.0	+4.0	0.0	0.0

countered in the process of manufacture. The most careful heat-treatment also is necessary to insure freedom from segregation. The slightest inhomogeneity is fatal to uniformity of results in practically every application—especially for chemical purposes.

Losses in acid solution, for instance, for different test-specimens made from the same alloy ingot, have been found to vary by over 1000 per cent. Properly prepared material, however, gives absolute uniformity of results.

CHEMICAL PROPERTIES

On page 595 is shown a test-certificate from the University of Michigan Chemical Laboratories which gives results obtained from a series of Rhotanium alloys, together with figures for gold, palladium and platinum for comparison.

When tabulated in terms of loss in milligrams per hour per 100 sq. cm., the results appear as in Table II. It is seen from these figures that for ordinary use with any of the above named reagents, excepting concentrated nitric acid, an alloy may be chosen of a composition that will give service equal to or better

run, with the temperature maintained within $\pm 25^\circ \text{C}$. of the figures given below. Losses at these various temperatures, in terms of milligrams per hour, per 100 sq. cm. of surface, are given in Table III.

Sample	1050° C.	1200° C.	1300° C.	1400° C.
Rhotanium No. 5	2.0	Melted	Melted	...
A	0.8	3.1	Melted	...
A ₅	0.6	2.0	Melted	...
B	0.4	1.4	6.0	...
C	0.4	1.3	4.0	7.1
D	0.2	0.6	2.82	5.8
Au
Pd	3.4 (gain)	14.0 (gain)	37.0 (gain)	120.0 (gain)
Pt	1.3	2.40(a)	3.1	4.5

(a) Burgess gives 0.71 to 2.79 mg. (Bureau of Standards, Scientific Paper No. 254).

After heating for 10 hours at these temperatures the surface of each specimen (melted and otherwise) was perfectly bright. At 1400° C. the crystalline structure was clearly shown, due to selective volatilization or grain growth, but no brittleness was produced. The gain in case of pure palladium is due, no doubt, to oxidation, although palladium also carbonizes very easily.

PHYSICAL PROPERTIES

The alloys A₅, B, C and D are practically white. C and D especially can only with difficulty be distinguished in appearance from platinum, and then only when in the form of sheet. Wires or articles of

¹ The name "Rhotanium" has been applied to this series of alloys. Alloys of different composition for distinct purposes are distinguished by sub letters as shown in the various tables of properties. This name has been registered, and all alloys, both as to composition and use, are covered by patent applications.

intricate design present a true platinum appearance. All are very malleable and ductile, and can be rolled, spun, or otherwise worked into any desired form.

Figures for some physical properties are given in Table IV.

TABLE IV—PHYSICAL PROPERTIES OF RHOTANIUM ALLOYS

ALLOY	Melting point ° C.	° F.	Sclero- Tensile		Electrical Conduc- tivity $\times 10^{-4}$	Temperature Coefficient
			Hard- ness	Strength Kg. per sq. mm.		
S	1150	2100	7	26
A	1220	2228	7	35	13.5	0.00097
A5	1280	2335	10	40	9.8	0.00065
B	1350	2462	13	45	7.85	0.00060
C	1410	2570	16	50	5.5	0.00050
D	1450	2642	17	51	3.8	0.00052
Au	1063	1945	5	21	45.5	0.00326
Pd	1550	2822	11	30	9.45	0.00328
Pt	1775	3191	9	24	9.94	0.00348

As may be judged from the above described properties these alloys are well suited to replace platinum in many of its applications in all fields, and have been so used for a long period with entire satisfaction. By taking advantage of the ease with which chemical and physical properties may be modified through adjustment in composition, various alloys of this series have operated fully as satisfactorily as platinum in chemistry, dentistry, jewelry, and in many electrical appliances.

Various grades of this material have undergone extended field trials, the results of which may be summarized as follows for the various fields of application.

CHEMICAL

Rhotanium cannot substitute platinum when exposed to the action of hot concentrated nitric acid, or when used as anodes in electrolytic work, but for all other purposes it is entirely satisfactory if the proper composition is chosen, and if properly manufactured. It is equal to platinum in the case of hot concentrated hydrochloric or hydrofluoric; hot dilute nitric; fused potassium bisulfate; hot concentrated sodium hydroxide solution; fused sodium carbonate; hot concentrated sodium sulfide solution; and in its resistance to oxidation at high temperatures. It is superior to platinum in its resistance to the action of hot concentrated sulfuric acid or fused sodium hydroxide. It is satisfactory as material for cathodes in the electrolytic determination of metals. Losses by volatilization at temperatures below 1300° C. are less than for commercial platinum.

Rhotanium may be rolled into sheets of any size, and may be formed either cold or white hot into any desired shape. It welds as readily as wrought iron at a white heat without the use of flux or other reagent. Due to greater strength and lower specific gravity, articles of rhotanium weigh only half, or less than half as much as similar articles of platinum. The specific gravity of alloys in this series varies from 18.5 to about 16.0, depending upon the composition; that of platinum is 21.5.

ELECTRICAL

Rhotanium is satisfactory within its temperature limitations as the material of resistor elements in electric heating units. It is not oxidized and is less volatile below 1300° C. than platinum. Its high resistance and low temperature coefficient are valuable in this connection.

It is satisfactory as material for contact terminals in many forms of automatic-electric devices and may be used in this capacity on certain types of telephones, switchboards, signal devices, lighting and ignition systems, and in most other cases except where it has been found necessary to use a high percentage of iridium alloyed with the platinum. Its behavior when tested on certain magnetos was satisfactory, but other experiments performed on a high-duty aeroplane engine magneto gave negative results.

DENTAL

Certain of these alloys have been in the hands of operating dentists for some time and have proved to be equally as good as platinum for many purposes. They have been used for pins and baked into porcelain teeth and as thin foil and heavy sheet for other types of construction, all with the most satisfactory results.

JEWELRY

Rhotanium is superior to pure platinum for use in jewelry. It is harder and stronger, and takes a better finish. It is absolutely not tarnishable or corrodible, and its color is practically platinum-white. It can be as readily worked as platinum, and scrap may be remelted for further use. It may be forged either cold or white-hot and may be "sweated" or otherwise treated as platinum without oxidizing or darkening in color. Finished articles of rhotanium jewelry of the more intricate designs can by no ordinary means be distinguished from platinum. This material passes the common jeweler's and platinum buyers' tests and there will no doubt be some confusion resulting from the passing of this material for platinum.

Exhaustive tests have shown that most of the uses for which platinum has heretofore been considered indispensable can be filled by one of these alloys, thus freeing platinum for those remaining applications where no other material can be employed.

The extent to which platinum may be replaced in this manner is limited by the amount of palladium available, and when it is considered that these alloys contain from 90 to 60 per cent of gold it is evident that the effective supply of platinum may thus be increased by many thousand ounces.

1706 GLENMONT ROAD
CLEVELAND, OHIO

A PRACTICAL METHOD FOR DETERMINING THE VISCOSITY OF STARCH FOR MILL PURPOSES

By G. M. MACNIDER

Received March 16, 1917

Several years ago the author described in THIS JOURNAL¹ a method for determining the viscosity of starch solutions for determining the value of different starches for cotton mill purposes. Since the publication of this article the author has had the opportunity of applying the method to similar mill work and has worked out a modification of the method which is described in this paper.

The original method is briefly as follows: 10 grams

¹Trans. Institute, 4 (1915), 317.

of the starch are weighed into a 600 cc. beaker, 300 cc. distilled water added (thus making a 4 per cent solution), heated over a Bunsen burner with constant stirring to the boiling point, and boiled 10 min.; 200 cc. of this solution are then poured into the cup of a Scott viscosimeter, the temperature being allowed to become constant, and 50 cc. run out into a graduate, the time being accurately measured with a stop-watch. The number of seconds required to deliver 50 cc. of the solution divided by the number of seconds required to deliver 50 cc. of boiling water gives the viscosity.

APPARATUS

The method makes a very satisfactory laboratory method for determining the comparative value of different starches, but in mill work it is frequently of importance to know the viscosity of the starch solution after it has been boiled with steam for an hour or more as is done in the use of the starch in preparing



FIG. 1

it for warp sizing, etc., in the mill. To accomplish this, a miniature size kettle was constructed, similar in every respect to the large kettles used in cooking starch in the mill. This kettle¹ (see Fig. 1) has a capacity of about 1 $\frac{3}{4}$ gallons and is equipped with double agitators of the propeller type, revolving in opposite directions. The steam for cooking enters through a perforated coil on the bottom of the kettle. In order to overcome variations in the amount of steam condensed the steam is passed through a trap just before entering the kettle. The time of boiling is one hour, the time being taken at the time the starch begins to boil. The amount of starch taken for a determination varies with the grade of starch. For thick boiling corn starch, potato starch, and similar

thick boiling starches 0.5 lb. of starch per gal. of water is used; for medium thin boiling corn starch, 1 lb. per gal. of water; for very thin corn starch and other chemically treated starches the amount is increased to 2 or 2.5 lbs. per gal. of water.

PROCEDURE

One gallon of water is measured into the kettle, the agitators started and the starch, accurately weighed, put into the kettle. The agitators are now run 10 to 15 minutes before turning on the steam in order to produce a perfectly smooth cream to avoid the formation of lumps. The steam is then turned on and the solution boiled for one hour after it comes to a boil. When the boiling is completed, some of the solution is drawn out into a beaker, quickly poured into the cup of a Scott viscosimeter and the viscosity determined as described in the original method.

The figures in Table I illustrate the application of this method in comparing several grades of thick boiling corn starches, using 0.5 lb. starch per gal. of water and boiling for one hour.

No.	STARCH	VISCOSITY
1	Regular Pearl Corn Starch.....	3.10
2	Powdered Starch.....	4.30
3	Purified Starch.....	4.30
4	Chemically Treated Starch.....	2.89
5	Highly Purified Starch.....	4.58

Some of the gluten and impurities of No. 2 were removed by the powdering process so that this starch shows a higher viscosity than No. 1. No. 3 was another form of starch which had been subjected to the same amount of purification as No. 2. While the viscosity of starch No. 4 was lower than that of starch No. 1, due to the chemical treatment, the actual value of starch No. 4 was greater. The actual mill practice substantiated these figures; *i. e.*, if under certain conditions a size mixing of starch No. 1 made on the basis of 0.5 lb. starch per gal. of water gave the desired results, if No. 2 or No. 3 were substituted, under the same conditions, it would be necessary to use less starch in order to obtain the same thickness of solution and consequently the same results; whereas, if No. 4 were substituted it would be necessary to use more starch.

No.	LBS. STARCH PER GAL. WATER	VISCOSITY
1	1 Lb.	2.45
2	same grade as 1, 1 Lb.	2.16
3	1 Lb.	1.94
4	2 Lbs.	1.27
5	same grade as 4, 4 Lbs.	3.54
6	(same grade as 5), 4 Lbs. (2 oz. KOH added to kettle)	2.63

Nos. 1 and 2 were the same grade of boiling starch; in using No. 2 in the mill it was found necessary to use slightly more than was used of No. 1; the figures show the difference. No. 2 was a higher fluidity or thinner starch than No. 1. Nos. 4 and 5 were the same grade of a very thin starch, the figures showing the difference in viscosity when the amount of starch used per gallon is doubled. No. 6 was the same as No. 5, but with the addition of 0.2 oz. KOH to the kettle. The viscosity figure shows the very marked thinning effect of this amount of caustic potash on

¹ This kettle was constructed by Mr. J. S. Drake of the Exposition Cotton Mills, Atlanta, Ga., and the author is indebted to Mr. Drake for valuable assistance and suggestions in working out the method.

the starch solution. It frequently becomes necessary to add to a starch mixing some reagent such as caustic alkali, chlorides of calcium, magnesium, zinc, etc., and it is very important to know just what effect the reagent will have on the thickness of the starch solution.

The advantages of this method over the laboratory method for mill work are as follows: the viscosity is determined when the starch has been boiled for the same length of time as it is boiled in preparing it for use in the mill and under the same conditions. The amount of starch used can be in the same proportion to the amount of water as in a regular size mixing; this makes the figures obtained by practical value as they show the viscosity of a size mixing. Also, in comparing two or more starches on such a basis, this fact that the viscosity figures represent the actual thickness of a size mixing makes it possible in case of a variation in viscosity to determine in the small kettle the amount necessary to use, thus saving the time and expense of experimenting on a large scale.

GREENVILLE, SOUTH CAROLINA

FULLER'S EARTH AND ITS VALUATION FOR THE OIL INDUSTRY

By THEODORE G. RICHERT

Received December 11, 1916

An important part of a modern oil refinery is the filtering department, where by means of fuller's earth the refined oils are bleached to the desired lightness in color. As many varieties of such bleaching agents are offered, it might be of interest to describe a cheap and quick method of determining, in the laboratory, the efficiency and economy of fuller's earth.

The earths for bleaching edible oils are clays which are used in the natural state as they occur or which sometimes are especially prepared in order to increase their bleaching power. They include hydrous silicates of aluminum, magnesium and calcium, containing small amounts of other substances, such as iron, sodium, potassium, etc.

Fuller's earth, owing to its colloidal character, when brought in contact with refined oil, forms, with the colloids soap and coloring matter, colloidal aggregates and settles out as such; after separating the oil and the fuller's earth, the oil has an earthy taste and a part of it remains with the fuller's earth.

Essential points in the use of fuller's earth in the oil industry are:

1. Precipitating of minutely suspended particles of soap left in the oil from the refining.
2. Removing of coloring matter, which, owing to the refining, is contained in the oil in an unstable state.
3. The earthy taste imparted to the oil should be removable by means of deodorization.
4. The loss of oil due to absorption should be as low as possible.

For trials like ours, Points 1 and 3 may be neglected, all fuller's earths have the ability of settling out the soap in sufficient degree and the earthy taste can always be removed by means of a well conducted deodoriza-

tion process. As to the other points, a valuation of fuller's earth concerning its bleaching power and its absorption of oil can be accomplished in the laboratory.

Owing to the varying behaviors of the refined oils, as well as to working conditions in the plants, it is impossible to determine and fix absolute values for these properties. The only alternative is to compare the results obtained from working a new unknown earth with the results of one already tested. The principal condition is that for all tests and all earths the same oil and methods be used.

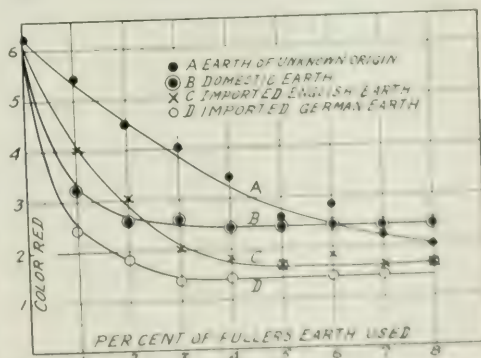
To determine the bleaching powers of different earths a number of bleaching tests¹ were made with a well refined cottonseed oil, using from 1 to 8 per cent of the earths (a greater per cent than 8 was not tested, since a higher amount is commercially prohibitory). In Table I, the earth B is a domestic, C an imported English, D an imported German earth; the origin of A could not be ascertained.

TABLE I. COLORS (LOVIBOND TINTOMETER) OF OILS BLEACHED WITH DIFFERENT PERCENTAGES OF FULLER'S EARTH

Bleached with Fuller's Earth	BRAND A		BRAND B		BRAND C		BRAND D	
	Yellow	Red	Yellow	Red	Yellow	Red	Yellow	Red
1.....	35	5.4	35	3.2	35	4.0	20	2.4
2.....	35	4.5	20	2.6	35	3.0	18	1.8
3.....	35	4.0	20	2.6	20	2.0	14	1.4
4.....	35	3.4	20	2.4	18	1.8	14	1.4
5.....	20	2.6	20	2.4	16	1.6	16	1.6
6.....	20	2.8	20	2.4	18	1.8	14	1.4
7.....	20	2.2	20	2.4	16	1.6	16	1.6
8.....	20	2.0	20	2.4	16	1.6	16	1.6

The results indicate the exhaustion and efficiency of the earth. The maximum effect is reached for Brands A, B, C and D with 8, 4, 5 and 3 per cent of earth, respectively.

To show even more distinctly the differences of the several tests, the results are plotted below, with the amount of fuller's earth used and the red color obtained as ordinates. The dotted line indicates the color for "White Oil"—20 yellow, 2.5 red.



The latter was first arrived at the first year of its course, and the latter is approximately the horizontal axis, the greater the bleaching power of the earth. In our case, Brand D is the most effective, as shown by the curve, which is the lowest. Brand A is highly effective, therefore, this curve is the highest. Brand C is the most effective, therefore, this curve is the second highest. Brand B is the least effective, therefore, this curve is the lowest. The dotted line indicates the color for "White Oil"—20 yellow, 2.5 red.

is a reliable agent; its run in the factory has confirmed its good qualities. *A* is a slow-acting earth; to obtain any tangible results large amounts are needed, a fact which prohibits its extended application.

Another feature of the curves is to show approximately how much of the different earths would be necessary to obtain the same results. For instance to bleach the oil of our experiment to a "White Oil," there must be used of Brands *A*, *B*, *C* or *D*, 5.8, 3.0, 2.4 or 1.0 per cent of earth, respectively.

To determine the loss of oil due to absorption, 300 g. of oil were agitated with 10 g. of each of the fuller's earth samples for a given time at a given temperature. Then the oil was filtered by means of a Buchner funnel.¹ When the earth seemed to be dry, vacuum was kept up for 15 min.; the earth was then removed from the funnel and weighed.

Now when there is known the loss due to absorption when working with one of the earths, it is possible to figure out the loss to be expected using another earth, provided the working conditions remain the same. For instance, the earth *C* was known to cause a loss of 8 per cent; the presumptive losses of the other earths based on this figure are shown in the following table:

TABLE II—ABSORPTION OF OIL BY FULLER'S EARTH

Brand	Earth plus Oil Grams	Oil Absorbed Per cent	Presumptive Loss Per cent
<i>A</i>	11.77	17.7	8.3
<i>B</i>	18.73	87.3	40.8
<i>C</i>	11.71	17.1	8.0
<i>D</i>	14.05	40.5	19.0

THE VALUATION

The value of fuller's earth and consequently the economy of its use is dependent on price, bleaching power, absorption value and the utilization of the residue. The latter, being for all earths practically constant, may be omitted.

On account of the impossibility of determining absolute figures for bleaching power and absorption value, the earth's worth can be so ascertained that it is assumed to bleach an oil to a certain lightness. The raw bleaching cost for 100 lbs. of oil is then:

$$V = \frac{x(100P + AO)}{100 + xA/100} \text{ cents,}$$

when x is the percentage of earth needed, A the presumptive loss, P and O the price in dollars for 100 lbs. of earth and oil, respectively; or, $xA/100$ in the denominator being negligible as compared with 100, the raw costs are simply:

$$V = \frac{x(100P + AO)}{100} \text{ cents.}$$

TABLE III

BRAND	Per cent of Earth	Price(a) of Earth for 100 lbs.	Presumptive Loss Per cent	Raw Bleaching Cost for 100 lbs. Cents
<i>A</i>	5.8	\$0.70	8.3	9.36
<i>B</i>	3.0	\$0.68	40.8	15.50
<i>C</i>	2.4	\$0.79	8.0	4.01
<i>D</i>	1.0	\$3.15	19.0	5.24

(a) All prices are figured f. o. b. Portsmouth, Va.

For the assumed case that a "White Oil" has to be made from our oil, the figures are collated in Table III, the price of oil being taken as \$11.00 per 100 lbs.

¹ See "Fuller's Earth," by Charles L. Parsons, Washington, D. C., Bull. 71, Bureau of Mines.

CONCLUSION

In spite of the highly developed bleaching power of Earth *D* its application is not to be recommended on account of its excessive price. An extended use would be desirable only with the dropping of its price to about \$1.90 per 100 lbs. or with an oil price of around \$4.50; in both cases the bleaching cost would then be about 4 cents. Brand *C* is the most economical of all; the higher amount of earth used is compensated by the low absorption. Brand *B* is not well recommended because of its high absorption value. Finally, Brand *A* is not suitable for practical work on account of the large amount needed, which calls for large sized filter presses.

In conclusion, it should be noted that the work in the actual run is usually less costly than the preceding figures show; the intense contact of earth and oil under pressure increases the effect. To state that the actual raw bleaching costs fluctuates between 50 and 75 per cent of the above figures would be a fair estimate.

P. O. Box 27, PORTSMOUTH, VIRGINIA

AN APPARATUS FOR THE PURIFICATION OF MERCURY

By HARRISON E. PATTEN AND GERALD H. MAINS

Received February 2, 1917

In this laboratory we have need of mercury in a very pure state not only for standard cells, and calomel half-cells, but also in rather large quantities for the filling of thermoregulators used in controlling constant temperature baths. The presence of even a slight trace of foreign metal, such as lead or zinc, after the mercury stands a short time in contact with air, gives rise to the formation of an oxide film on the surface which dirties the capillary tubes and interferes greatly with the delicacy of the thermoregulator.

We have tried out the various methods which have been proposed for the purification of mercury, and have used a number of the types of apparatus described in the literature. The well-known method of Lothar Meyer,¹ in which mercury is passed in a fine stream through a long column of dilute nitric acid, is slow, tedious, and cumbersome. The speed of operation is greatly increased by the modification of J. H. Hildebrand,² where the mercury is broken up into numerous extremely fine streams by passing it through muslin into the acid column. L. J. Desha devised a modification³ by which the mercury, after running through the nitric acid column, was automatically raised to the top and thus kept in continuous circulation. Loomis and Acree⁴ incorporated with the Desha apparatus the means of electrolytic purification, *i. e.*, making the mercury the anode in a nitric acid solution.⁵

Even after the above modifications, the purification demanded considerable watching and personal attention. Also there was no means provided for renewing the nitric acid without cleaning and refilling the entire apparatus. We have endeavored to construct a

¹ *Z. anal. Chem.*, **2** (1863), 241.

² *J. Am. Chem. Soc.*, **31** (1909), 933.

³ *Am. Chem. J.*, **41** (1909), 152.

⁴ N. E. Loomis and S. F. Acree, *Am. Chem. J.*, **46** (1911), 594.

⁵ Wolff and Waters, Bureau of Standards, Bull. **8**, 623; **4** (1907), 1.

purifier which would combine the spraying of the mercury through a column of dilute nitric acid, the automatic return and circulation of the mercury, the electrolytic purification, and the automatic renewal of the nitric acid in order to wash away the products of electrolysis and prevent re-solution of impurities. By means of the injector principle (used with some modifications of the Sprengel pump), the mercury is raised through a small-bore tube to the top of the apparatus in small globules in a current of air. During this process some oxidation of the impurities takes place,¹ which we have greatly increased by surrounding the return tube with a heating coil.

The purifier embodying these points has been in satisfactory operation for over eight months, during which time between 50 and 60 kg. of mercury have been run through the apparatus.

DESCRIPTION OF MERCURY PURIFIER

Plans of the apparatus with all necessary dimensions and enlarged details of the more important parts are presented below. The complete apparatus is shown in Fig. 1. It consists of the following principal parts: Mercury reservoirs, nitric acid fall tube, nitric acid reservoir, spray chamber, electrodes, waste tube, injector for returning mercury, and outlet for purified mercury. Fig. 2 is a detail of the main mercury reservoir and of the spray chamber, and shows the placing of the electrodes. Fig. 3 is a detail of the injector, injector cup, and connections. The glass work can be readily assembled by any glass-blower. A convenient stand for the apparatus may be built from wood, or metal rods and clamps may be used.

OPERATION—Impure mercury is placed in the main mercury reservoir *M*, and from this flows into spray chamber *S*, through a stopcock which regulates the speed of operation of the apparatus. Over the lower end of *S* is stretched a piece of bolting silk which breaks the mercury into a fine spray upon entering the nitric acid. The silk is fastened firmly to the end of *S* by silk thread, and a little flare at the end of the glass tube prevents any slipping. We have found No. 7 bolting silk very satisfactory, giving a fine spray and yet not readily clogging up. A No. 20 B. & S. gauge platinum wire is fused through the side of *S* into a mercury contact cup. This wire extends down into the mercury held on the silk. By connecting the wire to the positive pole of a source of current, the mercury, as it sprays through the silk, becomes the anode for electrolysis.

The spray chamber is seated into a ground glass neck on the fall tube *F*. This ground glass neck has a slot provided at one side (Section D, Fig. 2), through which the cathode wire is brought into the fall tube. The cathode is also No. 20 platinum wire, and is made into a loop encircling the end of *S* at the same level as the anode. An electrolyzing current of 1 ampere has proved satisfactory with the dimensions of the spray chamber used.

The overflow or waste tube *H* leads from the fall tube just above the electrode level, so that the products of

electrolysis are carried away by the stream of dilute nitric acid. The nitric acid used is a 2 per cent solution. This is fed from the reservoir *N*, into the fall tube at a slow rate, yet fast enough to prevent clogging about the cathode by separation of solid products of electrolysis, principally mercurous nitrate. In the particular apparatus used, it was found that an average rate of flow of 1000 cc. of nitric acid for a 7-hour period sufficed to maintain smooth operation. Some of the metallic impurities are deposited on the cathode. If the amount is excessive a silk bag placed around the cathode wire will prevent falling off of the deposit into the mercury below.¹

The height of the mercury column in the lower portion of fall tube *F* depends upon the mercury level in the injector cup *C* (Fig. 3), the difference in level being proportional to the weight of the nitric acid column in *F*. The mercury rises inside of the injector bulb *I* until it just reaches the top of the inner tube. This inner tube is brought around up to the top of the apparatus and is connected to the laboratory vacuum system. As soon as the mercury rises above the level, *ml*, in the injector bulb, a drop falls into the inner tube and is carried in a finely divided condition by the difference in pressure up to the auxiliary mercury reservoir *A*. The inner tube must be of $\frac{3}{16}$ in. inside diameter or less in order to elevate the mercury the required height.

A heating coil, *H*, surrounds the tube through which the mercury is elevated. This coil consists of a copper tube 4 ft. long, just large enough to slip over the glass tube, covered with a layer of asbestos, and then wound with No. 30 nichrome wire in two sections of 19 ft., each paralleled off of a 110-volt circuit. Since the resistance of this wire is 6 ohms per ft., the current in each section is then approximately 1 ampere. A layer of alundum cement holds the wire in place and prevents short circuits. Outside of this is placed a second layer of asbestos for heat insulation.

The finely divided mercury passing upward through the central glass tube in the coil becomes covered with a film, consisting of oxides of the foreign metals present and of mercurous oxide.

The mercury from auxiliary reservoir *A* flows down through a tube back to the main reservoir *M*. A stopcock in this tube serves to keep sufficient mercury in the auxiliary reservoir to prevent air being sucked in from the main reservoir. Also mercury may thus be held in the auxiliary reservoir while cleaning the main reservoir and spray chamber, or when inserting new bolting silk. The stoppers in the various tubes and reservoirs are of cork, except those in the auxiliary reservoir, which are of rubber in order to maintain the partial vacuum.

The optimum charge of mercury for the purifier is about 125 cc. or 1.5 kg. The mercury flows from the main reservoir, when regulated as to spray evenly and freely through the bolting silk, is approximately 30 cc. per sec. Thus all of the mercury circulates through the entire apparatus about one hundred times in a 7-hour period. The mercury is allowed to circulate

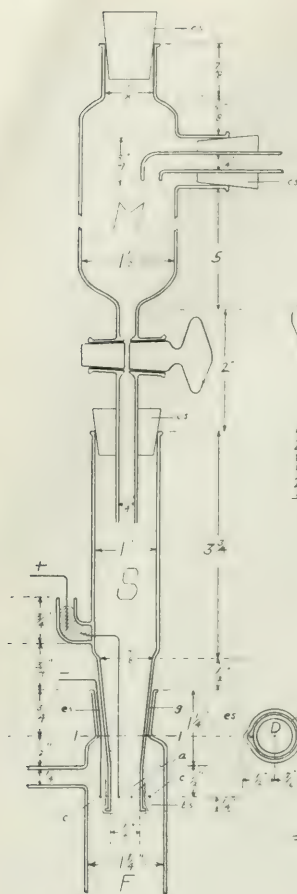
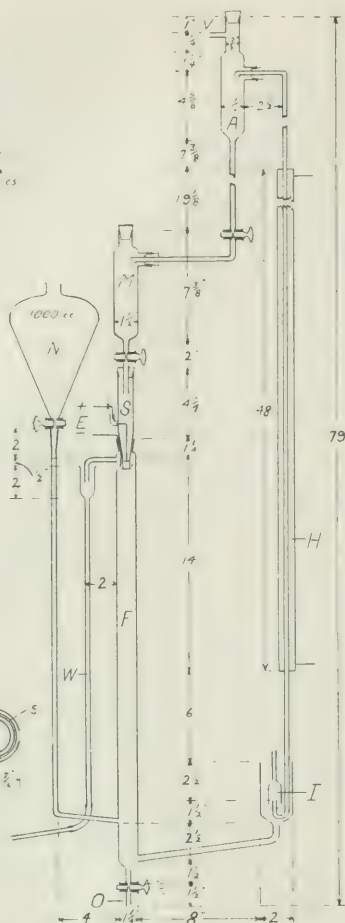


FIG. 2—DETAIL OF
RESERVOIR AND SPRAY CHAMBER

g, Ground joint
cs, Cork stoppers
S, Spray Chamber
D, Section through I-I
I, Injector Cup
M, Main Mercury Reservoir



We have used the mercury purified in this manner in our thermoregulators and found it to give satisfactory results. Calomel half-cells made up with this mercury have checked closely with each other and with cells made from pure mercury obtained from the Bureau of Standards. An attempt was made by using Hulett's method¹ for determining small traces of impurities, to distinguish between various stages of purification, but no clear-cut differences were obtained.

BUREAU OF CHEMISTRY, WASHINGTON, D. C.

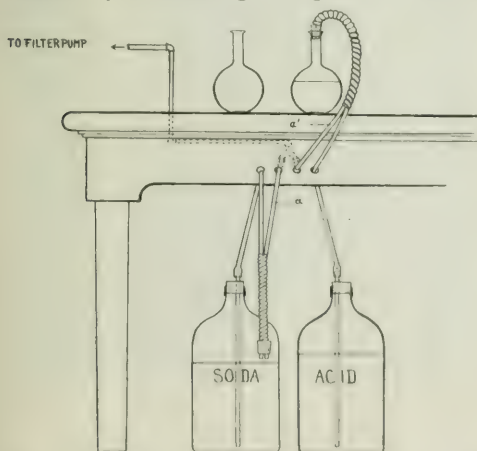
HANDLING LABORATORY SOLUTIONS BY SUCTION

By C. L. BEALS

Received February 10, 1917

To avoid lifting heavy bottles of solutions constantly employed in the laboratory, an ordinary filter pump provided with a few simple rubber and glass connections may be used to advantage.

The accompanying illustration shows an adaptation of the idea which has been successfully applied at our laboratory for dilute acid and alkaline solutions used in fiber determinations. The cumbersome supply bottles are placed out of the way under the bench. Each is fitted with a 2-hole stopper (one hole acting as an air vent) through which a glass tube extends nearly to the bottom of the bottle. These tubes are connected by means of $\frac{3}{8}$ -in. light pressure tubing to short glass nipples likewise extending through 2-hole stoppers of a size suitable for the flask in use. Nipples passing through the other holes of the stoppers are similarly connected by rubber tubing and a glass Y to the filter



pump. For convenience, the tubes leading from the rubber stoppers are bound together for a short distance with adhesive tape. To handle solutions, one has now only to place the stopper connected with the desired solution tightly into the service flask and start the filter pump. A vacuum tends to form in the system, which is made complete by closing one branch of the Y by pressure of the finger at α or α' ; the tube may be released. When sufficient solution has flowed into the service flask it is instantly stopped by releasing the

pressure, thus venting the system. The solution remaining in the tubing immediately drains back into the supply bottle. The apparatus works admirably and does away with pouring from heavy bottles or bothersome syphoning.

AGRICULTURAL EXPERIMENT STATION
AMHERST, MASSACHUSETTS

AN IMPROVED BUNSEN DIFFUSION APPARATUS

By JEROME S. MARCUS

Received February 27, 1917

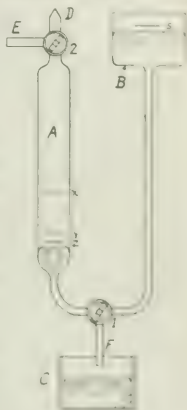
In a laboratory, where gas density is determined often and with only moderate accuracy, the Bunsen diffusion method has been found the quickest. There is no weighing, room temperature is used, and there are no liabilities of error from external conditions. The two chief factors of error are due to the difficulty of collecting over mercury and transferring to the apparatus the gas under investigation, and the irregularity of the action of the float.

The apparatus shown in the sketch was designed to eliminate both the float and the transference of mercury and gas, at the same time securing a more uniform pressure on all determinations than by the immersion method. Not only is the manipulation reduced to a minimum, but also the degree of accuracy increased.

The glass tube *A* is fitted at the top with a 3-way cock, opening to the orifice *D* and the tube *E*. At the bottom it is connected by the 3-way cock 1, to the mercury reservoir *B* and the tube *F*. The removable reservoir *C* may be any small vessel. For greater convenience the whole may be mounted on a board.

To standardize against air, cock 2 is opened to communicate with *E*, while the mercury is run out of *A* through *F* by cock 1. With 2 still open, 1 is turned to allow mercury to flow from *B* to *A* till the meniscus reaches the mark *z*. Both cocks are then closed, and *B* is filled from *C* to the mark *s*. At the same time both cocks are turned, so that *A* opens to *D* at the top and *B* at the bottom. By means of a stop watch, the time for the meniscus to move from the *y* to the *x* is determined.

To determine the rate of diffusion of the gas for the comparison to that of air, 2 is opened to *E* and *A* filled with mercury from *B* through 1. Cock 1 is then closed. The reservoir *C* is moved up to cover the bottom of *F* which is then connected to *A* by 1. This makes *A* the reservoir and vessel in which the gas is collected. *F* is composed of the narrow end of a glass tube and then graduated to *d* by *g*. The gas entering *A* drives out the mercury into *C* against the difference in pressure between that of the atmosphere and of the gas in *A*. The mercury levels are brought to the marks *z* and *s* as before and the rate of diffusion determined.



FORMAL OPENING OF THE NEW CHEMICAL LABORATORY UNIVERSITY OF CINCINNATI

The formal opening of the new chemical laboratory of the University of Cincinnati took place on Saturday, April 7, 1917. The exercises, presided over by Judge Rufus B. Smith, were held in McMicken Hall, Burnet Woods. The addresses were as follows:

"Presentation of the Building," Robert Hochstetter.

"Reply on Behalf of the Department of Chemistry," Lauder W. Jones.

"Reply on Behalf of the American Chemical Society," John Uri Lloyd.

Address—"The Swing of the Pendulum in Chemistry," Charles H. Berty.

The chemical laboratory was open for inspection from 9 A.M. to 6 P.M. A brief description of the laboratory is found following the addresses.

A dinner in honor of the occasion was arranged by the Cincinnati Section of the American Chemical Society, and was served at the Hotel Gibson. Dr. Alfred Springer acted as toastmaster. Addresses were made as follows:

"Chemistry in a University," Charles W. Dabney.

"The Relation of Chemical Industry to the University," Robert Hochstetter.

"The Transmutation of the Chemist," Lauder W. Jones.

PRESENTATION OF THE BUILDING

By ROBERT HOCHSTETTER

In the absence of Mr. Pollak, the Chairman of the Building Committee, the Board has requested me to act in his behalf.

In 1912, by act of Council, the City was authorized to issue \$250,000 worth of Bonds, to be used in the construction of a Chemical Laboratory.

This building (which we are dedicating to-day) stands as a monument to the untiring efforts of Dr. Jones and his associates and their devotion and loyalty to Science, Education and this University.

We are proud of the fact that our University has been so fortunate as to have such an able teacher and chemist to guide the students who have the privilege to come under his influence.

May this building continue to serve the cause of Science and Industry, and may the students repay our city in service and loyalty for the generosity of our citizens which made it possible to house a chemical department which is now second to none!

Our thanks, therefore, go out to Dr. Jones with the hope that he will continue to serve our University for many years to come in as efficient a capacity as he has in the past.

It is, therefore, with much pleasure that I, in behalf of the University Trustees, turn over the keys of the new laboratory to you, Dr. Jones, and may the good work you have so nobly begun be carried on indefinitely!

REPLY ON BEHALF OF THE DEPARTMENT OF CHEMISTRY

By LAUDER W. JONES

In reply to your very generous words, it is my privilege to speak not only for myself, but for the members of my staff, each and every one of whom has assisted in formulating and carrying into effect the plans of this new building. Permit me, therefore, to express to you our individual and composite appreciation of the trust which it is our honor to receive from you as representative of the Board of Directors of this University.

In accepting this laboratory for the services of chemistry and metallurgy, we are aware of the opportunities which you have granted us, and at the same time, of the responsibilities which you have imposed upon us. I assure you that it shall be our endeavor to use our opportunities wisely, and to assume our responsibilities willingly, and that, at all times, we shall strive to make this building, the home of the Department of Chemistry, a place

where the things accomplished shall be worthy of the University, and of the community which it is designed to serve.

Although every chemist has built laboratory-castles in the air, and has dreamed out plans for these ideal buildings, not many ever find themselves fortunate enough to see these dream textures fix themselves and become reality. Here, in Cincinnati, it has fallen to my lot to observe and guide a genuine transmutation of this very kind—to see a building develop from the idea of a building, through preliminary sketches, blue-prints, specifications, to the material stage as it stands now in brick, stone and mortar upon our campus. Not my laboratory-castle, perhaps, but better suited for the rough uses of daily life.

So, even though I must count my share in the bringing of these things to pass, a task, nevertheless it was a pleasant task, and one which I was not loath to undertake, since it had in-



DR. LAUDER W. JONES

Professor of Chemistry, University of Cincinnati

separably bound up with it something of the joy which an artist must experience in the creation of his work.

On this occasion, it may be interesting to relate briefly the important points in the historical development of the Department of Chemistry in this University. In 1873, the University Board decided to establish an Academic Department. By courtesy of the Board of High Schools, provisional arrangements were made under the management of Mr. G. W. Harper, Principal of Woodward High School, to offer courses of instruction in the High School. In October 1873, under the direction of teachers of Woodward High School, courses in ancient language, German, Mathematics, Chemistry and Physics were offered. Mr.

C. R. Stuntz was the first teacher of chemistry. His class numbered 13.

In 1874 regular courses of study were commenced with five recently appointed professors who offered the following subjects: Mathematics, Ancient Language, English, German, Physics and Chemistry. Dr. Frank Wigglesworth Clarke was chosen Professor of Physics and Chemistry. The Board of Education granted the University permission to use the 4th story of the Intermediate School located on Franklin St.

In October 1875, the first University building, on the McMicken grounds, near the Elm Street Incline, was completed. The Departments of Chemistry and Physics had quarters in the basement of this building. During this year there were in all 62 students enrolled in the academic department of the University.

In 1883, Dr. Clarke left the University to become associated with the U. S. Geological Survey in Washington, and Dr. Thomas H. Norton was appointed in his place.

McMicken Hall in Burnet Woods was completed and opened in September 1895, but the Departments of Chemistry and Physics could not be accommodated in the new building. The old University building on McMicken Ave. was rented by the University to the Board of Education for the use of the 6th District School, with the agreement that the Departments of Physics and Chemistry should occupy a portion of the building. However, in June 1895, a communication from Mr. Henry Hanna announced his intention of presenting to the University \$45,000 to be used for the erection of the "North wing of the New University Building." Work upon this building was commenced shortly afterwards, and in December 1896, the Departments of Chemistry and Physics were moved into Hanna Hall which they shared with the Department of Civil Engineering.

I have been told that many citizens wondered how the vast space in this building could ever be filled with students of chemistry. Professor Norton found himself supplied with room more than ample, but with equipment which was practically nil. An interesting item in the University budget for the year 1896 indicates how serious this need must have been. It reads: "For moving to Hanna Hall, \$9.30."

Hanna Hall was formally dedicated on May 13, 1897, just 20 years ago, lacking one month.

In 1900, Dr. Norton left the University to become United States Consul to Harput, Turkey. He was succeeded by Dr. Thomas Evans, who had been assistant Professor of Technical Chemistry in the department. During his term of office, the Engineering College, through the coöperative plan proposed by Dean Herman Schneider, started upon its successful career. Dr. Evans at the time of his death, in 1907, was Dean of the Engineering College.

In the fall of 1907, the Department of Chemistry was placed in my charge. At this time there were about 80 students enrolled in chemistry. But the rapid growth of the Engineering College, the affiliation with the Medical School and the organization of the pre-medical course, the introduction of courses in Domestic Arts, brought ever increasing numbers of students into the department, so that Hanna Hall, in spite of the fact that many rooms occupied by the Engineering Department were released and fitted up as laboratories, was no longer adequate to accommodate the students who presented themselves, and the erection of a more ample building for chemistry became a necessity.

In 1907, when Hanna Hall was occupied by the Department of Chemistry, there were 326 students in all academic departments of the University. In 1917, twenty years later, when the new building was occupied, 520 students enrolled for courses in chemistry and metallurgy, that is more than one and one-half times the total number of academic student 20 years ago.

"Chemistry concerns itself with the quantitative study of the change in composition and constitution which material sub-

stances undergo, and with the transformations of energy which accompany them."

The science of chemistry, therefore, is an organized body of knowledge which comprehends within it all of the facts, laws, theories, and hypotheses relating to these changes and transformations, arranged and classified in accordance with the method which custom and convenience have found best suited to meet the needs of those engaged in the study and practice of the science.

Chemistry is called an abstract-concrete science. Since it has for its realm all material substances and the changes in energy which accompany their transformations, there is nothing of a material nature which may not constitute a legitimate problem for investigation by a chemist. If investigations of this kind are conducted without the expectation of making a direct or immediate application of the results to some phase of our daily life, or of industry, the problem is often spoken of as belonging to "pure science." If, however, there happens to be in the mind of the investigator the idea of discovering something of commercial value or of utility to industry, the problem is said to be one in "applied science." Unfortunately, in America in particular, the opinion has been quite prevalent that between these two ways of choosing and pursuing research there exists a chasm which is spanned by no bridges.

A little reflection, however, will convince any reasonable individual that no such antagonism can exist. Michael Faraday, one of the world's greatest men of science, once made the statement that "There is nothing so prolific of utilities as abstractions." If we believe in the uniformity of nature and that the science of chemistry is unified knowledge, it is impossible to conceive of two sets of unrelated facts and laws, one in the possession of the "pure chemist" and the other the peculiar property of the "applied chemist." Even the so-called secrets of applied chemistry must be *explainable* by the laws of the "pure chemist." As a matter of fact, in the historical development of the science, applied chemistry came first. The workers in bronze during the bronze age were familiar with metallurgical processes and knew some of the properties of the alloy bronze. In the iron age which followed, the users of iron were perfectly familiar with the property of iron to corrode or rust. Ancient peoples who prepared sugars, gums, starches and dyes, knew intimately the properties and practical uses of these materials. These very substances to-day form the basis of many important industries presided over by applied chemistry.

The relations which exist to-day in nature are the same in essence as they were during the time of the aborigines. All of our laws, theories and hypotheses were latent in the nature of things, waiting for the mind of man to formulate them. We can imagine that very early in the history of the human race there came to be individuals who, in a crude way, observed that certain facts, well known to all their clansmen as of practical value, but looked upon by them as unrelated, in fact, passed analogies, and were correlated or correlated. This stage represents the beginning of the science of chemistry.

Thus, we see that the two phases of the subject, the pure and the applied, were mutually interrelated and dependent upon one another at a very early time, and in fact, through all ages, they have been inseparably intertwined. In 1811, when Hermann discovered benzene in the Luthmans' by-product coal tar, the fact was of interest at first to pure scientists alone. In 1856, Kekulé proposed the hexagonal formula for this substance, hence the two were again in the forefront of pure speculation and was of assistance to those engaged in pure abstraction of their hexagonal constitution of the "pure chemist," the vast industries poured under the name of coal-tar industries have developed.

After the death of Kekulé in 1896, his ideas were further developed

posed the benzene formula, Japp delivered a memorial lecture in England in which he says:

"Kekulé's work stands preëminently as an example of the power of ideas. A formula, consisting of a few symbols jotted down on paper and joined together by lines, has supplied work and inspiration for scientific organic chemists during an entire generation, and has afforded guidance to the most complex industry that the world has ever seen."

If you will agree with me that my arguments are sound, then it must follow logically that the new laboratory, which has been entrusted to me and to my staff, to-day, can render greater service to the community and at the same time advance the science of chemistry best, if it is so organized as to deny, absolutely, that there exists between theory and practice even so much as a discernible cleavage plane. For the well-being of both they must be wedded—they must take one another for better or for worse.

The consequences of this point of view are almost self-evident. It will be our duty to see to it that elementary students who take courses in chemistry shall receive a most thorough training in the fundamental facts and laws of modern chemistry. As the students advance, their individual preferences will require different outlets for their activities, but, in any event, the department must see to it that each one shall develop along the lines which are best suited to make him an independent thinker and producer in the fields of chemistry.

So, for the advanced students, we should encourage in some the pursuit of research which may be as abstract as he pleases to make it, while in other cases it may be intimately associated with the noise and clangor of industry, believing, at all times, that both pathways lead ultimately to the same goal, the advancement of the noble science of chemistry, as well as the happiness, prosperity and well-being of mankind.

REPLY ON BEHALF OF THE AMERICAN CHEMICAL SOCIETY

By JOHN URI LLOYD

One of my friends said to me, "Now, Lloyd, Professor Hertzy is going to tell us about 'The Swing of the Pendulum,' which subject takes in all there is in chemistry, so you won't have anything to say about chemistry." Then Professor Jones is going to give us the history of the Chemical Society in Cincinnati, and it will be well for you not to take up much time talking about that." "What am I to talk about?" "Well," said he, "it is to be expected that an old man will talk about the early days, and give incidents that the younger people haven't had an opportunity to hear about, connecting times gone by with the present." So I shall take my text from the following thought, "Remember now thy Creator in the days of thy youth," and aim to put what I have to say within the fifteen minutes given me.

I speak as one who looks back, before there was any University of Cincinnati, before there was even a systematic "Art" of Chemistry in Cincinnati. I remember when the study of chemistry was started here, and believe I know the "Creator" of it all. As I cast my mind back into those days, 1863-4, come to mind those known then as the chemists of Cincinnati. They were Edward S. Wayne, Chemist of the Ohio College of Medicine, Daniel Vaughan of the Eclectic Medical College, and Professor Adolph Fennell, father of Professor C. T. P. Fennell. This was before the Cincinnati College of Pharmacy was established. Dr. J. F. Judge, Dr. W. B. Chapman, and others were co-laborers on the staff that followed. There were also the chemists of the public schools, one of whom you will remember as Professor Stuntz. In those days, the chemist was expected to be a druggist or a teacher in a school. Nothing was

there such as we now have in professional chemistry. And yet the principles that dominated pharmacy and chemistry fifty years ago gave birth to the broader vision of the chemist of the present.

Dr. W. B. Chapman, who established himself as apothecary at 6th and Vine, where the Weatherhead drug store now stands, was one of the *educated* pharmacists in Cincinnati. There were but a few of these, the pharmacists of those days having, as a rule, undergone a very heroic apprenticeship. I can in my mind's eye see Dr. Chapman now. Well did he serve the people of Cincinnati. And with such an ideal before me, I think next of Professor Adolph Fennell, father of our present Professor Fennell, of the College of Pharmacy to-day. Many here cannot but remember him, kindly as a child, a talented, educated, German pharmacist-chemist, a good citizen, a man who did much in the beginning as a creator of that which followed. Comes now to view Daniel Vaughan, that man of extensive learning, who came down the Pike from Lexington, Kentucky, walking to Cincinnati, as also did Rafinesque, the botanist-scientist. Vaughan did what he could in behalf of chemistry, and, at the last he quietly starved and died in a little upstairs corner room at Sixth and John Streets, thus paralleling, in death as in life, the life of Rafinesque, for Professor C. S. R. Rafinesque died a pauper in the rich city of Philadelphia, his body being dissected as that of a homeless vagrant. The room where Vaughan died stands yet at Sixth and John Streets. Vaughan, recognized the world over as a great scientist and mathematician, it is true, starved to death in Cincinnati, but this was his own fault, because he was too proud to beg, too rich in intellectuality to consider physical pain. These men, and such as they, gave to us the chance that comes to us of Cincinnati to-day. Had it not been for them, there could have been no University at the date it was founded, such as stands on this beautiful hillside to-day. Their inspiration gave us Hanna Hall, and the inspiration of which they were a part, gave us that which followed Hanna Hall. Where we stand to-day was then country, only. Burnet Woods had not even been made a part of the city. Indeed, as I recall events, it was long a question whether Cincinnati would receive it as a gift. Fortunately, it was accepted.

Whatever is, had a beginning, but few realize how slight is that beginning. Like the seed from which grew the great redwood tree of the West, was the beginning of this great building here. Its beginning is the very commencement of cosmopolitan art, of alchemistic chemistry, and of connected sciences, which are one and all lost in the shadows of antiquity.

After the days of Chapman and Fennell and Wayne and Judge and Vaughan, those pioneers of the olden time, came the founding of the society that I am honored in representing to-day. The old building in which this start was formulated stands to-day down the hillside, pathetically pleading its own cause. I remember the problems with which McMicken University on the hillside then had to contend. She had no professor of chemistry. The public schools of Cincinnati gave to her the first teacher of chemistry. Give credit to Professor Stuntz, of Hughes High School, whose lectures were given, not in a grand edifice like this, but in the very basement of that old building to a class numbering a possible dozen.

The first authorized Professor of Chemistry in the Cincinnati University, was F. W. Clarke. But partly understood by the men among whom he moved, a pure scientist, his ideals were in investigating lines, not then conceived to be connected with commercial activity. For this reason he did not appeal to most people, but some, like myself, felt like taking off our hats when we met him. Professor F. W. Clarke was working on what he knew to be the very foundation of chemistry, but yet this was seemingly outside the lines of bread and butter, as chemistry was then looked upon.

Came then Professor Thomas H. Norton, and came soon an improvement in location in the building. He was given a much better place than down in the basement. Chemistry was no longer considered a spectacular study, for exhibition purposes as a lecture room show, a something with which to entertain children. Chemistry had now come to be viewed as a science destined to become a feature of the future, and to dominate every-day life. Professor Norton was a man well qualified to utilize chemistry for practical purposes. With him, by good fortune, came Mr. Hanna's gift, Hanna Hall. At that time I was very close to Norton. I knew what he was struggling to accomplish, and time and again spent afternoons and Sundays in his home when the new chemical department was being planned. I comprehend what he and Mrs. Norton did to found that department. Together they made charts for atomic and molecular weights. Together they worked on models to exhibit problems in stereo-chemistry. In other ways Mrs. Norton helped, preparing demonstration maps for chemical lectures explanatory of experiments. Professor Norton and his assistants had little in the way of apparatus, but with that little and what they added, they did well their work. Then came the call

room, look at that old laboratory in Hanna Hall, then consider this. View the apparatus in the great building constructed for chemistry, only. Dr. Jones sits beside us. His mind work stands before us as his monument. Every sphere of American scientific activity has been touched by him, and he has prepared these wonderful laboratories to give back from their outcome to those who have served him. The engineers in science, the whole world over, have contributed to what you find here. It is a monument to scientific Cincinnati, an honor to our people.

Now just a word concerning the American Chemical Society. An old man in the art, some call me, because I go back in study and research before there was any American Chemical Society. But in the way of reminiscences, I am not the only old man here. We have with us Dr. Alfred Springer, who can tell you better than can I, the story of the first meeting of the Cincinnati Chemical Society, which long antedated the birth of the American Chemical Society. The first meeting of the Cincinnati Society was called by him, at his home. The second meeting, at which the name "The Cincinnati Chemical Society" was adopted, was held at the home of Mr. Rhein, over his drug



CHEMICAL LABORATORY, UNIVERSITY OF CINCINNATI

to go to Syria, and Dr. Norton gave up his place to his first assistant, Dr. Thomas Evans. He, too, did well his work, but, unfortunately, was taken away from us, in the very strength of his life. But such work as his could no more die than does the redwood tree when it falls to earth, leaving its life seed to become a new tree.

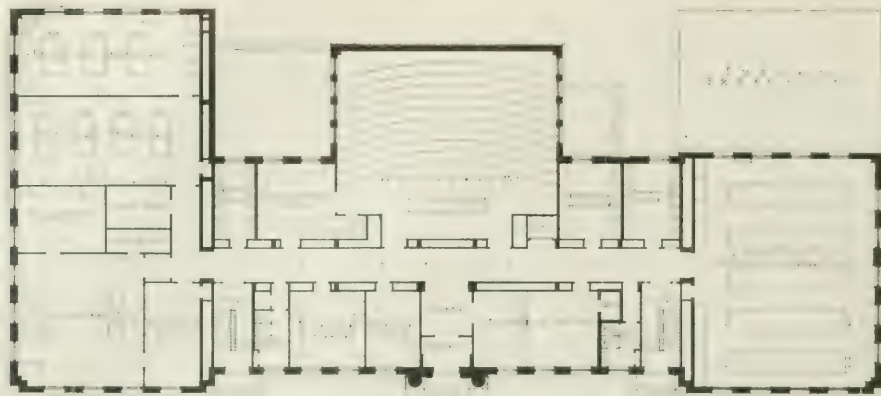
Came then our good friend, Professor Jones, and I must tell you something about the commencement of the chemical department of the building into which he went. When it was first built, there were so few students in that department that one day, as we stood in its uncompleted rooms, Norton said, "Lloyd, I wonder if it will ever be filled with a class. Haven't we bitten off more than we can chew?" In other words, shall I not be criticized for spending so much money on a laboratory? He did not foresee the stupendous growth that would so soon be accomplished.

Came finally Dr. Dalney, a President so competent to study men, and to put the right man in the right place. The Chemical Department that Norton felt might never be filled, grew until the students could not get into it. When you go from the

store, Fifth and Broadway. Subsequent meetings were held in the Ohio Mechanics Institute. When the time came at last for the organization of an American Chemical Society, we naturally became the first section of that society in this part of the West. To attend our meetings, came chemists from Columbus, Indianapolis, Lexington, and other cities round about.

I have presented but a superficial view of that which means to us from this great building. Remember, it is this Century in the day of this youth. We go to this in our youth, we concern chemistry. We are but freshmen, attending, but I believe, over a by and by that leads to upward progress. The path till now has been dark. What was before shall still be, velvet to mellow.

I hold in my hands a little paper on which is written the substance. These young men, Cincinnati, organized the American Chemical Society. In 1910 that same attention might be given to visitors at this meeting, a collection was taken, and a committee appointed, who were authorized to send all they needed. We took care of our students, too, then, prepared



FIRST FLOOR PLAN, UNIVERSITY OF CINCINNATI

satisfaction. After all the bills were paid, a fund of \$1500 was left. To whom did this belong? It had been contributed for a special purpose, which had been accomplished. It was decided, after much consultation, that this fund should form a nucleus to help needy young people who wished to attend the Chemical Department, and who would "make good" in life if given an opportunity. It was decided that this money be loaned them, the principal and interest to be returned to the University when in later years they were enabled to do so, through the equipment they had received. Can a more important fund be established than this? Is the equipping of these young people to be good citizens and so situated as to care for the interests of their country, not an opportunity? I will take the liberty of reading the names of four of those who by their contributions have increased this fund to the sum of \$2,000. These are Dr. Ernst Twitchell, Dr. F. W. Weissmann, Mr. Robert Hochstetter, and the firm of Ault and Wiborg. May I not be permitted to predict that those who can help this fund in the city of Cincinnati will be surprised, fifty years from now, to know what this nest egg has accomplished?

As a closing thought, may I not be personal? Much do I appreciate the opportunity of speaking here to-day. To appear on the same platform with the learned men of this great University, including its President, to know that I am listened to by Dr. Herty, past president of the American Chemical Society, to be introduced by Judge Rufus B. Smith, of the Board of Trustees, and to speak to an audience made up of intellectual Cincinnati, is indeed an honor that anyone might well hold precious.

THE SWING OF THE PENDULUM IN CHEMISTRY

By CHARLES H. HERTY

It is a peculiar pleasure to be present on this occasion which marks the formal opening of the new Chemical Laboratory of the University of Cincinnati. Too often of late have we read of loss by fire of historic laboratories; too often have we heard the lament of laboratories overcrowded with students. Here brick and mortar have been promptly joined and a fine housing given to the splendid corps of instructors whose work and whose policies have given to this institution as high rank in chemistry as developed in America. Here, too, has been happily worked out a combination of devotion to the advancement of chemistry as a science and to the application of chemistry in the service of mankind.

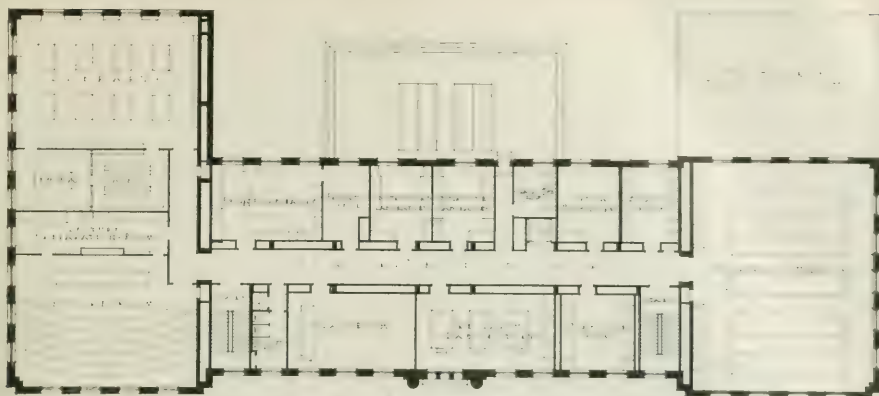
The erection of this building gives heart to the hope that the pendulum which has swung so strongly during the past two

and a half years towards the development of the chemical industries, is now about to begin an equally strong swing towards the betterment of conditions in our Universities—a betterment which should manifest itself in greater laboratory space and better equipment, in higher salaries for the teaching staff and in such increased number of instructors as will make possible more time for research. If the pendulum does not begin soon to swing strongly in this direction there is danger ahead.

CONDITIONS UP TO 1914

Up to the outbreak of the present great war the chemists of America had been working quietly but with zeal and effectiveness in university laboratories until we had reached the point where no longer was it considered necessary to go abroad to receive thorough and inspiring training in chemical research. This fact had not been widely advertised but it was evidenced by the constant increase in the proportion of young men receiving their higher training in the universities of this country, and by the constantly increasing prestige of the chemical journals of America.

So, too, in the industries of America, chemists had been busily and successfully engaged in solving the many problems of those industries which, because of our resources and environment, were of primary importance. Corn, the great staple of the Middle West, had been converted into a host of useful substances, through the transforming agency of our chemists. Cottonseed, so long neglected in the southern states, had become the raw material of a great industry whose output now approaches in value that of the lint column which for many years had alone given value to the cotton crop. The advances in metallurgy furnished brilliant examples of skill, ingenuity and sound chemical development. Petroleum refining had made possible the tremendous development of the automobile and allied industries. The tanning of leather had been placed upon surer foundations. The great industries of the heavy chemicals, acids, alkalis, etc., received a development of such consummate skill and magnitude of output as to assure success in other lines. At Niagara Falls an electrochemical industry was founded which stands to-day the greatest of its kind in the world, the products of this group now constituting essential equipment of many industries throughout the nation, and assuring us a degree of national preparedness, whose importance no one can overestimate in the great war into which we are entering. These are only a few illustrations of the many-sided and successful efforts of the industrial chemists previous to the outbreak of the present war.



SECOND FLOOR PLAN, UNIVERSITY OF CINCINNATI

The work, had been done quietly, earnestly and without advertisement and the nation accepted the results with but scant credit to those who primarily were responsible for the splendid achievements. It was, therefore, perhaps natural that with the shortage in coal-tar chemicals made manifest through the blockade of German ports, the nation should suddenly have awakened to the importance of its chemists and in that condition which is so often characteristic of rousing from sound slumber petulantly exclaimed: "Why have not our chemists provided us with a dyestuff industry commensurate with our needs?" Some rough jolts were necessary to make clear the situation that chemists alone cannot always develop industries, that combination of capital with chemical skill is essential and that capital is not inclined to invest in industries whose fostering, through adequate tariff legislation, has not only been neglected but strongly opposed by our own consumers. The full wakening, however, was not long delayed and with fine spirit consumers, capitalists, and chemists joined hands, effecting the development of a domestic dyestuff industry which has amazed the world, and which on the morrow, in the annual Easter parades, will give abundant evidence of its life and vigor.

EXPANSION OF CHEMICAL INDUSTRIES SINCE 1914

Along with developments in connection with industries using coal-tar products as raw materials, there has also been a great expansion in all other lines of chemical industries, which during the years 1915, 1916 and the first three months of 1917 has called for a direct investment in these industries of \$184,139,000. Not even the greatest optimist could have foreseen such an enormous expansion of the strictly chemical industries in so brief a time. The successful use of this vast sum has aroused the admiration of our people and to-day the chemist occupies a new plane in American public esteem, a position rendered all the more secure by the universal recognition of the important rôle the chemist plays in modern warfare.

To meet the universal demand for thoroughly trained men the industries have drawn heavily on university ranks. Men long habituated to the lecture room and university laboratory have taken new positions in the ranks of the industries and with characteristic American adaptability have fully met the new responsibilities. If this drain on University staffs goes much further there is distinct danger ahead to both the universities and the industries. In the universities should always be found men of the highest possible type, whose researches will carry forward the science of chemistry which usually precedes discoveries fundamental to the fullest development of the chemical industries. Such men attract and hold within universities for graduate work the best class of the undergraduate body upon which the future of chemistry in America will largely depend.

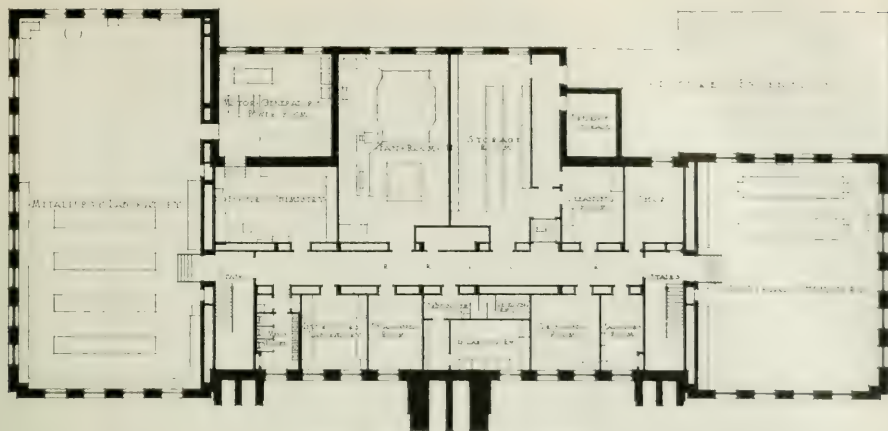
INCREASE IN CHEMISTRY STUDENTS

Furthermore, the wide advertisement which chemical prowess and prestige have recently received has resulted in largely increased numbers in chemistry classes working in laboratories taxed to utmost capacity. In order to secure facts in this connection a questionnaire, that most dreaded of all documents which pass through our mails, was sent to the registrars of all American colleges and universities listed in the report of the United States Commissioner of Education for the year ending June 30, 1916. In the hope of receiving reasonable returns the amount of statistics requested was very limited. Information was asked for the institutional years 1914-15, 1915-16, and 1916-17 as to the total number of students in chemistry, in chemical engineering, and in graduate courses in chemistry, and as to the amounts appropriated to chemistry departments (not including salaries) from funds other than fees paid by students.

Returns from this questionnaire have been slow in coming in and the information is far from complete. Nevertheless statistics have been received from one-third of our colleges and universities and fortunately these figures cover typical institutions, both the larger universities and smaller colleges being represented in approximately the same ratio as in the complete list of the Commissioner of Education.

The figures as to total students in chemistry are not suitable for use as misunderstandings arose as to whether the total number of individuals or the total enrollment of the classes had been requested. Nor are the figures as to appropriations to chemical departments suitable for specific use, as very few institutions answered this question. From those which did answer, however, it would seem that for the most part the chemistry departments of our colleges and universities subsist almost entirely, outside of the professors' salaries, on fees paid by the students. Appropriations from general university funds are in most cases negligible. It is to be regretted that a definite showing cannot be made in regard to this matter. To all who appreciate the unusual cost of material and equipment for research it must be plain that unless special appropriations are made from funds other than those received from students, the untimely prosecution of research must necessarily be hampered.

From this questionnaire, however, two reliable sets of figures have been received and these are exceedingly gratifying in view of the increased demand for trained chemists both in the control work and in research in the chemical industries whose continued development and expansion are so important at this particular time. For the session 1915-16 the registration of students in chemical engineering was 3 per cent greater than during the session of 1914-15, while the increase of 1916-17



BASEMENT PLAN, UNIVERSITY OF CINCINNATI

fully taught by a capable instructor. The actual increase in students, therefore, is in itself sufficient argument for more instructors.

In the third place adequate laboratory space and equipment should be provided to meet fully all needs. This *too* has been well met here in this commodious building, but in many *others* such is not the case. Finally, all these cramping and restricting influences *must* make themselves felt in handicapping the efforts of the teaching force to prosecute research to the fullest extent. For such work freedom from financial cares is necessary; time for concentrated thought and continuous experimentation cannot be dispensed with and space and necessary equipment cannot be ignored if that work is to be carried out under the most favorable conditions.

When I think of the exodus of men from the universities to the industries the cure seems to be the same as is now beginning to prove so effective in the problem of urban and country life. It took many years before we fully grasped the thought that the solution of the problem of country life lay in the making of country life more attractive. So in our educational circles, if the universities are to hold their men, conditions which have now become in many cases so hard must be improved.

I recognize fully the tendency for each of us to think that our own work is of greatest importance and should be therefore particularly cared for, and under normal conditions I should hesitate to make this *special* plea for increased funds for chemistry in our universities. But with the signing by President Wilson of that memorable resolution of Congress which enters this nation as an active participant in the great war, this country enters upon a new era, in which every energy of the nation must be devoted to complete consummation of the purposes for which we entered this war and at the earliest possible moment. In this task it is recognized by all that the chemist plays an extremely important role. Upon his inventiveness the issue may be largely determined.

REAL TEST OF EFFICIENCY OF AMERICAN CHEMIST NOW BEGINNING

A brilliant representative of the U. S. Navy, Admiral Fiske, I think, pointed out how often success in battle depends upon the unexpected use of some new discovery. Such a possibility will necessarily, through patriotic motives, lead our mind into many new channels, and the real test of the efficiency of the American chemist is now beginning. The test involves not only those men who are directly concerned with the manu-

facture of munitions, with the development of new explosives, with the perfecting of alloys to meet new demands, with the conservation of food, with the testing of army and navy supplies and with the guarding of the health of the field forces, but it also involves, fundamentally, the work of instruction in our colleges and universities which should be maintained at its very highest possible standard in order that this country, which we all desire to serve even at the cost of our own lives, may be served most efficiently.

With such thoughts in mind I share with you that feeling of deep gratification which must fill your hearts as a result of the recognition of the needs of chemistry as expressed in the appropriation from the funds of the University of Cincinnati which has enabled the erection and equipment of this building.

DESCRIPTION OF THE NEW CHEMICAL LABORATORY UNIVERSITY OF CINCINNATI

Taken from Circular issued by the University of Cincinnati

The new chemical laboratory of the University of Cincinnati has a total frontage of 207 ft. and is, practically, four stories high, since the basement is mostly above ground, and is utilized for laboratory purposes. The west wing is 92 ft. long by 48 ft. 9 in. wide. The east wing, which is to be completed later, is 57 ft. long by 48 ft. 9 in. wide. The cross bar connecting these two wings is 110 ft. long by 32 ft. wide. The total cost of the building was approximately \$250,000, including \$25,000 for special scientific equipment. It houses the Departments of Chemistry and Metallurgy. At the time of its occupation, in September, 1916, 220 students were enrolled in the various courses in chemistry and metallurgy.

FIRST FLOOR

The main auditorium for lecture purposes, which has a seating capacity of about 100, is located on the floor opposite the entrance. Adjacent to it is the lecture preparation room for setting up lecture apparatus. In the west wing are two laboratories for work in physical chemistry, and 10 laboratories for advanced metallurgy, together with a research laboratory for the Department of Metallurgy. In connection with these laboratories there is a dark room for microphotography, work, and a constant temperature room for work in physical chemistry. The offices on the floor are devoted to various purposes as follows: the business office in which the records of the department are kept on file and through which business is conducted; three

structors' offices and laboratories; two balance rooms, toilet and wash rooms. The east wing is devoted entirely to quantitative analysis.

SECOND FLOOR

The library of the department is located in the west wing. It has approximately 3,000 volumes. It contains sets of the important journals of chemistry and metallurgy, together with the current files of these journals and many reference books. In the west wing there is, also a lecture room seating about 80 students, together with its preparation room. This lecture room is equipped for demonstrating experiments, or processes, in electrochemistry and electrometallurgy; the switchboard control and recording instruments are visible to the class. The east wing is occupied by the laboratory of organic chemistry which is adjacent to a balance room, a combustion room and a room for sealed tube experiments and experiments with gases. The other rooms include two instructors' offices and laboratories, a special laboratory and office for the head of the department, a classroom, and a special methods room.

THIRD FLOOR

The elementary course in general chemistry is given in the laboratory located in the west wing. The table tops are provided at each working place with a hood in which a suction is produced by fan systems. The east wing contains a laboratory now used for qualitative analysis, and is equipped with the same kind of equipment as that of the laboratory of general chemistry. The stock-room from which supplies and apparatus are issued is on this floor; from this stock-room the materials used in all of the laboratories are distributed. A passenger elevator which serves to carry students from other floors, enabling them to reach the

stock-room without unnecessary delay, is adjacent to it. The stock-room is two stories high, the upper story being formed by a penthouse above the roof. In this second or balcony floor of the stock-room are located the controls for the distilled water system and the hydrogen sulfide generators, each in separate rooms in the attic. The fans connected with the various rooms in the building where suction is needed in addition to the general ventilation are controlled from the stock-room.

BASEMENT

The west wing is used entirely by the Department of Metallurgy. Here the rough and more elementary types of work are carried out, such as moulding and casting, the making of samples for testing in metallography, cutting of samples, heat treating, annealing, etc., and the use of gas furnaces, electric furnaces, pot furnaces, cupola, electric welders, etc. In a separate room in the rear of the building is located the electrical equipment for experimental work, consisting of motor generator sets, rotary converter with transformers and necessary switchboards. The laboratory for applied electrochemistry, situated in the cross bar, is also adjacent to the motor room. The east wing is planned for experimental work in industrial chemistry. It will contain typical units of machinery used in industrial work, such as stills, autoclaves, filter presses, nitrating kettles, pumps, fusion pots, vacuum dryers, centrifuges, grinders, etc. A shop, to be put in charge of a mechanic, is located near this room. In addition to these laboratories the basement contains a storage room for supplies, a cleaning room, a fire-proof storage room for combustible materials, a stock-room, a grinding room, instructors' office and laboratory, a storage battery room and the general ventilating system for the entire building.

ADDRESSES

THE CHEAP PRODUCTION OF ALCOHOL

By A. M. BRECKLER

Received March 19, 1917

The possible uses for denatured alcohol are two: as raw material in manufacture and as fuel.

After eight years of existence, the net result of the denatured alcohol act was the production of 17,000,000 proof gallons of denatured alcohol in 1914, most of which was used in the industries. Here it displaced the potable article, but with so little benefit to the ultimate consumer, according to the Commissioner of Internal Revenue, that in his report he advised a small tax to cover the cost of inspection by government officers during the manufacture.

In 1915, the manufacture of munitions had stimulated the production somewhat, but the benefits to the American people as a whole are doubtful and had the alcohol used in this industry (about 5,000,000 gallons) paid tax, a good portion of our present deficit might not have existed.

It is, of course, as a fuel for explosion engines that we look for the greatest demand for alcohol and it is the production of alcohol for this purpose which will eventually determine the price.

The total alcohol produced in 1914 in the United States from all raw materials was 182,000,000 proof gallons, equivalent to about 5 per cent of our present gasoline consumption. By far the largest source of this alcohol was grain, from which 142,000,000 gallons were produced. To produce enough alcohol to cover our gasoline demands as a motor fuel would take 16 per cent of our total cereal production or about 26 per cent of our total corn production.

The average cost of alcohol from grain (corn) has been 17.5 cents per proof gallon for the past five years. This probably

is a minimum figure as it is based on the cost in large distilleries and allows for the sale of the feed recovered at the average market price. The cost this season will not be far from 25 cents per proof gallon or about 45 cents per gallon of 90 per cent alcohol. If the alcohol is furnished in barrels, 2 cents must be added to this per proof gallon. This cost could not be cheapened materially. The overhead here figured is about 3 cents. So far as increasing the yield of alcohol per bushel, the possibility permits of an increase of only 5 per cent at most. It must be remembered that these figures carry no allowance for profit, selling expense and freight.

SOURCES OF CHEAP ALCOHOL

The possibility of making alcohol cheaper on the farm has been given prominence. The idea is to make alcohol and feed the slop to cattle. There are several reasons which would make this impractical in all except rare cases. The cattle fed on slop do not furnish meat which packs well. It is very tender and juicy and perfectly healthful, but becomes flabby on keeping. Therefore, it must be sold on a market which can absorb a large amount of it at a time. The experience of distillers who have fed large numbers of cattle (as many as 12,000 head at one distillery) is that such feeding is more or less of a speculation depending on the markets and the location of the plant, accessibility being necessary in order to enable them to take advantage of favorable prices. Aside from this there are fuel and water requirements which will be taken up later.

In 1912, the Minnesota Agricultural Experiment Station operated a 200-bushel distillery on grain. They employed an experienced distiller, had most careful chemical supervision of the plant and credited the feed at a very good price. Their yield was about 4 per cent under the average prevailing that season. The price charged for the corn was the average farm

price as against the market price. The net result was that they were unable to produce alcohol for what they could buy it. If under these favorable conditions, the alcohol cannot be produced at a profit, what can the farmer expect?

The other large source of alcohol is black strap molasses which five years ago was a drug on the market and sold as low as 2 cents per gallon at the sugar house. Coincident with the sudden increase in the demand for alcohol, the demand for black strap increased until to-day it is selling for 12 to 14 cents per gallon. The high price of sugar has stimulated the sugar houses to carry their extraction of sugar as far as possible and hence the yield of alcohol possible has decreased very much.

From black strap of good quality at 5 cents delivered, the cost of production would be around 10 cents per proof gallon, it is true, but if we assume that all the sugar produced in the United States and Cuba represents 80 per cent of that in the juice and all the remaining 20 per cent would be available for fermentation, we would have raw material available for about 162,000,000 gallons of alcohol or enough to supply about 5 per cent of our present demand for motor fuel. It is probable that not more than 25 per cent of this amount is actually available, owing to the increasing yields possible from better sugar extraction processes.

A third source of alcohol is wood waste. Enough money has been spent on sawdust plants to evolve several processes for cracking oils. The fact is that after seventy years of experimenting there are two plants running in this country and were it not for the high price of alcohol at the present time, it is doubtful whether they would run. The bulk of the material handled, the use of strong acids, the complex machinery for leaching and the rapid stripping of the timber tracts under cutting all operate against the process even were other conditions satisfactory. As both the plants now operating are financed by large corporations, it is evident that lack of money has not held the process back and it is very probable that if the process were really profitable, more plants would be in existence.

The sulfite liquors from pulp mills offer a cheap source of carbohydrates. None of the existing processes are exactly satisfactory. Just how much of this is available is a little uncertain. One thing is certain, that the amount of fermentable carbohydrates in this liquor is very variable. At present there are about three plants operating in America on this liquor.

Any process for making alcohol must give careful consideration to the question of yeast nutriment. As the amount of yeast formed is dependent on the volume of liquid rather than the concentration of the fermentable matter, the most economical process in this respect will evidently be that in which the concentration of the fermentable is the greatest practical. About 8 lbs. of dry yeast are formed from every 1000 lbs. of fermented liquor of which 6 per cent or $\frac{1}{2}$ lb. is nitrogen. If a liquid contains 10 per cent of fermentable, the amount of nitrogen required is one-thirtieth lb. per gallon 160 proof. The potash requirements are about one-fifth of the nitrogen. Just as much attention to yeast poisons is desirable. This is one of the drawbacks to the use of sulfite liquor for the production of alcohol. Even such a common substance as cranial acts as a yeast poison.

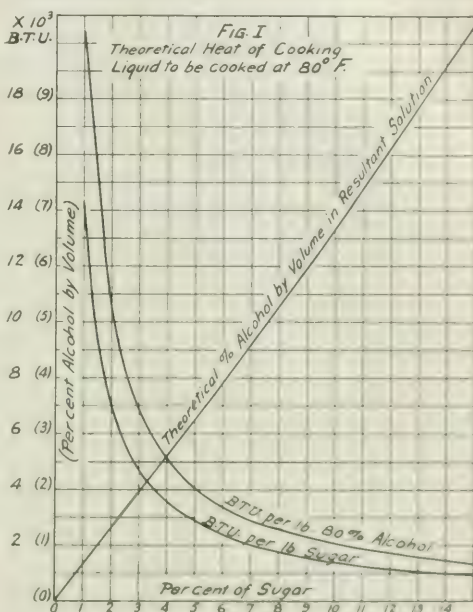
FUEL AND WATER SUPPLY IMPORTANT FACTORS

The factors which most often determine the feasibility of making alcohol from low grade material are fuel and water supply. The writer has prepared a curve, Fig. 1, showing the theoretical heat consumption at various concentrations for distillation of 1 lb. of 160 proof (80 per cent by volume) alcohol. This concentration was selected as being the lowest which would meet all fuel requirements and the highest which could be prepared with comparatively simple apparatus. The values for 95 per cent alcohol are about 1.5 times as great, owing to the heat necessary for the rectification and lower yield in gallons. The

factor 3.5 gives the minimum heat consumption while five times the theoretical would give about the average heat consumption.

For example, let us consider the distillation of 160 proof alcohol from sulfite liquor. As concentrated for fermentation, this liquor ordinarily contains 4 per cent fermentable. As this is hexose sugar, the resultant solution will contain theoretically 2.61 per cent alcohol. With a yield of 85 per cent (an average usually obtained), the resultant solution will contain about 2.2 per cent alcohol by volume. The theoretical heat of distillation per lb. 160 proof alcohol from such a concentration is 4,000 B. t. u. As the weight of one gallon of 160 proof alcohol is 7.2 lbs., the heat required under best conditions would be 126,000 B. t. u. while probably it would approach 180,000. Using a good coal running 13,000 B. t. u. per lb., the coal required under favorable conditions would be 10 to 14 lbs. Assuming such coal to cost \$3.00 per ton laid down at the paper mill, the costs under good conditions for distillation of 160 proof alcohol would run 1.5 to 2.1 cents per gallon.

Similarly it may be figured that 160 proof alcohol from sorghum



juice containing 15 per cent as hexose will cost 0.4 to 0.6 cent per gallon for distillation with coal at \$3.00 per ton. This probably represents as concentrated a liquor as it would be possible to ferment, since the resultant alcohol from weaker liquor would probably affect the yeast before the attenuation was complete. In Germany, where thicker mashes are used, the practice is to thin out with cold water during fermentation.

In the case of nearly any material containing starch and most other materials, a preliminary cooking is necessary and hence again the cost is greater the lower the concentration. Fig. 2 shows the B. t. u. per lb. hexose sugar and fructose (or 1 lb. 100 per cent alcohol) at various concentrations of sugar. Each multiplied by 1.11, of course, gives the heating concentration. The factor of 1.11 probably covers the steam losses in actual heat put under the vessels. Fig. 2 is based on cooking to 140°F. only. In a great many cases, the material is cooked to 140°F. in which case the figure given should be multiplied by 1.5 or more.

Considering the cost of softening (which is covered primarily only

mitted to the writer contained 5 per cent fermentable hexose. This gave a figure of 4,100 B. t. u. per lb. of 80 per cent alcohol theoretically, but as the average yield is 85 per cent of the theoretical, this would become 4,800 B. t. u. Multiplying by 7.2 and 2.5, we would have a theoretical consumption of 86,500 B. t. u. or 6.65 lbs. coal which, at \$3.00 per ton, represents 1 cent per gallon for cooking. If the mash should have to be cooked under pressure, the cost would be 1.8 to 1.7 cents per gallon 80 per cent alcohol, making a cost of 2.2 to 2.27 cents for cooking under atmospheric pressure and distilling, and of 2.9 to 3.4 cents at high pressure and distilling. In addition to this, power must be furnished for comminution, pumping, etc., all of which re-

The water required for condensing a gallon of 80 or 95 per cent alcohol and cooling to 80° F. is theoretically, as in Table I, assuming perfect efficiency. In practice, the amount found thus should be raised to the 3/2 power; this relation is based on experiments made by the writer in distilleries.

TABLE I GALLONS WATER REQUIRED TO CONDENSE ONE GALLON ALCOHOL AND COOL TO 85° F.

Temperature of Cooling Water:	55	60	65	70	75	80° F.
GALLONS WATER FOR ALCOHOL:						
80 Per cent by Volume	4.3	4.5	4.7	4.9	5.1	5.3
95 Per cent by Volume	3.4	3.6	3.7	3.9	4.2	4.3

It can be seen that a plant producing 100 gallons 80 per cent alcohol per day will require from 900 gallons water at 55° to 1,250 gallons at 80°, though probably the last figure is too low.

If the mash is heated considerably, more water will be required as is evident by Table II. It is not possible to correlate these figures with practice, unfortunately, as owing to the extreme viscosity of highly concentrated mashes, the factor is much greater here than that calculated as above, and owing to the more efficient apparatus used, the factor for thin mashes much less. At any rate, the figures given are minimal, though a safe margin would be five times the figures given.

MAXIMUM RAW MATERIAL COSTS

Assuming a concentration of 10 per cent fermentable in the liquid as finally prepared for fermentation, Table III represents about the maximum allowable cost per lb. fermentable for pro-

TABLE II GALLONS WATER PER GALLON 160 PROOF ALCOHOL FOR COOLING MASH TO 70° F.

Per cent Sugar in mash	Water at 55° F.	60° F.	65° F.	70° F.
1	112.5	116.2	120.2	124.4
2	56.3	58.1	60.1	62.2
3	37.5	38.7	40.1	41.5
4	28.1	29.1	30.1	31.1
6	22.5	23.5	24.0	24.9
8	18.8	19.4	20.1	20.8
10	16.1	16.6	17.2	17.8
12	14.1	14.6	15.0	15.6
14	12.5	12.9	13.4	13.8
16	11.3	11.6	12.0	12.4
18	10.2	10.5	10.9	11.3
20	9.4	9.7	10.0	10.4
25	7.5	7.7	8.0	8.3

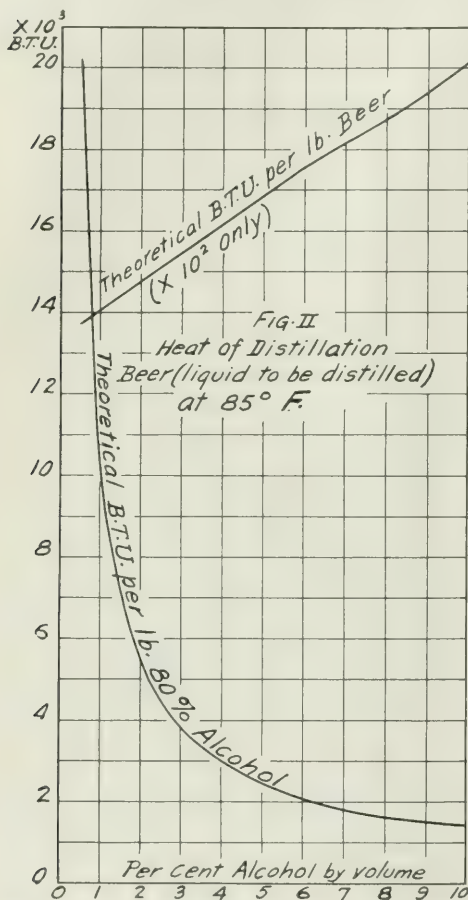
ducing alcohol of any given cost per proof gallon, assuming an 85 per cent yield. Any feeding value of the residue should be added allowable to raw material cost. As this table is based on an overhead of 2 cents per proof gallon, which is the minimum possible under the most favorable conditions, the figures for raw material cost give the maximum allowable value.

TABLE III MAXIMUM ALLOWABLE COSTS FERMENTABLE COST FERMENTABLE MINIMUM COST ALCOHOL per lb. Hexose Delivered per Proof Gallon

1.0 cent	9.6 cents
1.2	11.2
1.4	12.6
1.6	14.2
1.8	15.7
2.0	17.2
2.2	18.7
2.4	20.2
2.6	21.8
2.8	23.3
3.0	24.4

Let us suppose that we wished to compete with gasoline at 30 cents. Assuming that absolute alcohol and gasoline deliver the same amount of power per gallon, we must take the cost of alcohol at 15 cents per proof gallon. The raw material must, therefore, cost not over 1.7 cents per lb. fermentable. Alcohol potatoes contain 20 per cent starch. This is the equivalent of 22.2 per cent dextrose. We have the relation $0.222 \times 1.7 \times 0.38$ cent as the maximum allowable cost per lb. of potatoes delivered, provided the feed is not utilized. The feeding value of the residue of 1 lb. of potatoes is generally taken at about 0.1 cent. This would make the maximum allowable cost 0.48 cent or 28.8 cents per bushel delivered.

At present gasoline is selling about 20 cents per gallon. If the Utopian ideas of certain automobile manufacturers were realized, potatoes would have to be laid down at the distillery



quires fuel. In a grain distillery, the fuel required for this purpose is about half of that for all other purposes. It is, of course, difficult to state this cost for all materials, but this relation would probably not give excessive figures for any other material.

Coal, we can nearly always get, but unfortunately, the problem of cooling is just as pressing. Artificial refrigeration has never been used in distilleries in the United States because of its cost, most reliance being placed on water cooling. For plants which can obtain artesian water or lake water, or plants on the ocean, such a problem is not difficult, but for any proposed inland distillery too much consideration cannot be given to the matter.

for not to exceed 20 cents per bushel in order that alcohol might replace this gasoline. The average farm value for potatoes from 1907 to 1915 inclusive was 61.4 cents per bu. It is hard to see how the farmer could be stimulated to produce more potatoes if a lower price were offered as must be if potatoes are to figure as alcohol producers. The popular mind has become so obsessed with the idea of cheap alcohol from potatoes that it is forgotten that the German idea of cheap alcohol is alcohol at about 40 cents per gallon 180 proof.

CONCLUSIONS

Water, fuel and cost of raw material represent about all the factors susceptible of approximate calculation. In addition labor, insurance and depreciation must be taken into account. If starchy substances are used, malt or acids must be used for conversion which is an additional cost. It cannot be too strongly impressed on the prospective manufacturer that sporadic sources of material such as fruit, cornstalks, canning wastes, must always be used under the disadvantage of long periods of idleness resulting in increased depreciation, and disorganization of the working force.

It must not be understood that the writer intends to depreciate the possibility of producing alcohol at a cost to enable it to be used as a motor fuel. Quite the contrary. But it has seemed to him that unless more care is used in experiments on the production of alcohol that capital will abandon the field as unpromising. The newspapers are full of stories about the possibilities of production of cheap alcohol and even our own JOURNAL has not been entirely free from them. As a matter of fact, the production of cheap alcohol presents as many difficulties as the manufacture of cheap gasoline. The alcohol industry is one that requires experience as much as any other chemical industry and in spite of opinions to the contrary, uses at present about as scientific methods as any.

AUTHOR'S NOTE (Received May 16, 1917): Owing to recent increases in grain costs, it is probable that grain alcohol costs will be over fifty cents per proof gallon for the year 1917.

503 KENTUCKY TITLE BUILDING
LOUISVILLE, KENTUCKY

WILLARD GIBBS MEDAL AWARD

The Willard Gibbs Medal for the year 1917 was conferred upon Dr. Edward Williams Morley, former Professor Emeritus in Chemistry, Western Reserve University, Cleveland, Ohio, at the meeting of the Chicago Section of the American Chemical Society, held May 18, 1917, in the Louis XVI Room of the Hotel Sherman. One hundred and forty-six members and friends of the Chicago Section were present.

Mr. A. V. H. Mory, Chairman of the Chicago Section, opened the meeting and introduced Dr. W. A. Noyes, Professor of Chemistry, University of Illinois, and Editor of the *Journal of the American Chemical Society*, who made the presentation address. The medal address, entitled "Early Researches in Hydrogen and Oxygen," will appear in full in the *Journal of the American Chemical Society*, and we are printing below an abstract prepared by Dr. Morley at our request.

Dr. Morley spoke in his usual happy vein. He showed the distinguishing quality of his mind—that keen sense of proportion that made possible his great work, by fully appreciating the sort of treatment of his subject that would be most acceptable to a mixed audience, including many who had no knowledge of chemistry. There was a personal touch to Dr. Morley's talk that was much enjoyed and he skillfully employed an occasional narrative to drive the points home.

Letters of regret were received from a number of invited guests, including the presidents of the Middle West universities, and a number of the prominent chemists of the country, among them Secretary Charles L. Parsons.

At the speakers' table, besides the chairman, Professor Morley, and Professor Noyes, were President Stieglitz; Harry Pratt Judson, President of the University of Chicago; F. I. Moulton, President of the City Club of Chicago; John H. Long, Professor in Chemistry at the Northwestern University Medical College; William H. Burton, Vice-President of the Standard Oil Company of Indiana; and Edward Bartow, Director of the Illinois Water Survey, each of whom spoke briefly and entertainingly. President Stieglitz was able to give some interesting information concerning the work of our society in these stirring times.

The occasion was a memorable one and established even more completely, if it were possible, the high character of the Willard Gibbs Award.

Edward Williams Morley was born in Newark, N. J., in 1848. He received the degrees of A.B. (1869) and A.M. (1871) from Williams College, and an honorary Ph.D. from University of Wooster (1878). He has also received the honorary LL.D.

degree from Adelbert College (1891), Williams College (1901), Lafayette College (1907), University of Pittsburgh (1915), and the Sc.D. degree from Yale (1909). Dr. Morley was professor of chemistry from 1869 to 1906 at Western Reserve College, formerly at Hudson, Ohio, and afterwards removed to Cleveland. He also held the chair of professor of chemistry in the Cleveland Medical College from 1873 to 1888. Dr. Morley is an honorary member of the Royal Institute of London; corresponding member of the British Association for the Advancement of Science; associate fellow of the American Academy of Arts and Sciences; fellow of the American Association for the Advancement of Science, of which he was president, 1895–1896; a member of the National Academy of Sciences, American Philosophical Society, Astronomical and Astrophysical Society of America, the Chemical Society of London, and the American Chemical Society, of which he was president, 1899–1900.

Dr. Morley was honorary president of the Eighth International Congress of Applied Chemistry which met in New York City in September, 1912. The photograph of which a copy is shown here was made at about that time.

The *Chicago Chemical Bulletin* furnished us with the following brief account of Dr. Morley's most important work:

"The attention of chemists was first attracted by his work on a very accurate series of analyses of air which demonstrated that the per cent of oxygen in the air varies between narrow limits and is probably smaller in the higher strata of the atmosphere.

"In 1842 Dumas had made a series of determinations of the composition of water, on the basis of which the value 15.06 was accepted as the atomic weight of oxygen for nearly fifty years. Toward the end of this period a number of different chemists worked upon the problem and it gradually became clear that the value found by Dumas was in serious error, but it was not until Dr. Morley's paper appeared in 1858 that the chemical world accepted a quite different value as fully demonstrated. In an elaborate series of investigations, to which he gave more than ten of the best years of his life, the densities of hydrogen and of oxygen gases were determined with an accuracy that had not been excelled or even reached by any other observer. Dr. Morley also effected for the first time a complete quantitative synthesis of water, weighing both the oxygen and hydrogen used and also the water formed by their union. The result of all of his studies gave the value 15.89 for the atomic weight of oxygen, or, as it is now called, as the atomic weight of hydrogen and it being quite certain that these values will never be essentially changed.

"In the domain of physics the Michelson-Morley experiments, upon the transmission of light in the direction of the motion of the earth in space and at right angles to that motion, have been the basis of the modern theory of relativity and have gone far to undermine the confidence of physicists in the existence of the ether.

"Dr. Morley is not only one of the greatest of American chemists, but he is a man whose rare personal qualities have won for him a wide circle of friends."

INTRODUCTORY ADDRESS

By A. V. H. Mory

When William A. Converse, on retiring from the chairmanship and active work in the local section of the American Chemical Society, donated a sum to be used in founding a medal in the name of the Chicago Section for the encouragement of local talent, he builded better than he knew. Certain it is, his native modesty would have deterred him from presuming to found a medal of such dignity and importance as the Willard Gibbs Medal has come to be.

The committee appointed to draw up rules governing the award saw so many difficulties in the way of a local award by a local jury that it broadened the scope of the award. When the now honored president of our national society, Dr. Stieglitz, then chairman of the Medal Committee, proposed that the award bear the name of that most illustrious of American chemists, J. Willard Gibbs, the modest proposal of Mr. Converse then and there took on national importance.

A number of the most prominent chemists of the country were later invited to sit on the jury of award and the distinguished Swedish chemist, Arrhenius, was the first of those recognized in the bestowal of the Willard Gibbs Medal.

That there has been no lowering of the high standard thus set up is attested by the list of illustrious medalists that have followed—Theodore William Richards, Leo H. Baekeland, Ira Remsen, Arthur Amos Noyes, Willis Rodney Whitney, and last of all, our honored guest of the evening—Edward Williams Morley.

It goes without saying that the Chicago Section stands committed to a policy that insures the continued high character and dignity of the Willard Gibbs Medal. And it may be added that we, of the Chicago Section, including the founder of the medal, shall ever remain content to render such humble service as may be our privilege in simply providing, as it were, the machinery for bestowing the honors that the eminent jury shall elect to award.

PRESENTATION ADDRESS

By WILLIAM A. NOYES

There are a considerable number of fundamental physical constants which lie at the very foundation of all accurate scientific work. Among these the density of the common gases and the relative weights of the atoms of the elements have occupied a very prominent place in the attention of chemists. The earlier determinations of these constants were made by crude

and inaccurate methods and the values obtained were displaced by other, better values within a few years. Literally thousands of such determinations have been made, but the large majority, although they usually represent the work of many months, have been displaced by others within a few years or, at most, within a generation. Regnault in Paris in 1845 determined the densities of hydrogen and oxygen with such care that his work stood for a generation without serious question. About the same time Dumas, also working in Paris, determined the ratio of the atomic weights of hydrogen and oxygen and his result also stood for a generation, although we now know that it did not deserve the confidence which it received. Dumas himself considered that the value he obtained was in error, possibly as far as one part in 200. The fact that Regnault did not think of the compressing effect of the pressure of a ton or more on the outside of his empty globe, introduced an error in his value for the density of hydrogen which was almost identical with the error of Dumas's determination of the oxygen-hydrogen ratio. This accidental

agreement of two results, each of which was affected by a serious but different source of error gave chemists a very undue confidence and they allowed them to stand without serious question for forty years. After that a number of chemists and physicists gave to the world much better values for both constants. But Professor Morley was not content to give to the world values of the ordinary sort which might stand for a few years and then be displaced by others. He was willing to study, one after the other, and with almost an infinite patience, the sources of error in the determinations, and then he carried out his work with such an ingenuity in the execution of details, and with such accuracy, that at present there is no indication that the work will need to be repeated for a century.

I am glad to express in this way the estimate which the world places on the work of Professor Morley, but there is also a keen personal pleasure in being permitted to make this presentation. I have known Professor Morley for twenty-five years, and with the years there has grown an intimate personal friendship

which has become one of the most inspiring influences in my life. Professor Morley is a merciless critic—of himself. He has very little to say about the shortcomings of others, though few see more clearly what some of those shortcomings are. And so I take the greatest pleasure in presenting this medal to a personal friend, to a man who has done work of the very highest quality and to one who has given to the world values for two of our most fundamental constants which will always stand as very close indeed to the truth.

EARLY RESEARCHES IN HYDROGEN AND OXYGEN MEDAL ADDRESS¹

By EDWARD WILLIAMS MORLEY

The chemical principles involved in the synthesis of weighed quantities of water from weighed quantities of hydrogen and oxygen require no description; it is only the details of the manipulation by which errors were minimized which are interesting.

Pure hydrogen cannot easily be prepared by solution of a metal

¹ Author's abstract



EDWARD WILLIAMS MORLEY
WILLARD GIBBS MEDALIST, 1917

in acid. Carbon and carbon compounds derived from metallurgical operations introduce impurities which cannot be removed. If we remove carbon and carbon compounds, as by distillation of zinc in a vacuum, it is difficult to utilize the hydrogen produced in a given generating vessel to sweep out the nitrogen previously included and still have sufficient gas for the destined use. Electrolysis is accordingly a more convenient source. Electrolysis of caustic alkali would be convenient except that the presence of carbonate introduces impurity which cannot be removed. Dilute sulfuric acid is therefore to be preferred; it gives a gas which, of course, contains nitrogen; it contains vapor of water, and sulfur trioxide; it contains oxygen, ozone and vapor of hydrogen dioxide, diffused through the liquid from the other pole; it also contains sulfur dioxide and hydrogen sulfide. Prolonged evolution finally sweeps out nitrogen. Red-hot copper removes oxygen, ozone and hydrogen dioxide and converts all sulfur compounds into copper sulfide or hydrogen sulfide, which is easily removed by absorption in caustic alkali. Lastly, water is removed by phosphorus pentoxide.

Absence of nitrogen was proved by the absorption of a liter of the gas by means of hot copper, with eudiometric analysis of the one per cent of residue. It was proved that at last less than one part of nitrogen remained in two hundred thousand parts of hydrogen. But in the syntheses, the gas was next absorbed in palladium, the palladium tube was freed from accompanying nitrogen by a prolonged current after absorption had ceased, and this doubly purified hydrogen was utilized.

The amount of moisture remaining in a gas after drying with phosphorus pentoxide was measured; it was given by the loss of weight of a special absorption tube, and was about one milligram in 40,000 liters. The amount of pentoxide taken up by the gas was also determined and found also to be some such quantity as a milligram in 40,000 liters. It is probable that the milligram lost by the absorption tube and at first regarded as moisture was actually pentoxide, and that the amount of moisture remaining after drying with pentoxide is far less than a milligram in 40,000 liters.

The hydrogen used in syntheses was free from carbon compounds and compounds of sulfur. This was proved by burning a slow current of the hydrogen in an atmosphere of the oxygen produced in the same electrolysis. The combustion took place in a closed vessel, so that solution and absorption of possible products of combustion must have been complete. When some 600 cc. of water had accumulated, the liquid was examined; it contained no carbon dioxide and no oxide of sulfur; it contained 0.02 milligram of phosphorus pentoxide.

It was interesting to notice that in this experiment, when the platinum jet had been heated to incandescence in an atmosphere of pure oxygen for some ten days, the inside of the flask was covered with a rust-colored oxide of platinum. When the combustion was stopped, the current of hydrogen was maintained, and the oxide was immediately converted into a deep black coating of metallic platinum.

AUTHOR'S NOTE—Many other details of manipulation are described in the complete address, but they are mostly already on record and need not be here repeated.

CURRENT INDUSTRIAL NEWS

EXTRACTIONS OF LOW-GRADE LEAD ORES

At the Salt Lake City, Utah, Experiment Station of the Bureau of Mines, Department of the Interior, Mr. A. E. Wells, metallurgist in charge, reported as follows to the Washington office of the bureau:

The most successful results of the metallurgical research branch during the month were with low-grade lead ores which have failed to yield to flotation or leaching processes described in previous reports. By mixing these ores with sodium chloride and heating to temperatures of about 800° C. high extractions can be obtained with the lead irrespective of the type of gangue in the ore. The lead volatilizes as a chloride and any silver or gold present is likewise volatilized. These chlorides are precipitated from the fume by the use of the Cottrell precipitator. The precipitated lead chloride after a mixture with lime and a small amount of reducing agent is heated to a red heat when a slag of calcium chloride and metallic lead is formed. The calcium chloride is an advantageous substitute for sodium chloride in the first operation, and from 50 to 75 per cent of the chlorine is recovered in this manner. This process will have the advantage of producing bullion from either oxides or sulfite ores in localities which do not contain sufficient water for milling purposes. Cost calculations indicate a considerable possibility of this process being cheaper than water concentration followed by smelting.

COAL IN CHINA

The *Board of Trade Journal* of December 31, states that a Hong Kong contemporary had about that time published extracts from a report respecting the coal reserves of China, which had been drawn up recently by the Director of the Chinese Geological Survey. According to the report, coal seems to be very widely distributed in China. There is not a single province in which coal is not found. The northeastern provinces, Shansi, Chihli, Shantung and Honan are undoubtedly, the most im-

portant, the first named being the richest of all. Both Inner Mongolia and Manchuria are fairly well supplied with coal. The northwestern and southeastern regions are, however, much poorer, the geological formation being unfavorable. Both bituminous and anthracite coal occur in China, the latter being more extensive, as the coal in Shansi and Honan is largely anthracite. In fact, the latter variety has been more used in China, as it can be burned in open stoves without chimneys. The bituminous coal industry has acquired increasing importance in recent years as the coal now worked on a large scale is mostly of this variety and, out of twenty mines worked by machinery, only three are producing anthracite. The production of coal of all kinds in China in 1913 was about 15,000,000 metric tons (1 metric ton = 2,204.6 lbs.).—A. McMILLAN.

FRENCH RESINOUS PRODUCTS

According to a report in the *Oil and Color Trade Journal*, 51 (1917), 975, the output in the resin market for the coming year is very satisfactory. The Landes depots and warehouses report stocks of spirit of turpentine amounting to 3,000,000 kgs., to which there must be added 1,041,391 kgs. in Bordeaux warehouses, making a grand total of 4,000,000. Half of this total has already been sold so that only 2,000 tons are available to keep things going until the new season has opened. Hence prices are very firm at present and it is probable that a rise in price will take place and the present month may close with rates at \$45 to \$50 per 100 kilos. For dried sorts there is a pressing demand but very scant stocks. Lots on hand do not, probably, exceed 20,000 barrels of pitch and colophony. Prices are expected to advance from \$15 to \$20 per cased French tons. The market is greatly favored by the fact that sharp advances will probably occur in America due to higher freight and manure rates and to shipping losses. Artivads are also getting scarcer in England and America will probably be willing to replace American with French resins. M.

KAPOK FIBER

According to an article by Messrs. C. F. Cross and F. J. Bevan in the *Journal of the Society of Dyes*, 32, 274, true kapok is the seed-hair of *Eriodendron anfractuosum*, though other vegetable downings pass commercially as kapok. The chief use of the material is for stuffing lifebelts, etc., and the fiber keeps out of the water, not because it contains much water-repelling oils or resins (these are found up to 1.8 per cent), but because the fibers form thin-walled tubes filled with air. The fibers are remarkably uniform as regards diameter (0.021 to 0.028 mm.). The air is not expelled by immersion of the fiber in hydrocarbons. Sinking tests of kapok in water take very long times but, in aqueous alcohol of density 0.928, tests as to grade can be carried out expeditiously. In life-saving appliances 1 g. of kapok occupies about 15 cc., and a jacket containing 700 g. of this stuffing would have a floating power of 10.5 kg. After having been suspended in water for 72 hrs. with a weight of 9 kg. attached, the jacket still required 1.3 kg. more to submerge it and after 192 hrs., 0.9 kg. were required to sink the jacket. The references here mentioned are to tests carried out on kapok in the National Physical Laboratory, London, before the war.—M.

BRITISH MINERAL OUTPUT FOR 1915

The following table, taken from the annual report on mines and quarries for the year 1915, gives the production of the various minerals:

MINERAL	Quantity (Tons)	Value £	Quantity (Tons)	Value £
Alum Shale.....	6,078	607	7,911	791
Antimony Ore.....	421	39
Arsenical Pyrites.....	2,215	233
Arsenic.....	1,988	19,052	2,496	32,779
Barium Compounds.....	48,930	43,506	62,477	79,829
Bauxite.....	8,286	2,159	11,723	3,163
Bog Ore.....	2,342	585	1,986	496
Chalk.....	4,291,170	197,154	3,233,897	155,560
Chert, Flint.....	76,213	13,304	102,698	15,536
Chromite.....	100
Clay and Slate.....	13,124,361	1,731,779	8,871,821	1,172,877
Coal.....	265,664,393	132,596,853	253,206,081	157,830,670
Copper Ore.....	2,373	19,885	579	3,084
Copper Precipitate.....	185	5,529	243	9,938
Fluorspar.....	33,816	11,005	33,123	11,484
Gold Ore.....	47	318	5,086	3,389
Gravel and Sand.....	2,498,872	215,351	2,350,267	213,373
Gypsum.....	265,365	83,268	247,229	78,747
Igneous Rocks.....	7,135,243	1,369,242	6,085,415	1,200,212
Iron Ore.....	14,867,582	3,921,683	14,235,012	4,587,651
Iron Pyrites.....	11,654	4,759	10,535	4,873
Lead Ore.....	26,013	309,813	20,744	295,071
Lignite.....	300	150	1,783	536
Limestone.....	12,158,441	1,295,512	11,115,909	1,306,268
Manganese Ore.....	3,437	2,931	4,640	4,640
Natural Gas.....	87,000 c. ft.	Not stated	87,000 c. ft.	Not stated
Ochre, Umber.....	11,069	10,635	8,989	9,641
Oil Shale.....	3,268,666	837,249	2,998,652	836,393
Salt.....	2,069,989	560,893	2,005,605	607,251
Sandstone.....	3,464,528	1,057,096	2,520,856	758,325
Slate.....	318,912	806,196	226,037	452,819
Soapstone.....	180	90	850	575
Sulfate of Strontium.....	13,157	10,439	640	688
Tin Ore.....	8,085	661,865	8,144	668,609
Tungsten Ore.....	1,205	19,722	331	4,803
Uranium Ore.....	344	82
Zinc Ore.....	15,419	56,652	12,057	70,383
TOTALS.....		£145,863,332		£170,460,949

—M.

FOOD VALUE OF THE SOYA BEAN

In an article in *Compt. rend.*, 164 (1917), 300, the use of the soya bean as an article of food is strongly recommended. The author says that its food value has long been known in the Far East. It forms an important article of diet in the French Indo-Chinese colonies, in Cochín-China, China and Japan. The oil-content of soya beans is no less than 20 per cent and the protein content 40 per cent, whereas French haricot beans contain only 20 per cent of protein and 2 per cent of fat. The author further suggests that the soya bean should be cultivated in France. The nutritive value of the soya bean meal has led to its being used, in some degree, in military rations in the French army and its use for civilian purposes deserves wider application.—M.

SULFUR SUPPLY IN GERMANY

Before the war, says the *Iron and Coal Trade Review*, the Germans obtained annually about 900,000 tons of iron pyrites from Spain for the manufacture of sulfuric acid and they, themselves, produced about 300,000 tons every year at Megen in Silesia. In 1912 and 1913, however, they increased their purchases from Spain to 1,200,000 tons per annum. Owing to the stoppage of the Spanish supplies by the war, they had to look about for other sources and have, no doubt, found some in Poland and also in Greece and Turkey. Besides this, Germany has received about 400,000 tons of pyrites annually from Norway. The eminent French chemist, M. Cazeneuve, states that the Germans have succeeded in producing anhydride from plaster of Paris with the help of the electric furnace. It is also reported that a process is being carried on in Germany which consists in treating plaster of Paris with sand and producing silicate of lime and cement at the same time as sulfurous acid. The Norwegian supply of pyrites is not now available to Germany.—M.

ASBESTOS PACKING

According to A. Dubose in the *Journal de Caoutchouc et Gutta-percha*, attempts have been made with partial success to imitate klingerite, the asbestos preparation of German manufacture, which found favor prior to the war as an excellent packing for steam pipe joints. A sample of the product, 3.75 mm. in thickness, was found to consist of 15 layers of a thin asbestos felting, built up of the best long fibers mixed with 2 per cent of flax threads. Such layer was coated on both sides with some agglutinant which contained sulfur; this sulfur was to be slowly vulcanized, apparently while the material was being used, in order that it might become more resistant and impervious. An analysis of the sample gave: 80.5 per cent of asbestos, 2.2 per cent of cellulose (flax), and 17 per cent agglutinant (consisting of rubber and balata with a small percentage of sulfur, less than 0.5). The incorporation of the flax would render the packing stronger, more pliable, and increase the cohesion of the fine layers.—M.

CEDARWOOD OIL

We have received, says *Nature*, from Messrs. Flatters and Garnett, Ltd., Manchester, England, a specimen of their cedarwood oil for use with oil-immersion microscopic objectives. As the result of tests, the oil was found to be of good consistence and color, does not become cloudy in cold weather and has a high refractive index. The refractive index of cedarwood oil is stated to be 1.510, but that of the specimen examined was well above this, viz., 1.518. Hitherto, Great Britain has been supplied with immersion oil from the Continent, but this is a British-made oil which seems to fulfil every requirement. It is supplied in bottles at from \$0.18 to \$1.00 each, or in bulk.—M.

EXPORTATION OF JAPANESE CHEMICALS

According to a report in the *Chemical Trade Journal*, 60 (1917), 257, an order has been issued by the Japanese Minister for the Interior granting permission to export the following goods from Japan:

Acetate of lead	Castor oil	Oil of turpentine
Ammonia water	Cinchona bark	Potassium sulfate
Ammonium carbonate	Citric acid	Saccharine
Aspirin	Citrate of iron and ammonium	Sulfur
Bicarbonate of potash	Gum arabic	Tannic acid
Bicarbonate of soda	Hydrogen peroxide and preparations therefrom	Tartaric acid
Boric acid	Lactic acid	Urotropin
Bromine and salts	Lysol	Vaseline
Calcium	Camphor monobromatium	White wax
	Milk sugar (dactose)	Yellow wax

—M.

BRITISH BOARD OF TRADE

During the months February 15 to April 15, the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.

Animal traps for bears and pumas
Astrachan
Beech boards for brushes
Bellows suitable for use in damp places
Bleached white mercerized sewing yarn
Canvases

CHEMICALS: Alphanaphthylamine

Aluminum sulfate
Arsenic acid (sp. gr. 1.8)
Formaldehyde (40 per cent)

Dimethyl sulfate
Florida earth for bleaching oils
Carbonate of copper (commercial)

Carbonate of zinc
Selenium powder
Sodium perborate

Tin oxide
Ultramarine blue
Combs, white celluloid

Crepes paper
Dyes, blue and mauve for ink making

Enamelled tea kettles
Eyelet rivets
Fishing nets for sardine fishing

Fishing twine
Glass, hard, heat-resisting
Gramophone needles

Hand cleanser, suitable for motorists, mechanics
Handkerchiefs, colored cotton, for African native trade

Horseshoe nails
Iron or steel moulds for casting lead name-plates, numbers, etc.

Knitted fabric, for gas mantles
Leather boot laces
Leather tabs for metal key chains

MACHINERY AND PLANT FOR:

Cane plating
Converting mica into micanite and mica cloth

Cutting cartons for cardboard box making
Decorating ground nuts

Dry-cleaning garments
Embossing, printing and cutting out parcel seals

Hand-stapling, similar to Hotchkiss machines
Making India-rubber stamps

Making macaroni
Making paper spills
Making photographic and other lenses

Making rice-starch (for delivery after the war)
Making sheet-nets

Paper baling machines
Printing tickets from the reel

Printing, in one or two colors, and punching labels at same time, with or without embossing attachment

Stretching the corners of boxes, similar to Brechmer machine

Stuffing dolls' bodies
Micrometers

Mirrors, celluloid
Note-books, cheap

Stearine (240 tons)
Strawboard, millboard and substitutes therefor

Vacuum chambers for vacuum fash
Wax-tapers

Wood-moulds for buttons, large oval
—M.

DYE FROM RICE LEAVES

The discovery of a process of obtaining dye from the leaves of the rice plant is attributed to Mr. Shigeo Kumagiri, of the Japanese Department of Agriculture and Commerce. He claims to be able to produce a dark purple dye by a chemical treatment of the grass of this plant. When treated with acids, the new dye turns red. Experiments have shown that it can be used with success for various purposes in laboratories and also for coloring materials. In the opinion of a Japanese paper, the new discovery is not likely to prove of very great use as the leaves of the rice plant have to be gathered before harvesting. The production of the dye from such a source is, however, interesting.—M.

NORWEGIAN WHALE OIL PRODUCTION

Norway's production of whale oil during 1916, says the *Anglo-Norwegian Trade Journal*, was less than it has been for many years owing to several of the whalers being engaged in ordinary trade and to the difficulties connected with the fishing. The total production during the year amounted to 367,400 bbls. as against 475,000 bbls. in 1915, 575,000 in 1914, and 600,000 in 1913. It is necessary to go back to 1910 to find such a small production of oil. The catch at the South Shetlands aggregated last year 195,000 bbls., and at South Georgia 136,700 bbls., while the fisheries at Australia, Africa, the Faroe Islands and Alaska, only yielded 34,800 bbls. The world's production of whale oil in 1916 amounted to 634,500 bbls., of which 216,000 bbls. falls to the South Shetlands, 319,400 bbls. to South Georgia, 40,000 bbls. to Africa, 13,000 bbls. to Australia and 18,000 to Alaska. During 1915 the world's production was 630,000 bbls., during 1914 735,000 bbls. and during 1913 775,000 bbls. Compared with the world's production, the Norwegian production during 1916 was 58 per cent, during 1915 about 75 per cent, and during 1914 and 1913 about 78 and 77 per cent, respectively.—M.

FRENCH TUNGSTEN

The tungsten requirements of the French industries for 1917, says *Engineer*, are considerable, and the question of wolfram production in France has been taken up by the Government. An official has been specially appointed to keep in touch with producing companies, and formal assurance regarding the supply of labor has been given. An arrangement has been arrived at between the Vaubry et Cieux Co. and the Société du Giffre, an important tungsten producer for the more energetic exploitation of the concession. The deposits in the Valley of Cieux are said to contain tin and gold as well as wolfram. Considerable reserves of ore have been disclosed and, at the present time, the production is about 10 tons wolfram per month. It is hoped that by the installation of new plants the production will be increased to 30 tons per month. Other wolfram deposits have been worked in the department of Ille et Vilaine, and in the Haute-Vienne. The Puy-les-Vignes Mine in the latter district was the only French production since 1914. —M.

DETECTION OF COCONUT OIL

At the annual meeting of the Food Analysts held recently in London, Mr. G. D. Edrington read a paper on the same subject. The author had studied the methods of detection and description of pure coconut oil for the determination of coconut oil in mixtures, and also the examination suggested by Hildebrand and Bolton (Analyst 46 (1911), 344), but it had not been found possible to obtain satisfactory results by either method. In the present paper the composition of French and Danish coconut oil is given, and also the examination suggested by Hildebrand and Bolton. The value of these methods for the detection of coconut oil in mixtures is given. It is suggested that these methods and the method of Hildebrand and Bolton be used together.—M.

DEARTH OF RAW MATERIAL IN SCANDINAVIA

According to *Engineering*, 103 (1917), 175, the scarcity of raw materials is becoming more and more embarrassing in neutral countries, not only are the prices in many cases rapidly approaching an absolutely prohibitive limit, but many industries are on the verge of stopping or have done so. In this connection iron and coal play an important part. Some Danish cement works have had to stop, municipal power stations and gasworks are short of material and some large Swedish enameled-ware works have had to close down. In Denmark, Sweden and Norway, the telephone centrals are at their wits' end, being entirely unable to satisfy their new subscribers who have to wait for months before they can have their telephones installed. The makers are simply unable to get supplies of raw material. In Denmark the benzene supply is quite exhausted.—M.

JAVA CITRONELLA OIL

The exports of citronella oil from Java, says the *Oil and Color Trade Journal*, 51 (1917), 889, are now stated to have increased materially in 1915 over those in 1914 and a further increase was expected for 1916. The returns, so far available, show that the amount exported during the first six months of 1916 was 209,940 kilos, which, on an average of over 50 flasks (\$1.50) per kilo, will probably cause the year's export to exceed \$3,000,000. The exports have gone to France, Great Britain, Japan and the United States. Owing to the demand, the area of the grass plantations has risen to 2,500 hauses, and, in view of this increase in cultivation, it is probable there may be a fall in price of the oil. It is probable that Japan may take more, but the extra demand will not compensate for the falling off in other directions. Attempts to increase the Australian trade have not been very successful, as that country appears to be quite satisfied with Ceylon oil. —M.

ITALIAN OLIVE OIL PRODUCTION

According to the figures issued by the International Institute of Agriculture at Rome, the area of olive trees under cultivation in Italy in 1916 was 5,703,169 acres. This is only slightly less than the acreage of 1915 which was 5,704,158. The five years' average, 1909-1913, was 5,744,912 acres. The olive oil yield is estimated at 374,786,000 pounds in 1916 as against 300,401,802 in 1915 and 359,771,837 for the 1909-1913 average. The heavy rain and wind storms have injured the olive trees in some localities where the fruit has prematurely fallen.—M.

FRENCH BAUXITE

According to a report by the Secretary of the British Chamber of Commerce for the French Riviera, there exist rich deposits of bauxite in the territory behind the Riviera. Before the outbreak of war, these deposits were for the most part exploited by Germans and the yearly output is said to have amounted to 250,000 tons. A part of this was shipped direct to Germany, but most of it was transported by rail to Switzerland, where, it is understood, a German-owned plant had been erected for the extraction of aluminum by electrolysis. On the outbreak of war, the enemy mines were sequestered. In the neighborhood of the mines, sites are available for the erection of an electrolytic plant for refining the ore, and there exists an abundant water supply capable of providing the necessary power for such plant. In ordinary times, labor is plentiful and there is thus every facility for treating the ore on the spot. The ore could be delivered at Monaco, at which port wagons can be brought alongside the steamers at the quays.—M.

JAPANESE EXPORT TRADE

According to a report in the *Chemical Trade Journal*, 60 (1917), 158, the Japanese Government is evidently sincere in its efforts to develop and maintain the export trade of the country. It has been announced that the Department of Agriculture and Commerce is considering a measure for the improvement of the quality of the export goods with a view to retaining, at the close of hostilities, the oversea markets acquired by Japan during the war. Complaints, it is said, are too often heard of the poor quality of the goods Japan, at present, exports; so much so that it is generally feared that the trade, acquired during the war, may be eventually lost. The poor quality of certain Japanese goods is attributed to the backwardness of Japan's manufacturing and trading systems. It has been decided by the government to enforce thorough conditioning of all export goods and the particulars of a measure to be adopted are being considered. According to the official plan, the Association of Manufacturers, or their federations established in accordance with the law, will be empowered to condition all export goods on a compulsory system, and the government will exercise general supervision over the organization of conditioning houses and the actual management of business, at the same time giving bounties to these associations.—M.

ACETYLENE GENERATOR

An automatic acetylene generator, of which particulars are published by Messrs. Perkin and Co., Whitehall Road, Leeds, England, is provided with two generating chambers. Only one of these is in operation at any given time, but, when it is exhausted, the other is automatically brought into action. The first can then be recharged and set to come into operation without further attention when the carbide in the second has been used up, and the supply of gas is thus continuous. All the working parts are on the outside and, as the acetylene is automatically washed, scrubbed and cooled by the generator, purifiers are unnecessary. Carbide of any size, and not merely small pieces can be used for charging.—M.

NEW ELECTRIC FURNACE

Considerable numbers of a new electric furnace made by Messrs. T. H. Watson and Co., of Sheffield, are now at work in Great Britain, says the *Times Engineering Supplement* No. 509, 70. In it three-phase current is employed, and three single-phase transformers are connected with meshed primaries. The secondary windings are connected to an unequal star, from which two connections go to the top vertical electrodes of carbon, while the third is taken to the furnace hearth, which is made of a conducting mixture of dolomite and magnesia, and forms the third electrode. The proportions of the unequal star are so calculated as to give a balance on the primary supply phases when the upper electrodes are in equal adjustment. Thus, if one arc is broken, the others are not affected, and any current overload passing through any arc must traverse two transformers in series and in different phase thus giving a considerable buffer effect and tending towards the reduction of shock and the maintenance of a steady load. The electro-magnetic effects arising from the arrangement of the electrodes keep the bath of molten metal in continual circulation, the steel being thus uniformly heated and the intense heat of the arcs constantly absorbed. The hearth is always at least 20 in. thick and is not penetrated by water-cooled studs. These furnaces were originally designed to meet the requirements of the Sheffield steel industry, especially in connection with high-speed and high-grade alloy steels; one of them has already made over 950 heats of high-speed steel, and, though it was only designed to melt charges in three hours, it regularly turns out five charges in 12 hours. Its lining did not require renewal until after it had made 480 heats. Several standard sizes are made, rated at 10 cwt., 30 cwt., 3 tons and upwards. The electrical equipment for the 10 cwt. size has a capacity of 260 k. v. a., for the 30 cwt. of 520 k. v. a., and for the 3-ton of 800 k. v. a. For a 6-ton furnace 1,560 k. v. a. is provided, and it is furnished with four top electrodes, instead of two, as in the case of the smaller sizes.—M.

PETROLEUM PRODUCTION IN JAPAN

According to the annual report, the production of crude oil in Japan was 3,015,327 barrels in 1915, an increase of 272,807 barrels over the preceding year. The following figures show the production by districts in 1915 and 1914:

	1915	1914
Echigo	1,975,443 barrels	2,009,603 barrels
Akita	1,008,863 barrels	706,588 barrels
Fushu	2,098 barrels	2,455 barrels
Yamagata	451 barrels	428 barrels
Nagano	195 barrels	148 barrels
Hokkaido	9,287 barrels	5,987 barrels
Taiwan (Formosa)	18,970 barrels	17,314 barrels
Total	3,015,327 barrels	2,747,520 barrels

—M.

RENDERING COAL SOLUBLE BY OZONE

An interesting discovery, says *Engineering*, 103 (1917), 296, has been made by Dr. Franz Fischer, who has found that if ozone is brought in contact with coal in a glass tube at ordinary temperature, the surface of the coal undergoes a change in so far as it presents a fine brownish bloom which is soluble in water yielding a brownish liquid which is slightly acid. This discovery led to a test in which 9.6 g. of coal were exposed to the influence of ozone for 133 hrs., when only 0.7 g. of the original coal was left; hence 92 per cent was dissolved. The discoverer draws the conclusion from this that the principal component part of the coal is a transformed product of a former cellulose substance which can be rendered soluble by contact with ozone. To judge from the attributes of this new substance, it is assumed that the greater bulk is an acid which has been formed by the primary formation of ozonites which were subsequently decomposed by water. This test was made with Westphalian coal.

M

TRADE BETWEEN JAPAN AND SOUTH AFRICA

An extension of trade between Japan and South Africa appears, according to the *Times Trade Supplement*, likely to take place. Japan's purchasing power has increased during the war and several lines which can be supplied by South Africa with ease are in good demand in Japan. Some of these are asbestos, hides, aloes, wines, wattle bark and extract, and tobacco. The Japanese Consul in South Africa considers that there is a great future for export trade between the Union and Japan. An important new market will naturally supply a strong stimulus to production which it cannot be doubted will be capable of considerable extension after the war. Japan has already had dealings in some of the products of South Africa and the possibilities only need exploiting by properly organized methods. Japanese steamships have been attracted to South African ports in increasing numbers and there is every likelihood of Japanese shipowners interesting themselves in fostering trade between the two countries.—M.

TARPAULINS IN AUSTRALIA

A serious shortage of tarpaulins is reported in the Commonwealth of Australia—particularly Victoria—for covering grain when in transit on the railways. Not merely has it been found impossible to furnish coverings for the goods-trucks which have been added, but no renewals have been made to the stocks of tarpaulins which existed at the commencement of the war. The practice of the Railway Department has been to obtain the necessary canvas and itself complete the manufacture of the tarpaulins. Lately, however, supplies of any material at all suitable have been most difficult to obtain. Of a total quantity of 507,000 yds. of canvas which have been ordered by the Railway Department from different contractors since the outbreak of the war, only about 60,000 yds. had been delivered by the end of 1916. There seems little likelihood of any supplies of flax canvas becoming available yet for the purpose, but an inferior quality would be acceptable or, it is believed, any serviceable substitute which could be used to protect consignments of grain, bran and pollard.—M.

PETROLEUM PRODUCTION IN ARGENTINA

The production of petroleum in Argentina, which is monopolized by the Government, is now increasing very rapidly as will be seen from the returns of the last five years: 1911, 920 tons; 1912, 6,850 tons; 1913, 19,050 tons; 1914, 40,530 tons; 1915, 75,200 tons. The output for 1916 is provisionally estimated at 180,000 tons, which shows a large advance on last year. The director of the monopoly estimates that with an expenditure of three

million dollars in increasing the number of wells, a production of 480,000 tons could be secured in 1918 and of 900,000 tons in 1920. The Government has directed that the number of wells should be augmented upon the lines of this advice. The transport of petrol is effected by means of two tank steamers (capacity 4,000 tons) belonging to the government. Two other steamers are in course of construction.—M.

HIGH TENSILE vs. MILD STEEL FOR REINFORCED CONCRETE

In a paper read recently before the Society of Engineers in London, Mr. A. W. C. Shelf endeavored to show that, whereas it has been customary, at least in England, to use plain round mild steel bars for reinforced concrete, these are not the best for the purpose, but that greater efficiency and economy are obtained by physically developing mild steel bars in order to take out the first yield in the steel which is useless and has a detrimental effect on the concrete. When this first yield or stretch is taken out, a higher yield-point is obtained without any injury to the steel, so that it is safer to employ a stress of 20,000 lbs. per sq. in. (which results in a saving of 20 per cent in the weight of steel required) than it was to employ a stress of 16,000 lbs. per sq. in. before the steel was physically developed and, for this reason, the author of the paper is of the opinion that the existing regulation of the London County Council relating to the stress on steel should be altered to avoid the cramping of industrial progress.—M.

WATER-POWER IN NORWAY

According to a report in a contemporary, a special committee of the Norwegian Storting has recommended that concessions for the acquisition of waterfalls shall not be granted to foreigners or foreign companies except in very special cases as when, for instance, a going concern is desirous of obtaining possession of or regulating a waterfall. For Norwegian citizens, a concession is to be necessary in cases of waterfalls capable of yielding more than 5,000 natural h. p. The capital of companies or syndicates wishing to secure such concessions must be exclusively Norwegian and they must be domiciled in Norway and have an entirely Norwegian board of directors. The duration of the concessions is to be limited to 60 years. The state is to be entitled to secure the waterfall at latest in the 40th year after granting the concession; its option of purchase applies to waterfalls above 5,000 h. p., while, for smaller ones, the option rests with the corporation or municipality. The amount of power to be ceded to the state and municipalities by the possessor of a concession is to be 5 per cent.—M.

SCIENTIFIC SOCIETIES

CALENDAR OF MEETINGS

American Leather Chemists' Association: Fourteenth Annual Meeting, Atlantic City, N. J., June 7 to 9, 1917.

North Carolina Cottonseed Crushers' Association: Annual Convention, Norfolk, Va., June 19 to 20, 1917.

American Institute of Chemical Engineers: Ninth Semi-Annual Meeting, Buffalo, N. Y., June 20 to 22, 1917.

First Industrial Exposition and Export Conference, Springfield, Mass., June 23 to 30, 1917.

American Society for Testing Materials: Atlantic City, N. J., June 26 to 30, 1917.

American Chemical Society: Annual Meeting, Boston, Mass., September 10 to 16, 1917.

National Exposition of Chemical Industries: Third Grand Central Palace, New York City, September 24 to 30, 1917.

ANALYSIS OF SPELTER¹

Supplementary Note from the
Committee on Analysis of Non-Ferrous Alloys
Division of Industrial Chemists and Chemical Engineers

As a result of recent investigation it seems advisable to amend the report on "Spelter Analysis" [THIS JOURNAL, 7 (1915), 547] by inserting the following as a footnote after the second line, under the method for cadmium on p. 548.

"It is recommended that the acid be added slowly (4 or 5 drops at a time), it added rapidly on 10 cc. acid standing over night may be an insufficient time for the acid to dissolve the proper amount of zinc and small amounts of cadmium may remain in solution."

Wm. E. Fiske

Chairman, Committee on

Analysis of Non-Ferrous Alloys

¹ Approved by the Association of Industrial Chemists and Chemical Engineers, American Association of Economic Chemists.

DIVISION OF INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS—MINUTES OF BUSINESS SESSION 54TH MEETING AMERICAN CHEMICAL SOCIETY

The meeting was called to order with Chairman Dr. H. E. Howe presiding.

The minutes of the meeting at New York City were read by the Secretary and approved by the Division.

The Secretary reported on the financial condition of the Division as follows:

Cash on hand, September 25, 1916.....	\$ 19.47
Receipts in response to a request for funds.....	188.00
	\$207.47
Expenditure.....	30.00
Cash on hand, April 1, 1917.....	\$177.47

The Secretary also reported that the entire roll of members had been carefully gone over, all addresses being brought up to date and the names of members who have ceased to be members of the General Society dropped out. It was moved and seconded that the report be accepted.

The Committee on Soap and Soap Products presented a report of their work. This was turned over to the Supervisory Committee on Standard Methods of Analysis, Dr. Hillebrand, Chairman, and went to the Council direct.

After some discussion of the Committee situation it was unanimously decided to abolish the Divisional Committee on Standard Specifications and Methods of Analysis. Upon the suggestion of Dr. Hillebrand, Chairman of the Committee on Platinum, that this Committee be not reappointed because there seems to be no occasion for renewed work on the quality of platinum at the present time, it was moved and seconded that the Committee be not reappointed. Motion carried.

There being no further business to come before the Division the reading of the papers was proceeded with.

SAMUEL H. SALISBURY, JR.,

ATLAS PORTLAND CEMENT COMPANY
NORTHAMPTON, PA.

Secretary

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS NINTH SEMI-ANNUAL MEETING

The Ninth Semi-Annual Meeting of the American Institute of Chemical Engineers will be held at Buffalo, New York, June 20 to 22, 1917.

PROGRAM OF PAPERS

Address of Welcome. DAVID C. HOWARD, 1st Vice President Buffalo Chamber of Commerce.

Some Machinery Employed in the Manufacture of Glue. A. LOWENSTEIN.
Treatment of Sewage by Aeration in the Presence of Activated Sludge. III. EDWARD BARROW.

The Manufacture of Linseed Oil. GLENN H. PICKARD.

Trade Wastes Disposal. II. P. EDDY.

Chemical Engineering Aspect of Renovating a Sulfide Mill. H. K. MOORE.
Waste Heat Utilization. H. D. BAYLOR.

Symposium on Potash

The Possibilities of Developing an American Potash Industry. R. K. MERRILL.

A New Method of Potash Recovery from Feldspar. J. C. W. FRAZER AND E. MERRILL.

Potash from Waste Liquor of Beet Sugar Factories. H. E. ZITKOWSKI.

Joint subscription dinner of the Buffalo Engineering Society and the American Institute of Chemical Engineers. Addresses by F. A. Lidbury, President of the Buffalo Engineering Society, and President G. W. Thompson.

EXCURSIONS

Automobile trip around the city and inspection of the Buffalo Foundry and Machine Company Plant. A day at the Buffalo Canoe Club. Automobile ride to Niagara Falls. Car-ride around the great scenic gorge route.

AMERICAN LEATHER CHEMISTS' ASSOCIATION FOURTEENTH ANNUAL MEETING

The Fourteenth Annual Meeting of the American Leather Chemists' Association will be held at Atlantic City, June 7, 8 and 9, 1917, with headquarters at the Marlborough-Blenheim Hotel.

PROGRAM OF PAPERS

Anthrax and Disinfection of Hides. V. A. WALLIN.

The Future of Hide Supply (by Title). A. SEYMOUR-JONES.

Discussion. DR. HICKMAN of the Bureau of Animal Industry.

Comparative Analysis. R. H. WISDOM.

The Testing of Dyes for Leather. G. T. CREESE.

Solubility of Hide in Salt (NaCl) Solution and Effect of Alkali on

Soaking Dry Hides. L. BALDERSTON.

Nigrosines. J. MERRITT MATHEWS.

Analysis of Sulfonated Oils. W. K. ALSOP.

Effect of Hard Water on Tannins. T. A. FAUST.

Sulfuric Acid in Leather. C. R. OBERFELL.

Specifications for Kaolin Used in Tannin Analysis. R. W. FREY.

Analysis of Tannery Effluent. W. A. FOX.

Studies Conducted by the Public Health Service in Regard to the Sanitary Disposal of Tannery Wastes. H. B. HOMMON.

(The Public Health Service built an experimental disposal plant at an important tannery where these studies were conducted.)

Chemistry of the Manufacture of Tanning Extracts from Waste Sulfite-

Cellulose Liquors. H. H. HURT.

Drum Tannage. OSKAR REITHOF.

Borax and Boric Acid in the Tannery and Currying Shop. H. L. HARRIS.

Symposium on Anthrax

Anthrax. A. S. ROSS.

Practice and Theory on Treatment and Diagnosis of Anthrax. H. Z. FRISBIE.

The Nature of Anthrax and Anti-Anthrax Serum. J. REICHEL.

Discussions

Tanners and Chemists "Round Table" Discussion.

Discussion of Recently Advanced Ideas on Theory of Leather Formation.

JOHN ARTHUR WILSON, LLOYD BALDERSTON, WILLIAM KLABER,

H. C. REED, F. H. SMALL, ALLEN ROGERS, JOHN H. YOCUM,

ROBERT W. GRIFFITH.

PLATINUM IN JEWELRY

The members of the American Chemical Society will be very glad to learn that the Platinum Committee of the Jewelers Vigilance Committee has passed resolutions, which were presented to the Secretary of Commerce, in which they have shown a very proper attitude in recommending to the jewelry trade that the use of platinum in bulky and heavy pieces of jewelry be discouraged, and that jewelers also discourage the use of platinum in all non-essential parts of jewelry, such as scarfpin stems, pin tongues, joints, catches, swivels, spring rings, ear backs, etc., where gold would satisfactorily serve. Considering the fact that platinum is essential for the production of many of the munitions of war and that it is absolutely necessary for the development of our chemical industry and for the development of chemical knowledge, this action of the jewelers is to be highly commended and will be a great help toward discouraging the unnecessary use of platinum and result in a drop in its price and an increase in the stock supply available for the use of the government and our commercial laboratories. The jewelers should be credited with helpful motives, for they will undoubtedly yield up important profits by declining to encourage the desire for personal adornment and ostentatious display of wealth, which is the chief reason for the use of platinum in such articles as watch-cases, solid platinum rings, bracelets, mesh-bags, etc.

It is expected that these resolutions, added to those passed by the Daughters of the American Revolution, by the National Academy of Sciences, and by the American Chemical Society will help to overcome the abuse of platinum.

The needs of the government itself for platinum will undoubtedly be met during the present war without great sacrifice.

While the government itself uses comparatively little platinum, our sulfuric acid industry, especially for the strong acid used in the production of high explosives, is dependent upon it, and its high price makes it almost prohibitive for scientific research. No American man or woman will wish to feel that by wearing platinum they are interfering with the development of the country's industries and scientific standing, but such is inevitably the case.

CHAS. L. PARSONS, *Secretary*

The resolutions passed by the Platinum Committee of the Jewelers Vigilance Committee are as printed below:

RESOLUTIONS

WHEREAS, the Secretary of Commerce has requested the Platinum Committee of the Jewelers Vigilance Committee to bring to the attention of the jewelry trade of the United States the advisability of conserving platinum in order that our government may have larger supplies to draw upon for war purposes, and

WHEREAS, the jewelry trade has already clearly expressed its desire and determination to assist our government to the

extent of its ability in bringing the war to a successful termination,

Be It Resolved that we pledge ourselves to discontinue and strongly recommend to all manufacturing and retail jewelers of the United States that they in a truly patriotic spirit discourage the manufacture, sale and use of platinum in all bulky and heavy pieces of jewelry.

Be It Further Resolved that during the period of the war or until the present supplies of platinum shall be materially augmented, we pledge ourselves to discontinue and recommend that the jewelry trade discourage the use of all non-essential platinum findings or parts of jewelry, such as scarfpin stems, pin tongues, joints, catches, swivels, spring rings, ear backs, etc., where gold would satisfactorily serve.

Be It Further Resolved that the jewelry trade encourage by all means in their power, the use of gold in combination with platinum, wherever proper artistic results may be obtained.

Be It Further Resolved that copies of these resolutions be handed to the Secretary of Commerce, to the trade press, and be sent to all our trade organizations, and to the daily press, in order that they may have the widest possible dissemination.

NOTES AND CORRESPONDENCE

SPONTANEOUS COMBUSTION OF OLEIC ACID CONTAINING IRON

Editor of the Journal of Industrial and Engineering Chemistry:

A recent case engaging the attention of this laboratory was concerned with spontaneous combustion of oleic acid when applied to wool. The circumstances of the occurrence have enough of general interest to warrant publication.

The wool or other hair fibers were first oiled with 10 per cent of their weight of oleic acid, after which the oiled fiber was conveyed to bins through a tinned iron pipe by a current of air. The conveying pipes were very near a bank of heating pipes, the latter being employed to heat the mill.

This, of course, was bad practice, but the investigation was continued by an analysis of the oil employed. The iodine value was normal for commercial oleic acid, and the other constants showed nothing of a suspicious nature.

Samples of the various fibers employed—wool, mohair and the like—were then oiled with the oleic acid, and tested in Mackey's Cloth Oil Tester, as described in Vol. II, Allen's "Commercial Organic Analysis." The rise in temperature against time was normal, but the fact was disclosed that the finer fibers gave the greater rise. This fact we ascribed to more surface for oxidation being exposed for equal weights of fiber with similar weights of oil.

If the investigation had ended here, we should not have discovered the true inwardness of the case, but we were sufficiently interested to follow up the clue of more rapid oxidation the finer the fiber to which the oil was applied. To test this point, we next used cotton, and found a rapid and dangerous rise. This should not have been the case, if the oil were suitable. We checked the apparatus, using technically pure oleic acid of pharmaceutical grade, and got no dangerous rise. Thus, it was obvious that something about the oleic acid was wrong, notwithstanding the correct constants. Briefly, we found it to contain iron equivalent to 0.20 per cent ferric oxide.

We next made an oleate of iron, and dissolved it in the pure oleic acid, so that it contained the same amount of iron as the commercial sample. When the oil was applied to cotton, we found that it gave the same dangerous rise in the Mackey Tester as the commercial sample. Here, then, was an adequate explanation of the matter. The small amount of iron had functioned as a catalyst to promote oxidation.

Since this work was done, we have tested samples of oleic acid

from other sources, and have found in them amounts of iron of the same order of magnitude. Experiments have shown that the dangerous rise applies to these also.

We tried to remove the iron by shaking the oils with diluted hydrochloric acid, but without success. To do this successfully would probably necessitate getting the oil and acid in very fine emulsion.

CHARLES E. SWETT AND WALTER S. HUGHES

LABORATORY OF ARTHUR D. LITTLE, INC.
APRIL 28, 1917, BOSTON, MASS.

THE INCOMPLETE HYDROGENATION OF COTTON-SEED OIL—CORRECTION

Referring to the article under the above title (THIS JOURNAL, 9 (1917), 451) the following corrections should be made:

P. 451, Foot-note 1: second reference in third line should be dated 1906 instead of 1916.

P. 456, Table II: amount catalyzer in Run F was 2 per cent instead of 4 per cent.

P. 458, Table IV: iodine number of Sample 2, Run 1h, should read 83.6 instead of 83.1. Iodine number of Sample 6, Run 1i, should read 54.6 instead of 5.46.

Catalyzer referred to in Tables II and IV as "No. 1" should be understood to represent the type of catalyzer referred to in paragraph "2" of the section on "Catalyzers," rather than as one batch of material. Several batches of differing degrees of activity, are represented by it. The catalyzer referred to in the tables as "No. 2" is described in paragraph "1" of the section on "Catalyzers."

H. K. MOORE, C. A. RICHTER AND W. F. VAN ALSTINE

THE MANUFACTURE OF LINOLEUM AND ITS VALUATION—CORRECTION

In the article under above title, printed in THIS JOURNAL, 9 (1917), 6, the following corrections should be made:

Page 6, column 1, 2nd line, under "Process" (1st sentence): By 1 per cent increase, 2400 to the next round, 2400. By 1 per cent increase, 2400 to the next round, 2400.

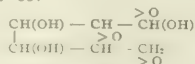
Page 6, column 1, 3rd line, under "Process" (1st sentence): "poison the soil" should read "poison the soil."

ARTHUR D. LITTLE

THE CHEMISTRY OF WOOD—CORRECTION

In the articles appearing under the above title in this issue, pp. 556 to 566, the following corrections should be made:

The formula on p. 557 should be:



On p. 560, 1st column, line 8 of text, $N/100$ should read $N/10$; same column, line 25, iodate should read iodide. Same page, Table I, "Hot Water" column, 4.87 should read 4.78.

On p. 561, Table II, last column, 4.23 should read 5.23.

The following foot-notes are to be inserted:

After 2nd paragraph, 2nd column, p, 562:

The excellent results obtained by Dox and Plaisance [*J. Am. Chem. Soc.*, **38** (1916), 2156] with thiobarbituric acid for determining furfural are

unfortunately not easily applicable to the concomitant determination of methylnifural

After 24 to 28 per cent, line 18, 1st column, p. 563:

In Technologic Paper No. 88, of the Bureau of Standards, "Studies on Paper Pulps," p. 9, the conclusion is drawn that alkaline processes of cooking pulp do not remove the furfural yielding complex to the same degree as the acid-sulfite process. Since as a rule only hardwoods are cooked by the soda process the resulting pulps would be expected to yield more furfural from the data given above.

On p. 565, last paragraph, the asterisks should be removed.

A. W. SCHORGER

FULLER'S EARTH, ETC.—CORRECTION

In my article in this issue, p. 599, the dotted line for "White Oil" (20 Yellow, 2.5 Red) has been omitted in re-making the drawing, so that the sentence referring to same should be omitted.

T. G. RICHERT

T. G. RICHERT

PERSONAL NOTES

The Council of National Defense announces the appointment of a sub-committee on chemicals, to serve under the committee on raw materials of the advisory commission, of which Bernard M. Baruch is chairman. Dr. William H. Nichols, of the General Chemical Co., of New York, is *chairman* of the new sub-division. Besides Dr. Nichols, the sub-committee is composed as follows:

Acids—E. R. Grasselli, of the Grasselli Chemical Co., Cleveland; Henry Howard, Merrimac Chemical Co., Boston.

Fertilizers—Horace Bowker, New York; Chas. E. MacDowell, President Armour Fertilizer Co., Chicago.

Alkalies—J. D. Pennock, Solvay Process Co., Syracuse.

Miscellaneous Chemicals—E. Mallinckrodt, Jr., St. Louis.

Professor Marston T. Bogert, Chairman of the Chemistry Committee of the National Research Council, has moved his office to Room 332, Munsey Building, Washington, D. C.

The Franklin Institute, acting through its Committee on Science and the Arts, has recently made the following medal awards, for especially meritorious papers published in its Journal for the year 1916: The Howard N. Potts Medal to Professor Ulric Dahlgren, professor of biology, Princeton University; Edward Longstreth Medals of Merit to Mr. George A. Rankin, late of the Geophysical Laboratory, Carnegie Institution of Washington; Prof. A. E. Kennelly, Messrs. F. H. Achard and A. S. Dana, Massachusetts Institute of Technology; Mr. John D. Ball, late of the General Electric Company, Schenectady, N. Y.; and Dayton C. Miller, Professor of Physics, Case School of Applied Science.

A number of platinum crucibles were taken from the laboratories of the Agricultural Experiment Station of the Rhode Island State College, Kingston, R. I., just prior to May 7th.

The following resolution was adopted by the Georgia Section of the A. C. S. through mail ballot: "*Resolved*: That the Georgia Section of the American Chemical Society, composed of experienced industrial, agricultural and research chemists, feeling that their services and laboratories can assist in preventing waste and promoting industrial efficiency, offer their services to the Government, individually and collectively."

Prof. J. H. Buchanan, of the food and sanitary chemistry department of the Iowa State College, and his assistant, J. W. Hawkes, were appointed to the Officers' Reserve Corps Camp at Fort Snelling and are at present in attendance.

Mr. W. P. Putnam, of The Detroit Testing Laboratory, Detroit, Michigan, has been elected President of the Detroit Engineering Society for 1917-18. The Detroit Engineering Society includes engineers of all branches of engineering, and numbers over 750 members of the leading men of the community in engineering work.

Prof. A. W. Smith, professor of industrial chemistry and head of the department of chemistry, at Case School of Applied Science, Cleveland, Ohio, was chosen by the Ohio State University as Exchange Lecturer during the week of April 16th to 21st. Dr. Smith lectured each day on chemical engineering topics. The College of Engineering at the Ohio State University made similar arrangements with other institutions, notably Purdue University and the University of Michigan, the lectures from those institutions being electrical and civil engineering. The arrangement is reciprocal.

Dr. H. P. Talbot (*Chairman*), Prof. M. T. Bogert and Dr. W. D. Richardson have been appointed by President Stieglitz as a Committee to consider the proposal of Dr. Bernhard C. Hesse for a Board of Control of National Policies. Dr. Hesse presents his plans in full in the April, 1917, issue of **THIS JOURNAL**, page 337.

Professors A. B. Lamb and G. B. Frankforter have been added to the Code of Professional Ethics Committee of the American Chemical Society.

During the past winter, the Wagner Free Institute of Science of Philadelphia has been giving, under the Richard B. Westbrook Foundation, which the Institute administers, special lectures by the members of its faculty. The Chemistry lectures were: "Food from the Air," by Henry Leffmann; "Chemistry of Bread-Making," by Chas. H. La Wall; "Catalysis in the Inorganic Field," by David W. Horn. The lectures will be published.

The Publicity Committee of the Philadelphia Section has elected Dr. Henry Leffmann as Chairman and has begun work. It includes representatives of all the important phases of applied chemistry.

On May 4th, McGill University conferred the degree of LL.D. on Dr. W. H. Ellis of the University of Toronto. Dr. Ellis is a past-chairman of the Division of Industrial Chemistry and Chemical Engineers.

President Stieglitz has appointed Dr. W. F. Hillebrand (*Chairman*), Dr. W. D. Bigelow and Dr. Charles Baskerville as an Advisory Committee to the Bureau of Standards on Analyzed Reagents in pursuance of a resolution passed by the Council at the Kansas City meeting.

Dr. Isaac F. Harris, formerly director of the Lederle Antitoxin Laboratories of New York and later director of the Arlington Research Laboratories of Yonkers, New York, has moved from Bronxville, N. Y., to New Brunswick, N. J., where he is head of the department of biochemistry in the research and biological laboratories of E. R. Squibb & Sons.

Mr. R. T. Will has resigned his position as general superintendent and chemical engineer of the General Coal Products Company of Pittsburgh, Pa., to establish offices and laboratories at Rochester, N. Y., for general testing and consultation in industrial and chemical engineering, under the name of "The Will Corporation." The new laboratories are located at 262 East Avenue.

The John Fritz Medal for 1917 was awarded to Dr. Henry Marion Howe for his investigation in the metallurgy of iron and steel. The presentation ceremonies took place on the evening of May 10th in the Auditorium of the United Engineering Building, 29 West Thirty-ninth Street, New York. Addresses were delivered by Dr. Rossiter W. Raymond, Dr. Ira N. Hollis, Judge Elbert H. Gary and Prof. Albert Sauveur.

The United States Civil Service Commission announces the following open competitive examinations: *Laboratory aid and junior chemist*, for men only, Naval Proving Ground, Indian Head, Md., salaries at \$3.28, \$3.84, \$4.48 and \$5.04 per diem. *Assistant chemist*, for men only, Picatinny Arsenal, Dover, N. J., salary \$1350 to \$1500 a year. Applications for the above positions should be filed at the earliest possible date. They will be rated immediately upon their receipt and appointments made immediately. *Junior chemist (qualified in fuels)*, for men only, Bureau of Mines, on June 6, 1917, salary \$1020 a year. *Assistant analytical chemist and mineralogist*, men only, salary \$1800 to \$2400 a year, on June 19, 1917; *Associate analytical chemist*, men only, salary \$2500 a year, on June 19; *Assistant chemical engineer (petroleum)*, men only, salary \$1800 to \$2100 a year on June 12; *Junior chemist*, men and women, salary \$1200 to \$1440 a year. Until further notice, applications for the last-named position will be received at any time. Papers will be rated immediately upon their receipt by the Commission in order that appointments may be made promptly.

Dr. Charles H. Herty addressed the National Association of Printing Ink Manufacturers during their recent Annual Convention at Delmonico's on the evening of May 7th. The subject of his address was "How the Spirit of Cooperation Can Help the American Color Industry."

On March 9, 1917, Dr. William Louis Jeffries died at Wilmington, Vermont, as a result of poisoning by hydrogen sulfide, while demonstrating the use of niter cake in sulfate pulp manufacture. Dr. Jeffries was educated first at Carson-Newman College, then at the University of North Carolina. From the latter institution he received the degrees A.B. and Ph.D., serving two years as instructor in chemistry. Since November 1915, he had been connected with the by-products division of the du Pont de Nemours Co., Wilmington, Delaware, in which capacity he had been very successful in finding new uses for niter cake. Dr. Jeffries was an enthusiastic member of the Alpha Chi Sigma fraternity and was actively engaged just previous to his death in bringing that organization of young chemists to offer the services of its members to the government in whatever capacity they might be used.

Dr. Wm. H. Taylor, who for 46 years was professor of chemistry in the Medical College of Virginia, and coroner of the City of Richmond, died on April 14th, at his home in Richmond. Dr. J. M. Whitfield, for several years city chemist of Richmond, has been made city coroner to succeed Dr. Taylor.

The University of Illinois Engineering Experiment Station has just completed a preliminary systematic study of the alloys of chromium, copper and nickel, and their properties. The work has been under the direction of Dr. D. F. McFarland, Assistant Professor of Applied Chemistry, and Dr. O. L. Harder, Fellow in Chemistry. Copies of Bulletin No. 93, containing the results of these tests, may be obtained without charge by writing C. P. Richards, Director of the Engineering Experiment Station, Urbana, Illinois.

Dr. L. F. Nickell of the department of chemistry, Washington University, St. Louis, has resigned to accept a position with the Monsanto Chemical Company of St. Louis in their research department.

Dr. E. C. L. Miller, who has been in California for the past year, is returning to the Medical College of Virginia where he resumes his duties as professor of physiological chemistry.

The Municipal Civil Service Commission of the City of New York announces the following opening competitive examination: Assistant Inspector of Combustibles, Grade 2 (Inspector of Combustibles), salary \$1200 to \$1500 a year. Applications will be received up to June 4th.

Mr. G. A. Burrell, consulting chemical engineer of Pittsburgh, and for eight years in charge of gas investigations of the Bureau of Mines, has been selected by Mr. Van H. Manning, Director of the Bureau of Mines, to take charge of research work on matters pertaining to gas warfare.

Dr. H. N. McCoy, who has been connected with the department of chemistry of the University of Chicago since 1901 and professor since 1911, has tendered his resignation in order to be free to devote more time to his important technical interests. His process of extracting radium from carnotite is being used by the Carnotite Production Company of Chicago in which he is a director.

At the Chemists' Club on Wednesday evening, April 25th, the Chemical Engineering Society of Columbia University held a dinner, at which former Professors M. C. Whitaker and F. J. Metzger were the guests of honor. The Society presented to each of them a silver desk clock, as a token of appreciation and gratitude for their work in building up the School of Chemical Engineering at Columbia, of which Prof. Whitaker was the head, before he recently resigned.

Mr. M. Landau, president of the Society, introduced Dr. C. F. Chandler, dean of the chemical profession, who acted as toastmaster. Dr. Whitaker, discussing the "Industrial Situation," told about the problems which manufacturers must meet, due to the activity of enemy agents. Dr. Metzger gave a short talk on "Chemical Engineering." Mr. A. F. Smithers, one of the graduating students, talked about "what Columbia has done for us." Mr. A. A. Haldenstein, also a Senior, spoke on "Our Responsibilities to Our Alma Mater."

Prof. D. D. Jackson, acting head of the School of Chemical Engineering, discussed "Preparedness for the Chemical Engineer." Dr. J. Teeple, gave the diners some excellent advice, when he responded to the toast, "Things to Remember." Prof. M. T. Bogert, Chairman National Research Council, spoke on "The Chemist in the Present Crisis." Professors Tucker and Neish both said a few words in appreciation of the work of Doctors Whitaker and Metzger.

Much credit is due the dinner committee, of which Mr. E. C. Brueckmann was chairman, for making the affair such a signal success.

Science reports that six professors of the University of Minnesota have been asked by the war department to act as a scientific research board for the district of the State of Minnesota. The duties asked of them will require a considerable portion of their time from now on. These men are Professor John I. Plattner, head of the department of research and instruction; Dean George R. Frankforter of the school of agriculture; Dr. J. G. Fowntine, head of the department of agriculture; Professor R. W. Fletcher, head of the department of agricultural chemistry; J. W. McKeehan of the department of physics; and F. A. McMillan, of the department of mechanical engineering. Dean Frankforter and Professor Fletcher acted upon a special jury board which made an inventory of Minnesota's resources last summer, and the system which they proposed at that time will be of incalculable value in the present crisis.

Dr. T. Brailsford Robertson, professor of biochemistry and pharmacology in the University of California, has donated to the Regents of the University of California his patents for the growth-controlling substance "Tethelin," which he has succeeded in isolating from the anterior lobe of the pituitary body and which has been employed to accelerate repair in slowly-healing wounds. The proceeds which may accrue from the sale or lease of these patents are to constitute a fund which will be entitled "The University of California Foundation for International Medical Research" and which will be expended in the furtherance of medical research, preferably research in the physiology, chemistry, and pathology of growth.

Dr. Wm. C. Carnell has resigned the position of Chemical Director of Harrison Brothers & Co., Inc., Philadelphia, to accept a similar position with the firm of Charles Lennig, Inc., Philadelphia, manufacturers of heavy chemicals.

Dr. E. P. Wightman, who has been acting professor of chemistry at Richmond College, session 1916-17, has accepted a position with the research department of Parke, Davis & Co., and will assume the duties of his new position June 1st.

At the request of the National Research Council, the faculty of Wesleyan University have appointed the following local committee, consisting of one representative of each of the scientific departments of the institution with the president, William Arnold Shanklin, *ex-officio*: Professors Walter G. Cady, physics, *Chairman*; William North Rice, geology; Raymond Dodge, psychology; Frederick Slocum, astronomy; Leroy A. Howland, mathematics; Moses L. Crossley, chemistry.

John Faxan Passamore died on March 9th at Wilmington, Delaware, after an illness of six weeks. He obtained his degree in Mechanical Engineering at Cornell University in June 1914. He was Assistant General Superintendent of Joseph Bancroft and Sons Co., Wilmington, Delaware, at the time of his death. Although only 25 years old, he was honored with the Presidency of the Departmental Association of the company, filling the position with marked ability for one of his years.

The New York University is planning the erection of a new chemistry building.

Mr. George D. Rosengarten has returned to Philadelphia very much improved in health.

INDUSTRIAL NOTES

Work has been begun on the erection of a large still-house on the property of the Benzol Products Company at Marcus Hook. It is expected that the building will be completed within six months. The Benzol Products Company, which manufactures coal-tar intermediates, is owned jointly by Semet-Solvay, Barrett and General Chemical interests, and is a constituent in the new National Aniline and Chemical Company, Inc.

The National Aniline and Chemical Company will remove its offices some time in June from 100 William Street, to a new building now being completed at 244 Madison Avenue.

In the West, the waters of various lakes besides Searles Lake are receiving considerable attention, and special mention should be made of Owens Lake, where three companies are now in the field. The last one entering is the California Alkali Company, now building its plant. The lake waters contain soda ash, sodium chloride, some borax, and some potash. The California Alkali Company is closely associated with the Great Western Electrochemical Company, and the salt obtained in the production of the various products will be shipped direct to the Pittsburg, Cal., plant of the Great Western Electrochemical Company and used there for the manufacture of caustic soda and chlorine products.

A fire which caused \$20,000 damage is reported to have occurred recently at the plant of the Albany Chemical Company, on Van Rensselaer Island.

The United Chemical and Organic Products Company has been chartered to manufacture glues, gelatine, etc., under the laws of Delaware, with capital of \$2,002,700.

The Manufacturers' Association of St. Louis has voted to protest against the proposed tax of 25 cents a gallon on denatured alcohol.

According to a report from Syracuse the Solvay Process Company is about ready to begin the production of potash at its new plant in Solduro, Utah, which is practically ready for operation.

Eimer & Amend are planning alterations and additions, costing \$100,000, to their buildings at Third Avenue and East 18th Street, New York City.

The Kalbfleisch Corporation, recently organized, has taken over all the interests of the Franklin H. Kalbfleisch Company,

Erie Chemical Works, the Kalbfleisch Corporation, and the Kaloid Company. The new corporation will thus own five plants, one each at Brooklyn, N. Y., Waterbury, Conn., Elizabethport, N. J., Erie, Pa., and Chattanooga, Tenn. The Brooklyn, Waterbury and Elizabethport plants turn out a line of acids and heavy chemicals. The Erie and Chattanooga works (the latter having been recently completed) manufacture the different grades of sulfate of alumina and alum.

The officers of the corporation are: Franklin H. Kalbfleisch, Chairman of the Board of Directors; Robert S. Perry, President; Alfred B. Savage, Vice-President-Treasurer; Richard Sheldrick, Secretary. The directors are the same with the addition of Harry L. Derby. Mr. Perry was formerly president of Harrison Bros. & Co., Inc., Philadelphia.

The Gold Leaf Natural Dye Company, of Manhattan, dyes, chemicals, etc., has been incorporated under the laws of New York with a capital stock of \$500,000. Incorporators: G. H. Bruce, R. L. L. Warner, H. Campbell, No. 150 Nassau Street.

The Brunswick Manufacturing Company, dyes and chemicals, has been incorporated under the laws of New Jersey with a capital stock of \$30,000. Incorporators: George R. Morrison, J. H. Helm, Horace E. Barwis, New Brunswick.

The Active Chemical Company, of Camden, has been incorporated under the laws of New Jersey, with a capital stock of \$150,000. Incorporators: E. C. L. Kressel, R. P. S. Miller, T. Harry Rowland, Camden.

The Bristol-Myers Company, of Brooklyn, has completed plans for additions to its chemical factory at Hillside, N. J., costing \$25,000.

The amount of capital stock in new dye companies, according to years during the war, including only companies of more than \$50,000 capital stock, has been as follows:

Year 1915	\$ 65,565,000
Year 1916	99,774,000
Four months 1917	24,398,000
Total	\$189,737,000

The Braeher Air Conditioning Corporation announce the opening of a branch office, with Mr. G. P. Upington in charge as District Manager, at 90 West Street, New York City.

GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

HYGIENIC LABORATORY

Changes in the Pharmacopoeia and the National Formulary. MARTIN I. WILBERT. Bulletin 107, 288 pp. Paper, 30 cents. This is a digest of the changes and requirements included in The Pharmacopoeia of the United States (ninth decennial revision) and in The National Formulary (fourth edition) with references to the titles not continued from the preceding editions.

"Because of the fact that The Pharmacopoeia and The National Formulary are in reality separate and distinct publications, it was thought that a comprehensive index of the articles described in recent editions of these two books would be of value to public health officials and to all who are in any way interested in the official standards and requirements for drugs and medicines. To provide a readily available means for determining the present status of any official or recently official article an alphabetical list of the titles included in the U. S. P. VIII, the U. S. P. IX, the N. F. III, and the N. F. IV, has been compiled with an outline of the changes and requirements that have been embodied in the revised editions of the U. S. P. and the N. F.

"In the compilation, the changes in strength and composition are indicated as concisely as practicable, and special attention is directed to changes in nomenclature of official articles as well as additions to and deletions from the list of articles included in the several books.

"The object in mind was to make this publication a practical companion and convenient reference book on the present status of any of the many articles included in either of the four books referred to.

"As noted above, this bulletin is designed to serve as an index to the several recent editions of the official standards and can in no sense be considered to take the place of either of these books. For detailed information regarding the composition, strength, tests, and other requirements in connection with the several official articles, readers are referred to The Pharmacopoeia and The National Formulary."

Pituitary Standardization. The Relative Value of Infundibular Extracts Made from Different Species of Mammals and a Comparison of Their Physiological Activity with That of Certain Commercial Preparations. GEORGE B. ROTH. Bulletin 109, I, 32 pp.

Pharmacological Studies with Cocaine and Novocaine. A Comparative Investigation of These Substances in Intact Animals and on Isolated Organs. GEORGE B. ROTH. Bulletin 109, II, 31 pp.

BUREAU OF THE CENSUS

Report on Cottonseed and Cottonseed Products. Post card announcement dated 10:00 A.M., April 24, gives the following figures:

	Shipped out Aug. 1 to Mar. 31	On Hand March 31
Crude oil (pounds).....	1,084,946,283	144,122,366(g)
Refined oil (pounds).....		320,930,168(b)
Cake and meal (tons).....	1,820,172	246,442
Hulls (tons).....	769,021	133,774
Linters (500-pound bales).....	999,430	136,907(c)
Hull fiber (500-pound bales).....	325,976	11,357(c)
Motes, grabbats, and sweepings (500-pound bales).....	18,196	11,485(c)
(a) Includes 4,438,521 and 7,423,786 pounds held by refining and manufacturing establishments on March 31, and 32,666,372 lbs. in transit to refiners and consumers.		
(b) Includes 10,567,250 pounds held by refiners, brokers, agents, and warehousemen at places other than refineries and manufacturing establishments and 8,477,746 lbs. in transit to manufacturers of lard substitute, oleomargarine, soap, etc., March 31.		
(c) Includes 11,995 bales of linters, 714 bales of hull fiber, and 110 bales of motes, grabbats, and sweepings stored elsewhere than at the mills.		

IMPORTS AND EXPORTS OF COTTONSEED PRODUCTS FROM AUGUST 1 TO MARCH 31

Imports: Oil (pounds).....	6,112,022
Exports:	
Oil (pounds).....	96,480,617
Cake and meal (tons).....	462,463
Linters—Unbleached (running bales).....	144,001
Bleached (running bales).....	96,041

Manufactured Ice. Report from Census of Manufactures, 1914, issued April 1917. The total cost of ammonia used in the ice and allied industries for the production of ice or refrigeration where ice is a subsidiary product, amounted to \$1,887,359.00. For this work 6,780,000 lbs. of anhydrous ammonia were used, about five-sixths of this in the ice industry and about nine-tenths of it in compressor systems. Aqua ammonia used amounted to nearly 2,000,000 lbs., practically all being employed in the ice industry. This material was used in approximately 5,000 machines which had a capacity of 130,000 tons of ice per day of twenty-four hours.

DEPARTMENT OF AGRICULTURE

Sugar-Cane Culture for Sirup Production in the United States. P. A. YODER. Bulletin 486, contribution from the Bureau of Plant Industry, issued March 19th, 46 pp. Paper, 10 cents. A description of the practices in vogue at the present time in the growing and handling of sugar cane where sirup is the main product.

A Study of American Beers and Ales. I. M. TOLMAN AND J. GARFIELD RILEY. Bulletin 493, contribution from the Bureau of Chemistry, issued March 21st, 23 pp. Paper, 5 cents. A technical study of this subject and of interest to brewers generally.

Studies on the Digestibility of Some Animal Fats. C. F. LANGWORTHY AND A. D. HOLMES. Bulletin 507, contribution from the States Relations Service, issued March 24th, 20 pp. Paper, 5 cents. This bulletin records studies of the digestibility of chicken fat, goose fat, brisket fat, cream fat in egg yolk, and fat or oil in fish. It is primarily of interest to students and investigators of food problems.

Yields from the Destructive Distillation of Certain Hardwoods. R. C. PALMER. Bulletin 518, contribution from the Forest Service, issued March 6th, 8 pp. Paper, 5 cents. This is the second progress report. Gives the results of experiments in destructive distillation of hardwoods and is of interest to manufacturers of by-product.

The Theory of Drying and Its Application to the New Humidity-Regulated and Recirculating Dry Kiln. HARRY D. HUBBARD. Bulletin 520, contribution from the Forest Service, issued March 11th, 11 pp. Paper, 5 cents. A practical discussion of a new method of kiln drying softwood lumber and of interest to manufacturers of lumber products.

Relation of the Water-Retaining Capacity of a Soil to Its Hygroscopic Coefficient. FREDERICK J. ALWAY and GUY R. MCDOLE. *Journal of Agricultural Research*, 9, 27-69 (April 9).

Fixation of Ammonia in Soils. I. G. MCBETH. *Journal of Agricultural Research*, 9, 141-151 (April 30).

PUBLIC HEALTH SERVICE

The Activity of Wild American Digitalis. GEORGE B. ROTH. *Public Health Reports*, 32, 377-80 (March 9). "From the above investigation we may conclude that the wild digitalis which is found in the Northwestern States may be utilized as a source of supply for making the various official preparations of digitalis, and that by using ordinary methods in handling and preparing the leaves we may secure a highly active product, which compares favorably with the activity of cultivated leaves grown under more favorable conditions."

Court Decisions Pertaining to Public Health. A Digest of the Judicial Opinions Published in the Public Health Reports During the Calendar Year 1916. JASON WATERMAN. *Public Health Reports*, 32, 453-75 (March 30).

Biological Products: Notice to Those Concerned. *Public Health Reports*, 32, 565 (April 20).

In view of the fact that some establishments licensed for the manufacture and sale of biological products located in Germany have not been inspected within the time required by regulation and on account of present conditions will be inaccessible to inspection for an indefinite period of time, the department has revoked the licenses of these establishments, and notification of this fact is hereby given to all concerned.

The establishments in question with their license numbers and products are the following:

No.	NAME	PRODUCTS
12	Chemische Fabrik auf Actien, Berlin, Germany	Antigonococcus vaccine, antistreptococcus serum, diphtheria antitoxin, and tuberculin
24	Farbwerke, vormals Meister, Lucius and Bruning, Höchst am Main, Germany	Antidysenteric serum, antimeningococcal serum, antipneumonic serum, antistreptococcal serum, antitetanic serum, diphtheria antitoxin, tuberculin
29	The Behringwerk, Marburg, Germany	Antitetanic serum and tuberculin
31	E. Merck, Darmstadt, Germany	Antimeningococcal serum, antipneumonic serum, antistreptococcal serum, diphtheria antitoxin, jequiritol serum, leucofermantin (antitryptic sheep serum), normal horse serum (liquid and dried), tuberculin, and bacterial vaccines prepared from colon bacillus, dysentery bacillus, gonococcus pneumococcus, staphylococci, streptococci, and typhoid bacillus.
32	Kalle & Co., Biebrich, Germany	Tuberculin (Rosenbach)
33	Pharmaceutisches Institut Ludwig Wilhelm Ganz, Oberursel bei Frankfurt a. M., Germany	Antidysenteric serum
55	Chemische Fabrik Ggstrow, Güstrow i. M., Germany	Staphylococcus vaccine

Detection of Hydrocyanic Acid Gas: Use of Small Animals for this Purpose. S. B. GRUBBS. *Public Health Reports*, 32, 565-70 (April 20).

BUREAU OF MINES

Analyses of Coals Purchased by the Government During the Fiscal Years 1908-1915. GEORGE S. POPE. *Bulletin* 119, 99 pp. Paper, 15 cents.

Combustion in the Fuel Bed of Hand-Fired Furnaces. HENRY KREISINGER, F. K. OVITZ and C. E. AUGUSTINE. *Technical Paper* 137, 61 pp. Paper, 15 cents. "The main object of the investigation described in this report was to determine the conditions governing the process of combustion in the fuel bed of a hand-fired furnace. The results of this investigation furnish data for correct design of coal-burning grates and furnaces and their efficient operation. They also cast light on the important problem of clinker trouble as related to fusibility of ash. They

further indicate the possibility of a high rate of gasification of coal in gas producers, as suggested in Bulletin 7."

Asphyxiation from Blast-Furnace Gas. FREDERICK H. WILLCOX. *Technical Paper* 106, 57 pp. Paper, 15 cents. "This report is issued by the Bureau of Mines in pursuance of its endeavors to increase safety and efficiency in metallurgical industries. It discusses the nature and causes of poisoning from blast-furnace gas, itemizes the places where gas may be expected to be encountered, suggests safeguards and points out the precautions to be taken in working about gaseous places."

Oxygen Mine Rescue Apparatus and Physiological Effects on Users. VANDELL HENDERSON and JAMES W. PAUL. *Technical Paper* 82, 83 pp. Paper, 15 cents.

GEOLOGICAL SURVEY

Tungsten Deposits of Northwestern Inyo County, California. ADOLPH KNOPF. *Bulletin* 640-L, from Contributions to Economic Geology, 1916, Part I, pp. 229-49. Published January 26, 1917. "Tungsten deposits were found in northwestern Inyo County, California, in 1913, but remained practically unknown until the spring of 1916, when they began to be energetically developed. By midsummer two mills, having a total daily capacity of 400 tons, had been completed and were in active operation.

"The ore bodies that are being mined are from 20 to 60 feet wide and from 150 to 200 feet long. They carry from 1.5 to 2 per cent of tungsten trioxide (WO₃). The area in which scheelite-bearing deposits have been found roughly forms a belt 20 miles long, but it is likely that the prospecting now going on will extend the dimensions of the field.

"The mining conditions are favorable; the climate is good, water is easily obtained, transportation facilities are adequate, and an electric transmission line transverses the belt, so that power is readily available. Timber, however, is lacking. The tungsten area adjoins a rich agricultural district."

Antimony in 1915. FRANK L. HESS. From *Mineral Resources of the United States, 1915, Part I*, pp. 837-843. Published March 13, 1917.

"Antimony prices in 1915 were probably the highest known since the metal became a regular article of commerce. The high prices led to the largest production the United States has made and probably to the largest world's production.

"According to figures collected by the United States Geological Survey the production of antimony ores in the United States in 1915 is estimated at 5,000 tons, containing 2,100 tons of antimony, valued at about \$425,000. The largest previous domestic production was in 1892, when 150 tons of metal were produced in San Francisco from Nevada ores and 380 tons of ore carrying 55 per cent of antimony were exported. Practically all operations of 1915 were new; most of them were small; and they were so widely scattered that it has been difficult to obtain accurate figures.

"For years large quantities of antimonial lead were imported into the United States as type metal, for which it is largely used. During 1912, 1913, 1914 and 1915 these imports have been much smaller, but the imports for 1915 were nearly double those of 1914."

Arsenic in 1915. FRANK L. HESS. From *Mineral Resources of the United States, 1915, Part I*, pp. 845-846. Published March 13, 1917.

"The output of arsenic in the United States in 1915, was much the largest yet made in this country and amounted to 5,498 short tons, valued at \$302,116, an increase of nearly 18 per cent over the production of 4,670 tons, valued at \$313,147, in 1914, and an increase of about 75 per cent over the largest previous

production, that of 1912, when 3,141 tons, valued at \$190,757, were produced.

"As usual, the arsenic was all saved as a by-product in the smelting of copper and gold and silver ores.

"White arsenic was not produced in the United States until 1901, when the Puget Sound Reduction Co., at Everett, Wash., made an output of 300 short tons, saved as a by-product in smelting gold and silver ores.

"Prices of white arsenic averaged from 2.45 to 2.83 cents a pound at the works. The prices in New York, according to the *Oil, Paint, and Drug Reporter*, were very steady, starting at 4 to 4.5 cents a pound in January, declining to 3.5 to 4 cents in August, and closing in December at 3.875 to 4.5 cents a pound. Lead arsenate was quoted at 5.5 to 6 cents a pound until November, when it rose to 6.5 to 7 cents a pound. Red arsenic (AsS) was quoted at 8 cents a pound at the beginning of the year, rising to 8.25 to 9 cents in November. No quotations were given in December."

Chemical Relations of the Oil-Field Waters in San Joaquin Valley, California. Preliminary Report. G. SHERBURNE ROGERS. Bulletin 653, 112 pp. Paper, 10 cents. "The writer studied the physical and chemical relations of the water and oil in these fields during the summers of 1914 and 1915. The chief conclusions concerning the chemistry of the waters, deduced by him from a study of several hundred analyses of water from different depths, are as follows:

1—Oil-field water is not necessarily salty, as is generally believed, and may not be even slightly salty to the taste. The degree of concentration of chloride in such water is governed primarily by local conditions and is not affected by the position of the water in relation to oil.

2—Sulfate, which predominates in most of the shallow ground waters on the west side of San Joaquin Valley, diminishes in amount as the oil zone is approached, and finally disappears.

3—The concentration of carbonate increases as the oil zone is approached but depends largely on the concentration of chloride.

4—The horizon, with respect to the oil zone, at which these alterations take place, is different in each field.

On the basis of these conclusions, which appear to be well grounded, at least for the area studied, the following practical suggestions may be made:

In drilling a well in untested territory it may be possible to obtain an indication of the presence or absence of oil and gas below by ascertaining by analysis whether the sulfate is diminishing and the carbonate increasing in the waters successively encountered. In some areas a significant change may be detected as much as 1,000 ft. above the oil; in others the upper limit of alteration may be within a few hundred feet of the oil.

The source of the water in a well that produces a mixture of water and oil may be determined, at least in a general way, by studying its chemical composition. In the Westside Coalinga field, for example, the source of the water may thus be determined rather definitely; in the Midway-Sunset field, where the distinctions are less sharp, the success of this method will depend largely on the number of authentic analyses that are available for comparison.

In this report the writer aims first to present the evidence on which the foregoing conclusions are based and to discuss the interpretation of water analyses and their value from the operator's standpoint, and second, to discuss the chemical relations of water and oil in so far as present information permits. It is hoped that this preliminary presentation will indicate the importance of experimental geochemical work in the interpretation of the organic constituents of oils and the inorganic

substances found in the oil-field waters. Enough is known already to warrant the belief that systematic experimental work in petroleum hydrology will yield results of practical as well as scientific value.

Cleveland Gas Field, Cuyahoga County, Ohio, with Study of Rock Pressure. G. SHERBURNE ROGERS. Application of Theory of Probability in Estimating Capacity of New Well. C. E. VAN ORSTRAND. Bulletin 661-A, 68 pp. Issued March 2.

Oil Resources of Black Shales of the Eastern United States G. H. ASHLEY. Bulletin 641-L, 33 pp.

Chromite. J. S. DILLER. Bulletin 666-A. The chromic iron imported into the United States in 1916 amounted to 114,655 long tons. During the same period the chromic iron produced and sold in the United States amounted to approximately 40,000 tons. The greatly increased trade, especially in steel, and the consequently larger demand for chromite have stimulated the search for it in the United States, as shown by the tenfold increase in production.

The ores west of Riddle are the richest yet mined in the States; in some places they run as high as 55 per cent chromic oxide, and much of the ore contains about 50 per cent. Most of the Oregon ore, however, like that of California, averages about 40 per cent of chromic oxide, and ore of that grade is commonly the basis of sale. The ore generally contains 38 to 45 per cent chromic oxide, 6 to 8 per cent silica, and 17 to 25 per cent alumina. It is claimed that the ore can be concentrated to a content of 55 per cent chromic oxide. If this can be done successfully, it will mean much for the chrome industry of the Pacific coast and will enlarge its possibilities to meet war demands. The difficulty with much of the chrome ore of the Pacific coast has been its low grade and its great distance from the principal markets. The low-grade ore, running 38 to 45 per cent chromic oxide, may be used to advantage chiefly for metallurgical purposes, such as grow out of war demands—for furnace lining and in the manufacture of chrome brick and chrome steel, for example—and by far the greater part of the California output is being so used. For chemical purposes, however, ore of higher grades is desirable, if not essential.

The prices of chromite in California on the basis of 40 per cent chromic oxide ranged in 1916 from \$14 a ton f. o. b. early in the season to \$20 toward the end of the year. To this must be added for the eastern buyer a freight rate for carload lots ranging from \$10 a ton to Chicago, to \$14.86 a ton to the eastern seaboard, thus making the California 40 per cent ore cost on the eastern seaboard from \$28.86 to \$34.96 a ton.

With the known supplies of chromite and others whose discovery within the limit of practicable transportation throughout the United States is confidently expected, there is good reason to believe that the domestic output of chromite could be so increased as to go far toward supplying the demand if in the event of war our imports, except those from Canada, were cut off.

The metallurgy of chromite has apparently been so developed in the hydroelectric process as to utilize to advantage relatively low-grade ores such as are most abundant in the United States, and the further development of that process on the Pacific coast, where water power abounds, would greatly diminish the handicap of long transportation.

Sulfur. PHILIP S. SMITH. Bulletin 666-B, 4 pp. Even under the conditions that now prevail this country exports much more sulfur than it imports. The exports are tabulated in round figures, to 1,000,000 long tons, valued at \$1,000,000 in 1915, to 1,100,000 tons, valued at \$1,100,000 in 1916, to 1,200,000 tons, valued at \$1,200,000, and in 1917 to 1,300,000 tons, valued at \$1,300,000. The great falling off of exports in 1917 may have been due in part to the increased use of sulfur in sulfuric acid in this country. In part, however, probably in large part, the

decrease was due to the difficulties and dangers of transportation to foreign ports.

The United States in 1913 produced about 350,000 long tons of pyrite and imported about 850,000 tons. If these figures represent the normal condition of the industry, it is evident that ordinarily the United States uses each year about 500,000 tons more pyrite than it produces. The imported pyritic ore has an average sulfur content of approximately 45 per cent, so that 225,000 tons of native sulfur would be required to make up this deficiency if the importation of pyrite were cut off. In 1916 we exported 107,000 tons of sulfur more than we imported. If the exportation of sulfur were prohibited, as it doubtless would be if imports of sulfides were cut off, this excess amount would therefore be available, and at the 1916 rate would make up nearly half of the deficiency that would be created by the shutting out of imported pyrite. The deficiency could be reduced still more by drawing on the reserves of sulfur already mentioned, but doubtless it would be far better not to use the high-grade native sulfur for many of the purposes for which pyrite may be used, but rather to save more of the sulfur from the sulfide ores and to hunt for and develop additional deposits of sulfides.

According to preliminary estimates the United States in 1916 produced about 4,500,000 tons of sulfuric acid of a strength of 50° Bé. and nearly 1,000,000 tons of acid of strength higher than 66° Bé. This amount exceeds the amount of similar acids produced in 1913 by more than 950,000 tons of 50° Bé. acid and by more than 900,000 tons of acid of strengths higher than 66° Bé.

Almost no sulfuric acid is imported into the United States, and but a relatively small amount is exported, even under the conditions now prevailing. The reports of the Bureau of Foreign and Domestic Commerce show that in 1916 a little over 600 tons of acid were imported and about 30,000 tons were exported.

Manganese. D. F. HEWETT. Bulletin 666-C, 12 pp. The largest domestic production of manganese ore for a single year was but 34,524 tons in 1887, and since that year, except for several brief periods, the domestic production has declined rather steadily.

In contrast with the domestic production, the imports of manganese ore, largely from India, Brazil, and Russia, have rather steadily risen in proportion to the production of steel. The extensive deposits of these countries are rich enough to permit the shipment of large quantities of ore without concentration.

MANGANESE RECOVERABLE FROM ORE PRODUCED IN THE UNITED STATES IN 1915, IN LONG TONS

Source	Ore	Manganese
Manganese ore.....	9,709	4,660
Manganiferous iron ores (a).....	48,193	9,040
Manganiferous silver ores.....	137,045	17,504
Manganiferous zinc residuum.....	189,318	23,053
		54,257
Manganese recoverable as alloys.....		36,792
Percentage of total manganese needed.....		21.0

(a) Exclusive of Marquette County, Mich., and Iron County, Mich.

The ferromanganese needed for the American steel industry has been supplied in part by imports of the alloy itself and in part by domestic manufacture from imported ore. It is evident that the domestic manganese ore is the source of little ferromanganese. The available data for spiegeleisen, however, show that prior to 1914 about half of the domestic product was made from domestic ore. During recent years the imports of spiegeleisen have been negligible. The available supply of these manganese alloys for 1915 and the approximate content in manganese is shown in the table. From these results, it has been calculated that for a four-year period an average of 14 lbs.

of manganese has been consumed for each ton of steel produced.

AVAILABLE SUPPLY OF MANGANESE ALLOYS IN THE UNITED STATES, 1915, IN LONG TONS

Imports	Quantity	Manganese Content
Ferromanganese.....	55,263	42,210(a)
Spiegeleisen.....	200	60(a)
Domestic production:		
Ferromanganese.....	144,260	110,134(a)
Spiegeleisen.....	114,556	22,808(b)

(a) Percentage of manganese estimated.

(b) Percentages of manganese submitted by makers.

The prevailing price of manganese ore has steadily risen since 1914, but the increases have lagged behind those in ferromanganese. For 15 years prior to 1914 the price per unit of 49 per cent ore in the United States ranged from 23 to 30 cents, but during 1916 it rose first to 45 cents and later to 65 cents. The price of 65 cents was maintained through the early months of 1917.

Soon after the war broke out the price of ferromanganese rose suddenly from \$40 to \$120 a ton for a brief period, then ranged from \$70 to \$115 for more than a year. During 1916 prices ranged from \$115 to \$175 a ton, except for a short time in April, when \$400 a ton was recorded. This great rise was probably caused by Germany's declaration of a blockade of England. In February 1917, the price reached \$250 a ton.

The price offered for standard 18 to 22 per cent spiegeleisen has also increased from about \$25 a ton in 1914 to \$50 in 1916 and \$65 in 1917.

Platinum. JAMES M. HILL. Bulletin 666-D, 4 pp. It will be noted that the normal annual addition of crude platinum to the world's supply has varied between 260,000 and 313,000 ounces. This supply is augmented by the platinum produced by refiners of copper matte and gold bullion. United States refiners of gold and copper produce annually about 1,500 ounces of refined platinum as by-products, chiefly from copper ore, of both foreign and domestic origin.

That the supply of new platinum has not been sufficient to meet the requirements is indicated by the very extensive trade in scrap or used metal. Figures are not available for such trade in foreign countries, but in the United States the yearly sales of secondary platinum normally amount to about 40,000 ounces; in 1916 they increased to 49,400 ounces.

The United States at present is not supplying 10 per cent of its platinum requirements, and while there is some assurance that by systematic geologic investigation, already planned, new placer deposits that will yield platinum may be found and that by a study of the methods of saving platinum a greater yield from all deposits may be had, yet the issue must be squarely faced that in all probability the domestic supply cannot be made adequate to meet the requirements of normal times.

Salt, Bromine and Calcium Chloride. R. W. STONE. Bulletin 666-F, 4 pp. The United States furnishes practically all the salt consumed by its people. In 1916 more than 99 per cent of all the salt used in this country was made here, and the value of the salt exported was more than twice as great as that of the salt imported.

The production in 1916 is estimated at 43,000,000 bbls. of 280 lbs., or nearly half a barrel for each individual in the country, compared with 38,000,000 bbls. in 1915.

Prices of salt are increasing and may continue to increase so long as the present unsettled conditions continue. Some grades of salt have doubled in value since 1915; others have increased 50 per cent. This increase is chargeable not only to increased demands of labor and cost of supplies but also to the larger margin of profit to which producers feel entitled under present circumstances. Heavy charges against the cost of production

are wages and fuel. Labor is demanding and receiving higher pay, and coal at some salt works has been hard to get and expensive. One producer reports coal increased in cost from 80 cents to \$5.50 a ton.

In 1915 there was a significant increase over the production of the previous year, the total output in the United States being 855,857 lbs., valued at \$856,307, or about \$1 a pound. The comparatively low price indicated by the total figures is due to the fact that considerable bromine was sold at prices specified in contracts made before the demand increased, and to the further fact that the figures indicate prices at point of production and hence do not include the cost of freight. The price of bromine during the first half of 1916 ranged from \$4.75 to \$6.50 a pound in New York, as a result, at least in part, of the unprecedented demand from abroad. In March, 1917, it had fallen to \$1.30 a pound.

The quantity of calcium chloride produced from natural brines and sold in the United States has recently been about 20,000 short tons a year, valued at \$6 to \$6.50 a ton. This does not include the output obtained in the manufacture of soda, as calcium chloride so obtained is not an original constituent of brine. Large quantities made in the manufacture of soda have been wasted, and it is hoped that new uses may be found for this by-product.

Since the first half of 1916 there has been a demand for this material which has raised the price. In March, 1917, 70 to 75 per cent fused calcium chloride was quoted in the New York market at \$26 to \$30 a ton, and granulated calcium chloride has recently been quoted as high as \$40 a ton. Fused lump calcium chloride that used to retail for 15 cents a pound was quoted in April, 1917, at 90 cents. It is believed that the supply can easily be kept ahead of the demand.

Sand and Gravel. R. W. STONE. Bulletin 666-G, 3 pp. The sand industry in all its branches grows normally with increase of population. Severe business depression decreases the production of building sand more than that of sand for some other uses, such as engine sand, which is used wherever trains and trolley cars run. Business acceleration increases the output and use of all kinds of sand. The value of all the sand and gravel produced in 1915 of which the United States Geological Survey has a record was over \$23,000,000. The statistics for 1916 are not yet available (April, 1917).

"The glass-making industry is in no way dependent on foreign supplies for its sand, salt cake, soda ash, and limestone. Our resources in these materials are ample. Most of the output of glass sand comes from a belt of states extending from New Jersey to Missouri.

"The output in 1916 approximated 2,000,000 tons and was thus larger than it has ever been. On account of the higher wages and the increased cost of machinery and of all supplies, particularly coal, the price of glass sand, which has been decreasing in the last few years, showed an upward tendency in 1916."

The new requirements of armament and munitions have caused foundries and machine shops to increase their output, and this activity is in turn reflected in the molding sand industry. The total production in 1915 was 3,500,000 tons, more than two-thirds of which came from New Jersey, New York, Pennsylvania, and Ohio. This was 750,000 tons more than the output of 1914. The statistics for 1916 are not yet available (April, 1917), but it is confidently expected that they will show 4,500,000 tons produced in that year.

Sand suitable for grinding and polishing, ranging from small gravel for use in sand blast work on heavy casting, to the fine material used for giving a polish, is abundant, and the country produces about 1,000,000 tons annually. Pennsylvania is the leading producer and in some years furnishes one-half of the output. The present activity in the production of armament

will call for an increased production of this material, for it is the practice in large foundries to clean castings by sand-blast.

Asbestos. J. S. DILLER. Bulletin 666-H, 4 pp. The United States is one of the largest manufacturers of objects made from asbestos, but it is not a large producer of crude asbestos. The supply of asbestos of all grades in Quebec, Canada, is so large and so conveniently obtained and the quality of the Canadian asbestos is so excellent as to delay the development of asbestos deposits in the United States. The demand for high-grade asbestos has always been active, but recently, under the stimulus of war conditions abroad, it has become still greater, and the available supply, although larger than before, is frequently not equal to the demand. In 1916 the total output of asbestos in the United States was 1,479 short tons. The imports during the same time, almost wholly from Canada, amounted to 116,162 short tons, making a total supply available for manufacture in the United States of 117,641 tons.

"The prices for asbestos produced in the United States during 1916 are said to have ranged, according to grade, from \$15 to \$1,000 a ton. In 1915 normal prices ranged from \$10 to \$400 a ton.

With a view to increasing the available supply of asbestos, especially the spinning grades, which are so much in demand, all areas of peridotite and pyroxenite rocks more or less altered to serpentine should be prospected for cross-fiber veins of asbestos in which the fibers are three-fourths of an inch or more in length. The content of such fiber necessary to yield a profit may be less than 1 per cent of the whole rock quarried, and in obtaining it a much larger percentage of mill fiber will most probably be taken out.

Although the Arizona chrysotile fiber is excellent for certain purposes and finds a ready sale to those who need it for electric insulation, its mode of occurrence necessitates expensive operation and small production, and it should be mined with especial reference to avoiding waste and obtaining all within reach.

Talc and Soapstone. J. S. DILLER. Bulletin 666-I, 2 pp. The total domestic production is nearly twelve times the total imports, over one-third of which came from Canada. The tale of New York is an especially good paper filler and is largely used for that purpose, although much goes into paints. The output of Vermont is used for the same purpose and also for foundry facing, rubber goods, and coating walls. A small amount is used for crayons. Talc for pencils, crayons, burners, and insulators comes almost wholly from North Carolina and Georgia and is cut in Chattanooga. The demand for talc of the highest grade is greater than the supply. Much of the material for toilet powders is imported. With the exception of compact material for pencils, burners, and insulators and the best grade for toilet powders the United States has a large reserve in nearly all the producing States. It is believed that by more searching field investigations the domestic output even of pencil and gas burner talc as well as the best toilet powder grade may be greatly increased. The "foot-case" grade of ground talc, now so extensively used in the Army, may be fully supplied in this country. Although the war has greatly increased production it has not greatly increased the price except in emergencies.

In 1916 there was a small production of soapstone in California, but almost the entire output of the United States came from Virginia, where there were four producing quarries. The total yield, including that of California, was 164,000 short tons. The United States has large reserves of soapstone and more necessary, greatly increased its output.

Phosphate Rock. R. W. STONE. Bulletin 666-J, 3 pp. In 1914 the United States was producing annually about 3,500,000 tons of phosphate rock of which 90 per cent came from Florida, Tennessee, and North Carolina. Phos-

produced more than 75 per cent of the total output, including the great bulk of the material exported, which was over 40 per cent of the total. With the beginning of the war the facilities for shipping phosphate rock to Europe were greatly decreased. Many Florida plants were shut down, and they have not resumed operations.

The proportion of exports to total production dropped from about 42 per cent in 1912 and 1913 to 35 per cent in 1914 and less than 14 per cent in 1915. In 1915 the total production was only 60 per cent of that in 1913. In 1916 the industry was in some areas practically demoralized, but there was nevertheless a gain over 1915. The total output in 1916 was 1,980,000 tons, valued at \$5,897,000.

Any statement as to probable developments in the phosphate industry when peace is declared is largely conjecture. So long as the war continues phosphate rock cannot be sent to the large consumer, Germany, and high ocean freight rates greatly restrict and practically stop shipments to other European countries. Furthermore, the demand for sulfuric acid for use in making munitions has raised the prices of acid so high that manufacturers of acid phosphate have been obliged to curtail production. This has reduced the quantity of rock phosphate used by manufacturers of fertilizers and increased the quantity of rock ground for direct application to the soil. It seems reasonable to believe that at the end of the war European nations will want increased quantities of phosphate, for their stores of food-stuffs will be low and intensive cultivation of the soil will be necessary. The demand will again fall largely on the Florida and South Carolina deposits, which are close to the seacoast, and the phosphate industry in those States may then look for marked improvement.

Coal. C. E. LESHER. Bulletin 666-M, 7 pp. This separate is devoted to a discussion of commercial conditions, the character of coal application, and the causes of coal shortage. It is essentially an appeal to the consumers of coal to operate in reducing the likelihood of a coal shortage during the coming winter by proper purchase and storage of their fuel supplies at suitable times.

Mineral Production of the United States in 1915. Introduction by H. D. McCASKEY. Summary by MARTHA B. CLARK. From Mineral Resources of the United States, 1915, Part I, pp. 116-95a. Published April 16, 1917. This is the summary section of the two volumes on Mineral Resources indicating by materials, years, and states, the statistics for production, import, export, and other features of interest. The total mineral production summarized amounted to \$2,400,000,000 for 1915.

Cadmium in 1915. Production and Resources. C. E. SIEBENTHAL. From Mineral Resources of the United States, 1915, Part I, pp. 979-981. Published April 30. In 1915 the metallic cadmium produced in the United States amounted to 91,400 lbs. valued at \$108,000, an average of \$1.19. During the same period 10,600 lbs. of cadmium sulfide valued at \$10,000 were produced. The last reports from Germany (for 1913) indicate the metallic cadmium produced in that country, which is the only other producer of this metal in quantity, as 82,000 lbs. which that year was valued on an average of 78 cents per lb.

COMMERCE REPORTS—APRIL, 1917

Large coal deposits have been discovered in Iceland. (P. 14)

Coincident with a short lemon crop in Sicily, it has been found that the lemon essence had an abnormally high optical rotation. (P. 19)

A plant is to be established at Curaçao, Dutch West Indies, for the extraction of **tannin** from *divi-divi*; and of dyes from dyewoods. (P. 45)

A plant is to be erected in Norway for the production of fuel

from peat and wood waste by the "Rosendable" method. (P. 175)

Two varieties of the lumbang nut are found in the Philippines, the "triloba," a hard nut, and the "trisperma" a soft nut. The oil of the soft nut dries more rapidly than that of the hard nut, and resembles **tung oil**. Some planting has been done, but in general the nuts are gathered from native trees, the industry being very poorly organized. (P. 216)

Efforts are being made to develop in Siberia such industries as **paper, leather, brick, iron**, etc. In several districts coal and iron deposits are in close proximity. (P. 232)

Efforts are being made in Australia to develop the manufacture of **paper** from "lalang grass," which grows over large areas, and resembles **esparto**. (P. 247)

Barytes deposits of Manchuria are now being developed. (P. 274)

The recent development of the Russian chemical industry is chiefly in the production of **heavy chemicals and raw materials**, especially for explosives and dyestuffs. (P. 281)

In a review of the **platinum** deposits of the world, by James M. Hill, the sources in Russia, Colombia, Brazil, Australia and the United States are described. (P. 298)

The Mersey Chemical Works, near Liverpool, built by the Badische Anilin und Soda Fabrik, has been purchased by an English firm to be used now for **explosives** and later for **dyes and intermediates**. (P. 321)

Bauxite is now being shipped from British Guiana to the United States. (P. 331)

An extensive deposit of **scheelite** has been discovered in New Zealand. (P. 361)

A marked shortage in the production of **kauri gum** in New Zealand is reported. (P. 365)

Brazil has become the principal source of **manganese** ore, of which it now exports annually 500,000 tons, compared with 122,000 tons in 1913. (P. 379)

In order to increase the available supply of **tin cans** for packing perishable foods, steps have been taken by the Department of Commerce and the manufacturers to increase the use of substitutes for tin, *e. g.*, **paper**, as containers for non-perishable goods. (P. 389)

SPECIAL REPORTS ISSUED IN APRIL

SPAIN—15a	BRITISH INDIA—50a
CANADA—23a	CHINA—52a
HONDURAS—31a	NEW ZEALAND—61a
BOLIVIA—39a	BRITISH EAST AFRICA—65a

STATISTICS OF EXPORTS TO THE UNITED STATES (Pp.)

ITALY—184	SPAIN—Sup. 15a	CHINA—Sup. 52a
Tartaric acid	Spain ore	Antimony
Beeswax	Almond oil	Albumen
Hides	Olive oil	Aniline dyes
Sienna	Iron oxide	Camphor
Umber	Garnet	Cantharides
Pumice	Lavender oil	Gall nuts
Mercury	Thyme oil	Indigo paste
Soap		Licorice
Soap stock	CANADA—Sup. 23a	Musk
Talcum	Coal and coke	Rhubarb
Citrate of lime	Hides	Sodium benzoate
Licorice	Leather	Turmeric
Sulfur	Aluminum	Gold
	Asbestos	Hides
	Copper	Pig iron
	Gold	Peanuts
COLOMBIA—278	Iron and Steel	Soya bean oil
Gold	Nickel	Castor oil
Hides	Silver	Cottonseed oil
Ipsacae		Peanut oil
Platinum	HONDURAS—Sup. 31a	Rapeseed oil
Rubber	Copra	China wood oil
Sugar	Hides	Silver
Mangrove extract	Fustic	Vegetable tallow
	Rubber	Zinc ore
	Sarsaparilla	Anised oil
BRITISH INDIA—Sup. 50a		Cassia oil
Cashew nuts	BOLIVIA—Sup. 39a	Paper
Castor seeds	Tin	Sugar
Coconut oil	Tungsten	Tin
Copra	Copper	
Indigo	Antimony	
Lemon grass oil	Lead	NEW ZEALAND—Sup. 61a
Nux vomica	Bismuth	Copra
Rubber	Silver	Hides
Sienna	Zinc	Kauri gum
Hides	Gold	Bullion
Turmeric	Molybdenum	

NEW PUBLICATIONS

By IRVING DeMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- Agricultural Economics.** E. G. Nourse. 8vo. Price, 12s. Cambridge University Press.
- Agriculture in Oxfordshire.** J. ORR. 8vo. 239 pp. Price, \$2.90. Oxford University Press, New York.
- Bituminous Materials: Laboratory Manual of Bituminous Materials.** PAVROV HUBBARD. 8vo. Price, 6s. 6d. Chapman & Hall, London.
- Chemistry of Materials of the Machine and Building Industries.** R. B. LEONOU. 8vo. 449 pp. Price, \$3.00. McGraw-Hill Book Co., New York.
- Drugs: Popular Drugs: Their Use and Abuse.** SYDNEY HELLIER. 8vo. Price, 1s. T. Werner Laurie, Ltd., London.
- Dynamics: Elementary Course in Lagrange's Equations and Their Applications to Solutions of Problems of Dynamics.** N. W. AKIMOFF. 8vo. 195 pp. Price, \$2.00. Philadelphia Book Co., Philadelphia.
- Engineering: An Epitome of Engineering.** RAMACHANDRA IVOR. 3rd Ed. 8vo. 197 pp. Price, 4s. Higginbotham & Co., Madras.
- Explosives.** ARTHUR MARSHALL. 2 Vol. 2nd Ed. 8vo. 424 pp. Price, \$16.00. P. Blakiston's Son & Co., Philadelphia.
- High Speed Internal Combustion Engines.** A. W. JUDGE. 8vo. 350 pp. Price, \$5.50. The Macmillan Co., New York.
- History of the American Society of Mechanical Engineers from 1880-1915.** F. R. HUTTON. 8vo. 355 pp. Price, \$5.00. American Society of Mechanical Engineers, New York.
- Hydraulics: Treatise on Hydraulics.** MANSFIELD MERRIMAN. 10th Ed. 8vo. Price, 17s. 6d. Chapman & Hall, London.
- Inorganic Chemistry: Industrial and Manufacturing Chemistry. Part II.** G. H. MARTIN. 3rd Ed. 8vo. 527 pp. Price, 35s. Crosby Lockwood & Son, London.
- Laws of Physical Science.** E. F. NORTHRUP. 12mo 210 pp. Price, \$2.00. J. B. Lippincott Co., Philadelphia.
- Machines: The Theory of Machines.** R. W. ANGUS. 8vo. 340 pp. Price, \$3.00. McGraw-Hill Book Co., New York.
- Meat Hygiene: Textbook of Meat Hygiene.** RICHARD EDELMANN. Rev. Ed. 8vo. Price, 21s. J. and A. Churchill, London.
- Mechanical Appliances.** G. D. HISCOX. 4th Ed. 8vo. 396 pp. Price, \$3.00. Norman W. Henley Publishing Co., New York.
- Milling: Modern Milling.** ERNEST PULL. 8vo. 207 pp. Price, \$3.00. The Macmillan Co., New York.
- Mine Supplies: The Efficient Purchase and Utilization of Mine Supplies.** H. N. STROCK and J. R. BILLYARD. 12mo. 97 pp. Price, \$1.25. John Wiley & Sons, New York.
- Municipal Engineering Practice.** A. P. POLWELL. 8vo. Price, 15s. Chapman & Hall, London.
- Organic Chemistry: Industrial and Manufacturing Chemistry. Part I.** G. H. MARTIN. 3rd Ed. 8vo. 776 pp. Price, 25s. Crosby Lockwood & Son, London.
- Pavements: A Textbook of Brick Pavements.** C. R. MANDIGO. 12mo. 126 pp. Price, \$1.50. Western Paving Brick Manufacturers' Association, Kansas City.
- Physical Chemistry of Vital Phenomena.** J. F. McLENDON. 8vo. 240 pp. Price, \$2.00. Princeton University Press, Princeton, N. J.
- Physical Measurements.** R. S. MINOR. 4 Vol. 8vo. Price, \$2.60. The Author, Berkeley, California.
- Plants Poisonous to Live Stock.** H. C. LONG. 8vo. 119 pp. Price, 6s. Cambridge University Press.
- Refrigeration: The Elements of Refrigeration.** A. N. GREEN. 8vo. Price, 17s. Chapman & Hall, London.
- Science: A List of Books on the History of Science.** A. G. S. JORDISON. 4to. 139 pp. Price, \$0.25. John Crerar Library, Chicago.
- Soil Biology: A Laboratory Manual.** A. L. WHITING. 12mo. 182 pp. Price, \$1.25. John Wiley & Sons, New York.
- Spectroscopy: Collected Papers on Spectroscopy.** G. D. LIVING and JAMES DEWAR. 4to. 366 pp. Price, \$9.00. G. P. Putnam's Sons, New York.
- Steam Boilers: Their Construction, Care and Operation.** C. F. SWINGLE. 12mo. 303 pp. Price, \$1.50. Frederick I. Drake & Co., Chicago.
- Steam Turbines.** W. J. GOODE. 8vo. 519 pp. Price, \$4.00. Longmans, Green & Co., New York.
- Stresses in Structural Steel Angles.** L. A. WATERBURY. 8vo. 17 pp. Price, \$1.25. John Wiley & Sons, New York.
- Tanning: Practical Tanning.** L. A. FLEMING. 615 pp. Price, 30s. Crosby Lockwood & Son, London.
- Technical Chemists' Handbook, Tables and Methods of Analysis for Manufacturers of Inorganic Chemical Products.** GILBERT LECHE. 2nd Ed. 12mo. 293 pp. Price, \$1.00. D. Van Nostrand Co., New York.
- Theoretical Chemistry from the Standpoint of Avogadro's Rule and Thermodynamics.** WALTER NERNST. 12mo. 880 pp. Price, \$2.00. The Macmillan Co., New York.

- Thermochemistry: A Textbook of Thermochemistry and Thermodynamics.** OTTO SACHUR. 8vo. 439 pp. Price, \$3.50. The Macmillan Co., New York.
- Water-Supply.** W. P. MASON. 4th Ed. 8vo. Price, 16s. Chapman & Hall, London.
- Wheat and Its Products.** A. MILLAR. 12mo. 134 pp. Price, \$0.85. Sir Isaac Pitman & Sons, New York.
- X-Rays.** G. W. C. KAYE. 8vo. 2nd Ed. 385 pp. Price, \$3.00. Longmans, Green & Co., New York.

RECENT JOURNAL ARTICLES

- Alloy or Carbon Steels vs. Carbonized.** E. F. LAKE. *The Iron Age*, Vol. 99 (1917), No. 18, pp. 1068-1071.
- Aluminum-Dust Precipitation Tests.** P. H. CRAWFORD. *Mining and Scientific Press*, Vol. 114 (1917), No. 15, pp. 515-517.
- Autoclave: A Convenient Form of Autoclave.** W. MOREY. *Journal of the Washington Academy of Sciences*, Vol. 7 (1917), No. 8, pp. 205-208.
- Bearing Bronzes and the Microscope.** C. H. BURROUGHS and VERNER SKILLMAN. *The Iron Age*, Vol. 99 (1917), No. 16, pp. 945-947.
- Boiler Practice in Textile Mills.** G. W. PERKINS. *Textile World Journal*, Vol. 52 (1917), No. 23, pp. 45-47.
- Chemistry and American Industry.** A. S. CUSHMAN. *Journal of the Franklin Institute*, Vol. 183 (1917), No. 5, pp. 557-574.
- Coal and Ash Transportation at Producers.** H. V. SCHNEPPE. *Blast Furnace and Steel Plant*, Vol. 5 (1917), No. 5, pp. 199-202.
- Condensers: Condenseur amovible universel.** M. VIORREUX. *Bulletin de la Société Chimique de France*, Vol. 21 (1917), No. 2, p. 450.
- Copper: Recent Progress and Problems in the Metallurgy of Copper.** E. R. WEIDLEIN. *Kansan Chemallurgist*, Vol. 2 (1917), No. 1, pp. 8-11.
- Corrosion and Electrical Properties of Steels.** ROBERT HADFIELD and EDGAR NEWBERRY. *Proceedings of the Royal Society, Series A*, Vol. 93 (1917), No. 647, pp. 56-67.
- Electric Furnace in Making Special Steel.** C. C. LYNDE. *Blast Furnace and Steel Plant*, Vol. 5 (1917), No. 5, pp. 214-216.
- Enameling: Application of Electricity to Enameling and Japanning.** W. S. SEELY. *The Electrician*, Vol. 14 (1917), No. 8, pp. 170-173.
- Exfoliation and Carbon Concentration in the Case-Hardening of Steel.** E. P. SIESSER. *Metalurgical and Chemical Engineering*, Vol. 16 (1917), No. 8, pp. 425-433.
- Ferromanganese in the Iron and Steel Industry.** R. J. ANDERSON. *Journal of the Franklin Institute*, Vol. 183 (1917), No. 5, pp. 579-592.
- Fixation of Ammonia in Soils.** I. G. McBETH. *Journal of Agricultural Research*, Vol. 9 (1917), No. 5, pp. 141-151.
- Flotation: The Disposal of Flotation Products.** R. S. LEWIS. *Mining and Scientific Press*, Vol. 114 (1917), No. 4, pp. 475-484.
- Flotation: Percentage of Oil in Flotation.** H. A. MURRAY. *Engineering and Mining Journal*, Vol. 103 (1917), No. 18, pp. 779-781.
- Furnace: Test of Recuperative Gas Oven Furnace.** W. C. BUELL, JR. *The Iron Age*, Vol. 99 (1917), No. 18, pp. 1082-1084.
- Gases in Cast Iron.** E. A. CRISTE. *The Iron Trade Review*, Vol. 60 (1917), No. 1, pp. 925-926.
- Gearing Development through Treatment.** W. H. PHILLIPS. *American Ship Builder*, Vol. 16 (1917), No. 8, pp. 112-114.
- Grading of Crushed Stone and Gravel Feldspar, Fireworks and Flour.** E. S. WARD. *Metalurgical and Chemical Engineering*, Vol. 16 (1917), No. 8, pp. 449-453.
- Grain Size Determination and Standardization.** ZAV JEFFRIES. *Metal, Iron and Chemical Engineering*, Vol. 16 (1917), No. 9, pp. 595-598.
- Handling Ashes at Steel Plants.** H. E. BUNCH. *The Iron Age*, Vol. 99 (1917), No. 16, pp. 939-931.
- Heat Balance of an Absorption Plant.** J. C. SMALLWOOD. *Power*, Vol. 45 (1917), No. 15, pp. 482-484.
- Ores: Characteristics of Magmatic Sulfide Ores.** C. E. THOMAS, JR. and A. F. ROBERTS. *Mining and Scientific Press*, Vol. 114 (1917), No. 16, pp. 530-531.
- Oxidation and Reduction in Physical Chemistry.** J. O. HEDGECOCK. *Modern Physical and Chemical Chemistry*, Vol. 16 (1917), No. 4, pp. 50-59.
- Petroleum: Chemical Nature of Petroleum Cracking.** ROY GRANT. *Hydrocarbon Chemistry*, Vol. 2 (1917), No. 1, pp. 1-10.
- Potash: Recovery of Potash as a By-Product in the Manufacture of Cement.** J. I. BUCKLEY. *1917 Proceedings, American*, Vol. 46 (1917), No. 9, p. 57.
- Pounds of Air per Pound of Coal.** A. J. ALLEN. *Power*, Vol. 45 (1917), No. 1, pp. 5-11.
- Refractories: A Study of Silica Refractories.** J. E. McLENDON. *Power*, Vol. 45 (1917), No. 60, pp. 50-51.
- Refractory Linings and Materials.** W. A. HATHAWAY. *Modern Engineering and Construction*, Vol. 8 (1917), No. 4, pp. 10-11.
- Size Experiments: A New Test for Size Experiments.** A. A. GARDNER. *Power*, Vol. 45 (1917), No. 1, pp. 12-13.

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON MAY 20

INORGANIC CHEMICALS

Acetate of Lime.....	100 Lbs.	4.50	@	4.55
Alum. lump ammonia.....	100 Lbs.	4.00	@	4.25
Aluminum Sulfate, high-grade.....	Ton	70.00	@	80.00
Ammonium Carbonate, domestic.....	Lb.	10 1/2	@	11
Ammonium Chloride, white.....	Lb.	16 1/2	@	17
Aqua Ammonia, 26° drums.....	Lb.	6	■	6 1/4
Arsenic, white.....	Lb.	17	@	17 1/2
Barium Chloride.....	Ton	85.00	@	90.00
Barium Nitrate.....	Lb.	10	@	11
Barytes, prime white, foreign.....	Ton	30.00	@	40.00
Bleaching Powder, 35 per cent.....	100 Lbs.	3.75	@	4.00
Blue Vitriol.....	Lb.	9 1/2	@	10
Borax, crystals, in bags.....	Lb.	7 1/4	@	8 1/2
Boric Acid, powdered crystals.....	Lb.	13	@	13 1/2
Brimstone, crude, domestic.....	Long Ton			45.00
Bromine, technical, bulk.....	Lb.	83	@	1.00
Calcium Chloride, lump, 70 to 75% fused.....	Ton	30.00	@	32.00
Caustic Soda, 76 per cent.....	Lb.	6.15	@	6.35
Chalk, light precipitated.....	Lb.	4 1/2	@	4 1/2
China Clay, imported.....	Ton	18.00	@	30.00
Feldspar.....	Ton	8.00	@	15.00
Pulver's Earth, foreign, powdered.....	Ton			35.00
Glauber's Salt, in bbls.....	100 Lbs.	65	@	70
Green Vitriol bulk.....	100 Lbs.	1.05	@	1.10
Hydrochloric Acid commercial, 18°.....	Lb.	1 1/2	@	1 1/2
Hydrochloric Acid, C. P., conc., 22°.....	Lb.	1 1/4	@	2
Iodine, resublimed.....	Lb.	3.50	@	3.55
Lead Acetate, white crystals.....	Lb.	15	@	15 1/2
Lead Nitrate.....	Lb.	15 1/2	@	16
Litharge, American.....	Lb.	11	@	11 1/2
Lithium Carbonate.....	Lb.			1.25
Magnesium Carbonate, U. S. P.....	Lb.	24	@	26
Magnesite, "Calcedined".....	Ton	60.00	@	65.00
Nitric Acid, 36°.....	Lb.	6 1/4	@	6 1/4
Nitric Acid 42°.....	Lb.	7 1/2	@	8 1/2
Phosphoric Acid, sp. gr. 1.710.....	Lb.	3 1/2	@	3 1/2
Phosphorus yellow.....	Lb.	1.15	@	1.25
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, casks.....	Lb.	36	@	37
Potassium Bromide (granular).....	100 Lbs.	1.00	@	1.10
Potassium Carbonate, calcined, 80 @ 85%.....	Lb.	48	@	70
Potassium Chlorate, crystals, spot.....	Lb.	57	@	60
Potassium Cyanide, bulk, 98-99 per cent.....	Mixture	2.15	@	2.20
Potassium Hydroxide, 88 @ 92%.....	Lb.	85	@	87
Potassium Iodide, bulk.....	Lb.			2.90
Potassium Nitrate.....	Lb.	31	@	34
Potassium Permanganate, bulk.....	Lb.	3.85	@	4.00
Quicksilver, flask.....	75 lbs	105.00	@	106.00
Red Lead, American, dry.....	Ton	18.00	@	20.00
Salt Cake, glass makers'.....	Lb.	11 1/2	@	11
Silver Nitrate.....	Oz.			46 1/2
Soapstone in bags.....	Ton	10.00	@	12.50
Soda Ash, 58%, in bags.....	100 Lbs.	2.80	@	2.90
Sodium Acetate.....	Lb.	8 1/2	@	9 1/2
Sodium Bicarbonate, domestic.....	100 Lbs.	2.10	@	2.25
Sodium Bichromate.....	Lb.	15 1/2	@	16
Sodium Chlorate.....	Lb.	23 1/2	@	24 1/2
Sodium Fluoride, commercial.....	Lb.	12 1/2	@	13 1/2
Sodium Hyposulfite.....	100 Lbs.	1.85	@	2.00
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	4.05	@	4.15
Sodium Silicate, liquid, 40° Bé.....	100 Lbs.	1.25	@	1.50
Sodium Sulfide, 30%, crystals, in bbls.....	Lb.	2 1/2	@	3
Sodium Bisulfite, powdered.....	Lb.	0 1/2	@	0 1/2
Strontium Nitrate.....	Lb.	28	@	30
Sulfur, flowers, sublimed.....	100 Lbs.	3.05	@	3.45
Sulfur, roll.....	100 Lbs.	2.85	@	3.25
Sulfuric Acid, chamber, 66° Bé.....	Ton	30.00	@	32.00
Sulfuric Acid, oleum (fuming).....	Ton	40.00	@	42.00
Talc, American white.....	Ton	10.00	@	12.00
Terra Alba, American, No. 1.....	100 Lbs.	85	@	90
Tin Bichloride, 50°.....	100 Lbs.			17.50
Tin Oxide.....	Lb.	65	@	66
White Lead, American, dry.....	Lb.	10	@	10 1/2
Zinc Carbonate.....	Lb.	25	@	27
Zinc Chloride, commercial.....	Lb.	16	@	17
Zinc Oxide, American process XX.....	Lb.	13	@	14

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	54	@	56
Acetic Acid, 56 per cent, in bbls.....	Lb.	50 1/2	@	51
Acetic Acid, glacial, 99 1/4%, in carboys.....	Lb.	28	@	30
Acetone, drums.....	Lb.	27	@	29
Alcohol, denatured, 180 proof.....	Gal.	72	@	74

Alcohol, grain, 188 proof.....	Gal.	3.04	@	3.06
Alcohol, wood, 95 per cent, refined.....	Gal.	1.00	@	1.02
Amyl Acetate.....	Gal.	3.60	@	3.80
Aniline Oil.....	Lb.	30	@	30 1/2
Benzoic Acid, ex-toluol.....	Lb.	6.75	@	7.50
Benzol, 90 per cent.....	Gal.	59	@	60
Camphor, refined in bulk, bbls.....	Lb.	89	@	90
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	42	@	44
Carbon Bisulfide.....	Lb.	6 1/2	@	7
Carbon Tetrachloride, drums, 100 gals.....	Lb.	16	@	17
Chloroform.....	Lb.	60	@	61
Citric Acid, domestic, crystals.....	Lb.	74	@	75
Cresote, beechwood.....	Lb.	1.90	@	2.00
Cresol, U. S. P.....	Gal.	1.25	@	1.30
Dextrine, corn (carload, bags).....	100 Lbs.	6.05	@	6.10
Dextrine, imported potato.....	Lb.	15 1/2	@	16
Ether, U. S. P., 1900.....	Lb.	23	@	30
Formaldehyde, 40 per cent.....	Lb.	17	@	18
Glycerine, dynamite, drums included.....	Lb.	56 1/2	@	60
Oxalic Acid, in casks.....	Lb.	45	@	47
Pyrogallol Acid, resublimed bulk.....	Lb.			3.25
Salicylic Acid.....	Lb.	1.10	@	1.25
Starch, cassava.....	Lb.			—
Starch, corn (carload, bags) pearl.....	100 Lbs.	4.75	@	4.80
Starch, potato.....	Lb.	13 1/2	@	15
Starch, rice.....	Lb.	10 1/4	@	11
Flour, sago.....	Lb.	6	@	6 1/2
Starch, wheat.....	Lb.	5 1/4	@	6 1/2
Tannic Acid, commercial.....	Lb.	45	@	50
Tartaric Acid, crystals.....	Lb.	79	@	80

OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	55	@	60
Black Mineral Oil, 29 gravity.....	Lb.	13 1/2	@	14
Castor Oil, No. 3.....	Lb.	24 1/2	@	25
Ceresin, yellow.....	Lb.	16	@	19
Corn Oil, crude.....	100 Lbs.	15 1/2	@	16
Cottonseed Oil, crude, f. o. b. mill.....	Gal.	1.10	@	1.11
Cottonseed Oil, p. a. y.....	Lb.	16 1/2	@	16 1/2
Menhaden Oil, crude (southern).....	Gal.			80
Neat's foot Oil, 20°.....	Gal.	1.60	@	1.65
Paraffine, crude, 118 to 120 m. p.....	Lb.	7 1/4	@	7 1/2
Paraffine Oil, high viscosity.....	Gal.	29 1/2	@	30
Rosin, "F" Grade, 280 lbs.....	Bbl.	6.50	@	—
Rosin Oil, first run.....	Gal.			37
Shellac, T. N.....	Lb.	57	@	58
Spermaceti, cake.....	Lb.	25	@	—
Sperm Oil, bleached winter, 38°.....	Gal.			nominal
Spindle Oil, No. 200.....	Gal.	24	@	25
Stearic Acid, double-pressed.....	Lb.	23	@	23 1/2
Tallow, acidless.....	Gal.	1.40	@	nominal
Tar Oil, distilled.....	Gal.	30	@	32
Turpentine, spirits of.....	Gal.	48	@	48 1/2

METALS

Aluminum, No. 1, ingots.....	Lb.	59	@	61
Antimony, ordinary.....	Lb.	26	@	27
Bismuth, N. Y.....	Lb.	3.00	@	3.10
Copper, electrolytic.....	Lb.			32
Copper, lake.....	Lb.			32
Lead, N. Y.....	100 Lbs.	10	@	10 1/2
Nickel, electrolytic.....	Lb.	55	@	56
Platinum, refined, soft.....	Oz.			105.00
Silver.....	Oz.			74 1/4
Tin, Straits.....	Lb.	66	@	66 1/2
Tungsten (WGs).....	Per Unit	17.00	@	18.00
Zinc, N. Y.....	100 Lbs.	9	@	9 1/2

FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	5.75	@	6.00
Blood, dried, f. o. b. Chicago.....	Unit			4.85
Bone, 4 and 50, ground raw.....	Ton	32.00	@	38.00
Calcium Cyanamid.....	Unit of Ammonia			—
Calcium Nitrate, Norwegian.....	100 Lbs			—
Castor Meal.....	Unit			—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	8.00	@	10
Phosphate, acid, 16 per cent.....	Ton	14	@	15
Phosphate rock, f. o. b. mine.....				—
Florida land pebble, 68 per cent.....	Ton	2.00	@	2.25
Tennessee, 78-80 per cent.....	Ton	5.00	@	5.50
Potassium "muriate," basis 80 per cent.....	Ton	38.00	@	400.00
Pyrites, furnace size, imported.....	Unit			nominal
Tankage, high-grade, f. o. b. Chicago.....	Unit	4.85	@	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

AT EASTON, PA.

Volume IX

JULY 1, 1917

No. 7

Editor: CHARLES H. HERTY

Assistant Editor: LEOLA E. MARES

Advertising Manager: M. A. WILLIAMSON

ADVISORY BOARD

H. E. BARNARD, H. K. BENSON, F. K. CAMERON, B. C. HESSE, A. D. LITTLE, A. V. H. MORY, M. C. WHITAKER

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly; single copy, 60 cents.
Price per single copy to American Chemical Society members, 50 cents. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted.
Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

All communications should be sent to The Journal of Industrial and Engineering Chemistry.

Telephone: Vanderbilt 1930

35 East 41st Street, New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

First Place to Government Needs.....	636
Greetings to Professor Grignard.....	636
Chemical Statistics Assured.....	636
The Tariff Commission and Schedule A.....	636
The September Meeting.....	637
Concerning the Exposition of Chemical Industries.....	637
Another Possible Form of Cooperation between Universities and the Chemical Industries.....	638
Friendly Confirmation of a Policy.....	638

THE PRESENT STATUS OF AMERICAN CHEMISTS AND WAR SERVICE.....	639
--	-----

ORIGINAL PAPERS:

Results of Recent Investigations of the Smelter Smoke Problem. A. E. Wells.....	640
The Nature of Cement Mill Potash. R. J. Nestell and E. Anderson.....	646
Some Relations of the Effect of Overheating to Certain Physical and Chemical Properties of Asphalts. A. W. Hixson and Harold E. Hands.....	651
Observations on the Action of Sulfur Monochloride on Bituminous and Tarry Substances and Hydrocarbon Oils. Joseph V. Meigs.....	658
The Physical Testing of Paper as Affected by Humidity. Ross Campbell.....	658
The Occurrence of Germanium in Missouri and Wisconsin Blends. G. H. Buchanan.....	661
Phosphor Tin and a Volumetric Method for Its Analysis. Richard Edwin Lee, W. H. Fegeley and Frank H. Reichel.....	663
The Electrometric Titration of Zinc. F. Russell v. Bichowsky.....	668
A New Method of Separating Zinc from Cadmium and the Latter's Determination Iodometrically. Eric John Ersson.....	671
The Chemical Examination of Natural Brines. O. R. Sweeney and James R. Withrow.....	671
Seasonal Distribution of Soil and Fecal Strains of the Colon Aerogenes Group in Surface Waters. Myrtle Greenfield and W. N. Skoufup.....	673
The Examination of Canned Salmon for Bacteria and Toxins. L. D. Bushnell and C. A. A. Uhl.....	688
The Industrial Chemistry of Chicle and Chewing Gum. Frederic Danneberg.....	699

Reversion of Acid Phosphate. Carlton C. James.....	682
A Rapid Method for the Determination of Water-Soluble Arsenic in Lead Arsenate. H. A. Scholz and P. J. Waldstein.....	682

LABORATORY AND PLANT:

Safeguarding the Eyes of Industrial Workers.....	683
Recovery of Molybdenum Residues. Victor Lenher and M. P. Schultz.....	684
Note: Organic Chemical Reagents for Scientific and Technical Laboratories. Roger Adams.....	685
An Evaporating Bath of Sea Sand Heated by Steam. P. P. Peterson.....	686
An Improved Form of a Fumeless Digestion Apparatus. J. S. McHargue.....	686
A Note on An Automatic Suction Attachment for an Ordinary Pipette. J. P. Schroeder.....	687

ADDRESSES:

Potash and a World Emergency. W. C. Ebaugh.....	688
The Recovery of Potash from Beet-Sugar House Waste Liquors. H. E. Zitkowski.....	692
The Influence of Pigments on Rubber. Maximilian Toch.....	693
Industrial Waste Disposal. Harrison P. Eddy.....	696
The Economic Resources of the Kansas City Zone. Arthur J. Boynton.....	700
The New Zinc Fields of Kansas-Oklahoma. Winthrop P. Hayes.....	706
The Legal Status and the Character of Work Done by the Kansas State Board of Health Water and Sewage Laboratory. C. C. Young.....	708
Some Machinery Employed in the Manufacture of Glue. Arthur Lowenstein.....	710

CURRENT INDUSTRIAL NEWS

OBITUARIES.....	711
Julius O. Schlotterback.....	711
Alois Von Isakovics.....	716
NOTES AND CORRESPONDENCE.....	716
WASHINGTON LETTER.....	717
PERSONAL NOTES.....	718
INDUSTRIAL NOTES.....	719
GOVERNMENT PUBLICATIONS.....	724
NEW PUBLICATIONS.....	725
MARKET REPORT.....	728

EDITORIALS

FIRST PLACE TO GOVERNMENT NEEDS

It is the desire of THIS JOURNAL to be of any service possible to the chemists of our government who are charged with the investigation of special problems connected with the war; likewise to serve those chemists who in university and private laboratories are patriotically coöperating with the government in the solution of such problems. In this spirit we therefore gladly depart from normal editorial policy and beg to tender to all such chemists throughout the continuance of the war this first portion of the editorial section for announcing any needs which may arise in the prosecution of their important work.

Dr. W. F. Hillebrand, Acting Director of the Bureau of Standards, under date of June 14, 1917, asks that publicity be given to the following:

GAS INTERFEROMETER NEEDED

The National Bureau of Standards requires for immediate use in an important military investigation several gas interferometers and desires information as to where such apparatus can be purchased or borrowed. The apparatus needed is the Rayleigh gas interferometer with gas tubes 100 cm. long of the form built by the Zeiss Company, or an apparatus equivalent to this. Any information relating to such apparatus should be forwarded to the Director, Bureau of Standards, Washington, D. C., Attention of Gas Laboratory.

GREETINGS TO PROFESSOR GRIGNARD

Among the distinguished members of the scientific commissions from France and England now visiting this country, chemists will be especially interested in the presence of Professor V. Grignard of France. He has come to us at the request of the National Research Council to confer with the Chemistry Committee of the Council and with our War and Navy Departments, and to give us the benefit of the experience which two years of war have brought to the chemical profession in his country. Appreciation of Professor Grignard's brilliant achievements in chemical research and respect for his sound judgment, make doubly warm the hearty greetings which all American chemists extend to him.

CHEMICAL STATISTICS ASSURED

It is a great pleasure to be able to announce the completion of the two thousand-dollar fund for the coöperation of the American Chemical Society with the Bureau of Foreign and Domestic Commerce in the compilation of a census of imports of chemicals other than dyestuffs in a typical pre-war fiscal year. The hope expressed at the conclusion of the rather despondent editorial on this subject in the June issue has been justified; the full amount has been pledged, and the work can now promptly begin.

The detailed itemization of these imports, together with the amounts of each, will constitute a valuable and safe guide to those who patriotically desire for our country national self-containedness in its chemical industries.

There is a deeper significance in this movement, however, than the compilation of such a census. The fund subscribed by representatives of the chemical industries is proof of a desire not only for information from government records on the basis of which new lines of needed manufacture may be inaugurated, but also for prompt and regular issuance of statistics on current imports, which will give invaluable aid to the continued, healthy growth of all of our chemical industries. If those in charge of and responsible for such matters will but compare the character of the information on imports now furnished our chemical manufacturers with that which the German government has for years furnished its manufacturers, they will readily see to how great an extent we have been handicapped by lack of such basic facts. The many problems now to be solved concerning the character of the classifications and itemizations of this census will determine the form of the statistics on current imports. Again we express a hope, namely, that complete statistics on current chemical imports will soon become an asset of the American chemical manufacturer.

THE TARIFF COMMISSION AND SCHEDULE A

Soon after its organization the Tariff Commission announced that it would begin at an early date a thorough investigation of Schedule A (chemicals). To aid the Commission in this complex field an expert adviser was to be appointed. In this connection the following letter was received, under date of May 31, 1917, from Dr. F. W. Taussig, Chairman of the United States Tariff Commission:

My dear Dr. Herty:

It will interest you, I believe, to know that the Tariff Commission has appointed Professor Grinnell Jones to act as Special Expert in connection with its inquiries upon the chemical industries of the country and Schedule A of the existing tariff act.

As you know, the Tariff Commission conferred with Professor Stieglitz and the Advisory Council of the Chemical Society and secured from the Council lists and recommendations of chemists whose services would be helpful to the Commission. Some of the gentlemen suggested proved not to be able to give continuous service, such as is necessary for the work of the Commission, and we finally selected Professor Jones. We are glad to have been able to act in coöperation with the Chemical Society and are indebted to you for the suggestion which led to this coöperation. There is no reason now why public mention of the action taken by the Commission should not be made.

This action of the Tariff Commission gives rise to several very pleasant reflections.

Heartiest congratulations to Professor Grinnell Jones upon the unsolicited opportunity thus afforded for public service of nation-wide import! Likewise congratulations to the Tariff Commission upon having secured for its expert adviser in matters pertaining to the chemical industries one of the brilliant young chemists of America whose attainments and character assure thoroughness, accuracy of detail, breadth of vision, uncompromising rectitude and patriotic loyalty!

The fine suggestion by Dr. B. C. Hesse for a Board of Control for the Society in national matters, as presented at the Kansas City Meeting of the Council, has already borne fruit. Pending the determination of certain constitutional questions the Council appointed a committee along the lines suggested by Dr. Hesse to advise the President of the Society on all matters of national bearing. When, therefore, President Stieglitz received from Chairman Taussig a request for immediate nominations for this office the machinery was already provided to give prompt recommendations.

We are confident that all will appreciate the action of the Tariff Commission in thus seeking the counsel of the organized body of American chemists. Too often appointment to public office is accompanied by an unseemly scramble of office seekers for recommendations and for political influence, not to mention persistent personal pleas. All such have here been avoided.

Another reflection, to which we are always glad to give expression, is the value of organization. Sometimes in the past we have heard men say, "Why should I spend my money on dues to the American Chemical Society? I get the benefit of the journals in the library of the Company (or University)." We believe that the present phenomenal growth of the membership of the Society is due to a constantly increasing appreciation of the fact that the Society is more than a mere publisher of journals; more and more its function as a great national force is being recognized, and as it expands to a more complete inclusion of all American chemists that force correspondingly increases. In such days as these no man can afford to live to himself or for himself alone.

THE SEPTEMBER MEETING

On Saturday, May 26, 1917, the Directors of the Society, at a special meeting, considered in all of its bearings the holding of an Annual Meeting this fall. As a result of their deliberations it was decided that the meeting should be held at Boston in September as previously voted by the Council.

The Council will meet on the afternoon and evening of Monday, September 10, 1917. The meetings of the Society will take place on September 11, 12 and 13. The Northeastern Section has been requested by the Directors to omit the usual annual banquet and excursions, and to arrange a program characterized by simplicity and seriousness, and bearing as fully as possible on questions concerning the activities of chemists both in the government service and in the industries during the present war.

The General Meeting will be held on Tuesday morning. This will be followed in the afternoon by a general conference to be opened by Dr. W. H. Nichols, Chairman of the Committee on Chemicals of the National Defense Council, and by Dr. M. F. Bogert, Chairman of the Chemistry Committee of the National Research Council, the conference then to be continued from the floor. It is expected that an informal, yet together meeting of a social character will be held on Tuesday

evening, at which time opportunity will be given for informal discussion of problems of the day.

Wednesday morning will be devoted to divisional conferences, and the afternoon to divisional meetings, with papers, or a continuation of the conferences, as the divisions may decide. The presidential address will be delivered on Wednesday evening.

Thursday, both morning and afternoon, will be given to divisional meetings.

We feel confident that the decision of the Directors to hold the Annual Meeting, and along the lines above mentioned, will receive the hearty endorsement of all members of the Society. The gravity of the times makes fitting the elimination of the usual social functions; at the same time it is the compelling reason for a thoughtful assembly of chemists. In the conferences planned opportunity will be given for sounding the keynote of the present situation and for adjusting viewpoints to the new conditions under which we are now working. The country needs the judgment of its chemists on many phases of war conditions. This judgment can best be reached through the inspiration of the spoken word in the conferences, where opportunity will be afforded for interchange of views by men from all sections of the country. This meeting will be no holiday occasion—it should prove a well-spring of strength for our country.

CONCERNING THE EXPOSITION OF CHEMICAL INDUSTRIES

In the midst of the present general upheaval of normal conditions there has been evident from time to time somewhat hysterical agitation of certain ideas which, while of undoubted value, by no means admit of general application. For example, it has been suggested in some quarters that under present conditions the Third National Exposition of Chemical Industries should be abandoned. Against this suggestion, fortunately confined to a very limited number of proponents, we wish to enter most earnest and emphatic protest. This unhesitating protest is based upon the record of what the two previous Expositions have proved themselves to be and upon the thought and purpose which underlie the great expansion already assured this third occasion.

There can be no difference of opinion as to the impropriety of holding this year expositions of the usual popular type. While nominally based upon some historic event of our national life, and while marking through various exhibits certain definite steps forward in industrial life, nevertheless, such expositions really serve as occasions for holiday trips, for recreation, for holiday or simply for amusement. As a result we are in no mood for such events.

The National Exposition of Chemical Industries, on the other hand, has an entirely different purpose. From the outset it was charged with the responsibility of stimulating the nation, to have never sought to make of its exhibit a "show," but from common sense and to the belief that the American people would be thoughtfully interested in exhibitions arranged with illustrations of the real progress in industry which

holds within itself so much of fascinating interest and which, at the same time, has such deep significance for our national welfare. Results have proved that this conviction was fully justified.

It was further believed that through this popular insight into the work of the chemist there would be brought about a truer conception of the function of the chemist in all phases of industrial life. In this way the exposition has already stimulated the establishment of laboratories for control and for research in many industrial organizations which hitherto had never had the benefit of this means of efficiency and rational advance.

The spirit of the Exposition has never been one of self-glorification of an industry which seeks to flatter itself by boasting of past accomplishments, but rather has been that of a fearless exhibition of shortcomings, in order that the way might be clearly indicated for future effort. The Exposition has portrayed the splendid achievements of the past only for the purpose of gaining courage and confidence for the greater work of the future.

Up to the present the development of the ideals of the Exposition has been chiefly along the lines of products manufactured and the machinery utilized in their production. If, however, the full service of the Exposition is to be rendered it must act as a coordinating influence in the cooperation of all those factors which go to make up a truly great chemical industry. To the expert knowledge of the chemist and the skill of the machine builder must be added the confidence of capital and an intimate knowledge of the sources of raw materials. It is hoped that this third Exposition will result in marked progress in these two lines. Of all periods in our history this is the most urgent for such progress to be made. The real sinews of war must be furnished by the chemical industries; whatever contributes to their welfare brings the day of a righteous peace nearer.

For these reasons we feel that the Third National Exposition of Chemical Industries should be held next September as planned, confident that its continued growth and evolution will be attended by results of deepest significance to the welfare of our country.

ANOTHER POSSIBLE FORM OF COÖPERATION BETWEEN UNIVERSITIES AND THE CHEMICAL INDUSTRIES

We have recently received a letter from a member of the chemistry staff of a well-known university from which the following paragraph is quoted:

I wish to come into closer touch with industrial plants as an actual worker during the summer months' vacation. This would give me a more intimate knowledge of present works conditions and thus enable me better to prepare and advise my students to meet the present industrial demands. It would temporarily help to relieve the apparent present stress in some industry until the younger and less experienced men were broken in, would increase my effectiveness in the preparation of chemical engineers, and I could assuredly give full value for any compensation advanced me.

It is fully realized that this is not the first time such a desire has been expressed, and that in the past

the temporary character of the proposal has proved a bar to its acceptance. However, the changes in the personnel of plant forces due to enlistment and to the draft may give rise this summer to abnormal conditions which might be relieved temporarily by additions from university forces. Certainly such plant experience would be reflected in better teaching during the next collegiate year, and in this matter the industries have a very direct interest.

The correspondent above quoted, asks this question—"Can you suggest any man or men to whom such a proposition might appeal to the extent of their offering such employment?"

Unfortunately, we had at the time no information which was of any value. This very shortcoming suggests a possible service and we therefore gladly offer to act as a clearing house of information on this subject for those professors and instructors who may care to file their names with us and for those in the chemical industries who may desire to have a list of such available men.

FRIENDLY CONFIRMATION OF A POLICY

In the June issue we urged the members of the Society to exert their personal influence in maintaining, and, indeed, in increasing the list of our advertisers under the new rates recommended by the Society's representatives. It is too early as yet to ascertain the extent of the response to this appeal. It is, nevertheless, a satisfaction to have received such an endorsement of the spirit of the appeal as was contained in the "lead-off" editorial of the *Manufacturers Record* in its issue of June 16, 1917. This is reproduced here with a few eliminations:

TO USE "THEIR PERSUASIVE POWERS"

The *Journal of Industrial and Engineering Chemistry*, published by the American Chemical Society, announces that, in view of increased cost of operation, the Publication Committee has recently decided to advance its rates 40 per cent, to take effect immediately; and in publishing this statement the *Journal* appeals to members of the Society to render valuable aid by "using their persuasive powers" in holding all former advertisers, and by urging those not now advertising to become advertisers in the *Journal*.

THE MANUFACTURERS RECORD has not as yet advanced its rates to meet these new conditions, notwithstanding the great increase in the cost of publication of this as of all other papers, but whenever it is compelled to do so, it trusts that it can appeal to its readers, as the *Journal of Industrial and Engineering Chemistry* has appealed to the members of the American Chemical Society, to use their "persuasive powers" to induce all advertisers to continue to advertise, and to induce those who are not now advertising to use the advertising pages of the MANUFACTURERS RECORD.

If we can have the hearty coöperation of all of our readers in furtherance of efforts to increase advertising and to make advertisers know the value to the readers of the MANUFACTURERS RECORD of these advertisements, we shall be glad to have learned the lesson from the *Journal of Industrial and Engineering Chemistry*.

A good example is being set to other publishers in facing the issue of higher cost of publication and the necessity for higher advertising rates, and in appealing to the readers of the publication to coöperate in holding and securing advertising in the publication. Success to this excellent campaign!

THE PRESENT STATUS OF AMERICAN CHEMISTS AND WAR SERVICE

For the information of all chemists there is given below the "Report on the War Service for Chemists" and the "Plan for the Impressment of Chemists for War Service as Chemists and for the Preservation of the Supply of Chemists", as recommended to the Council of National Defense by a committee consisting of William H. Nichols, M. T. Bogert, A. A. Noyes, Julius Stieglitz and C. L. Parsons. The documents were drafted after careful consideration of the experience of our Allies. Dr. William H. Nichols, chairman of the Coöperative Committee on Chemicals of the Advisory Commission of the Council of

National Defense, has embodied this material in his report with the recommendation that it be adopted by the Council of National Defense. That body has not yet acted upon the report, nor has any action been taken in regard to the status of chemists as a class; it is possible that the cases of chemists, drafted will have to be considered individually. Whatever action is taken, it must receive the approval of the President before becoming a fixed policy. The wording of this report, and the lack of final action thereon, would seem to make clear the patriotic duty of chemists at this time—WAIT! [EDITOR]

REPORT ON THE WAR SERVICE FOR CHEMISTS

Chemists and chemical engineers are normally needed in almost all branches of industry (including the standardization and control of food products) for the successful operation of processes, the detection and speedy correction of difficulties and the improvement of products. England, France, and Italy found it necessary to recall all chemists from the ranks; Canada does not allow chemists to enlist; chemists have saved Germany up to the present time.

There was a decided shortage in the supply of chemists in the United States even before April 1914. The war has made the shortage acute, and it is certain that our own war needs and industries necessary to war will absorb chemists as rapidly as they can be trained.

It takes from four to seven years to train a chemist. The shorter time is for college graduates and chemical engineers who become wholly useful only after a further year of experience in a manufacturing plant or laboratory (corresponding to the hospital year required of medical students). The longer time is for the training of research men taking the doctorate degree in chemistry, on whose shoulders ultimately the vast need of the government and the industries fall for meeting and solving new difficulties and problems of organized research.

When chemists of mature years are called in for service in government laboratories, their places must be filled by younger men to keep the machinery working. It is, therefore, of the greatest importance that steps be taken:

1st—To keep and impress into service in chemical lines chemists drawn by the draft for service in the United States Army or Navy.

2nd—To provide means for keeping open sources of supply of chemists from universities, colleges, and schools of technology, and to procure volunteers in chemistry.

A tentative plan for accomplishing these results is hereby appended and recommended.

WILLIAM H. NICHOLS, *Chairman of the Chemistry Committee, National Defense Council*, Past President Society of Chemical Industry, President 8th International Congress of Applied Chemistry.

MARSTON T. BOGERT, *Chairman of the Chemistry Committee, National Research Council*, Past President American Chemical Society.

A. A. NOYES, *Past President American Chemical Society*.

JULIUS STIEGLITZ, *President American Chemical Society*.

CHARLES L. PARSONS, *Secretary American Chemical Society*.

PLAN FOR THE IMPRESSMENT OF CHEMISTS FOR WAR SERVICE AS CHEMISTS AND FOR THE PRESERVATION OF THE SUPPLY OF CHEMISTS

I—There shall be organized a Committee of three to advise the President of the United States through the War Department on requests for exemption of chemists. This committee might well include besides a Government representative two chemists, one a chemical engineer or technical chemist, the second a university man. These men should be nominated to the President by the Council of National Defense.

II—Requests for exemption of individual chemists shall be made to this committee by:

- (1) Government, State or Municipal Laboratories and Bureaus.
- (2) Heads of manufacturing plants on the basis of the imperative need of these men for their successful operation.
- (3) Presidents of Universities, Colleges, and Schools of Engineering or Mining on the basis of proficiency, promise and ability of candidates for college or university degrees, specializing in chemistry. Men recommended under this head who are candidates for the doctorate degree shall not be over 26 years of age when they receive the degree, and men who are candidates for a four-year college degree shall not be over 23 years of age when they are to receive the degree.

III—(1) Chemists under 21 and over 30 years of age and chemists between 21 and 30 who have not been drafted may enroll with the above committee as volunteers in chemistry subject to the same conditions as the enlisted and exempted men.

(2) Students in chemistry under 21 years of age may enroll with the above committee for a "chemistry reserve" under the conditions specified in II (3).

IV—Men thus enrolled and accepted under the provisions of the above paragraphs shall wear as chemists and shall be subject to the orders of the government as to location and hours of service and shall be entitled to wear a badge or other insignia indicating their official status (nature of branch and position of other European countries). Students enrolled in a "chemistry reserve" shall be subject to the same conditions as above for other reserves of the government and shall also be entitled to wear some insignia or badge indicating their enrollment.

ORIGINAL PAPERS

RESULTS OF RECENT INVESTIGATIONS OF THE SMELTER SMOKE PROBLEM¹

BY A. E. WHEELS

Received June 1, 1917

At many of the smelting plants throughout the United States, the smoke problem continues to be one of considerable importance. In fact, due to the increased tonnages of ores being handled during the last two years at many plants, some damage has been done by smoke where formerly no serious smoke troubles were encountered, and the problem in those places has assumed serious proportions. Elsewhere the problem has become important mainly because a greater number of those people engaged in agricultural pursuits in the vicinity of smelters have heard through various sources that the smelter smoke might be injurious to crops and to live stock; thus, whenever any adverse condition arises in districts contiguous to smelters, it has become the custom to blame the smelter smoke first, before trying to determine the true causes. Careful investigations in many cases have proved that the causes were wholly foreign to the smelter smoke. Whether actual damage has been on the increase, due to increased smoke output, or whether there has been a greater tendency on the part of the farmers and stock raisers to lay their natural crop and stock troubles at the door of the smelter smoke, the result has been that at many plants it has become necessary for the companies to enter upon careful investigations to determine the facts.

Believing that an outline of these investigations as carried out by the lead and copper smelting companies would be of interest to those who are directly concerned with the metallurgy of zinc, an attempt has been made in these pages to present this outline in as brief a form as possible.

As metallurgist on the smoke problem for the United States Bureau of Mines, the writer has been associated directly or indirectly with nearly all these investigations, and in many cases has assisted in the work. Co-operation with the smelting companies is possible in nearly every instance, because it is evident that the companies wish to have the true facts determined concerning the conditions in the zones around their plants. They are ready to face squarely any facts so determined which might be considered even detrimental to their interests, and are showing a willingness to go as far as practicable toward the ultimate solution of the problem by the elimination of the substances that are found to be the causes for damage. In general it might be stated that the companies are ready to meet the situation fairly, and that wherever there is a possibility of injury resulting from their present methods of operation, they are ready to make decided improvements. These improvements often involve expenditures of money beyond those yielding any financial return.

As this can be but a brief presentation of some of the most important features of the smoke problem, it will be necessary to dismiss with a few words any consideration of the dust and metallic fume element of the smoke, as this element is of minor importance.

DUST AND METALLIC FUME ELEMENT OF MINOR IMPORTANCE

The investigations that have been conducted during the last few years, including those of the Selby Smelter Commission,¹ American Smelting and Refining Co., etc., have proven conclusively that as far as damage to vegetation is concerned, dust and fume particles or acid mist are practically negligible quantities. The effect of dust and fume particles upon animal life is another matter. No doubt some injury has been done and may now be done in certain places to animal life by the toxic salts in the smelter emanations where there have been large accumulations of these toxic salts on vegetation. Generally speaking, however, wherever the amount of dust and fume being emitted is so large as to constitute a menace to live stock in the community, it is found that the value of the solids being lost would pay a reasonable return on the investment necessary for installations to recover them, without any damage consideration being involved. In most cases it is a comparatively easy matter to recover the greater portion of the solids, and at the present time there is no excuse for a smelter turning large amounts of the solid constituents of the smoke into the atmosphere, especially if those solids are known to be causing injury to live stock.

SULFUR DIOXIDE PROBLEM MOST IMPORTANT

The most important problem, therefore, is the sulfur dioxide problem. At many plants where large quantities of sulfide ores are being handled serious efforts are being made to utilize the waste sulfur dioxide through the manufacture of sulfuric acid, liquid sulfur dioxide and even elementary sulfur. Technical methods have been worked out for accomplishing the last two schemes, and small scale commercial plants erected. Two of the largest copper smelters of the west, namely, Anaconda and Garfield, have recently made heavy investments in acid plants. However, many plants are situated at such great distances from the markets for these products that only a comparatively small amount of the available sulfur dioxide can be utilized. It is recognized that although the amount of the waste sulfur gases that will be utilized in commercial products will be steadily increasing, yet for many years to come the smelters will be obliged to waste large quantities of sulfur dioxide into the atmosphere. Thus, investigations are in progress to determine how, under different climatic and topographic conditions, these volumes of sulfur dioxide, whether large or small, can be discharged into the atmosphere without causing injury to vegetation in the surrounding country.

¹ See THIS JOURNAL, 7 (1915), 41, for abstract of Selby Smelter Commission report.

¹ Presented at the Symposium on the Chemistry and Metallurgy of Zinc, 56th Meeting American Chemical Society, Kansas City, April 12, 1917.

Published with the permission of the Director of the Bureau of Mines.

EFFECTS OF BLEACHING ON YIELD

In this connection it is necessary to determine first of all what are the effects, both in regard to superficial bleaching and in regard to the economic results on yield, of applying various concentrations of sulfur dioxide to various forms of plant life and under different atmospheric conditions. If the time were available, it would be interesting to discuss the earlier methods that were used in this country and in Germany for determining the effect of sulfur dioxide on vegetation, and to show wherein the vast amount of data that were determined by these investigations are of no value as furnishing data upon which to base definite conclusions. It is necessary to dismiss any consideration of these investigations with the brief statement that in none, whether the tests were made in cabinets, glass jars or in smoke houses, were normal field conditions even approximated, nor was there any knowledge of the actual concentration of the sulfur dioxide in contact with the plants, nor of the atmospheric conditions. A knowledge of the attendant atmospheric conditions is of the greatest importance.

The first research work along the line of making determinations under actual field conditions was that done by the Selby Smelter Commission. In these determinations, known volumes of air containing known definite concentrations of sulfur dioxide were blown for definite periods of time under known atmospheric conditions over plants growing normally in the field. A cabinet framed with wood and with celluloid sheets for the sides was placed over the plants during the period of investigation, which varied between two minutes and eight hours. Check plots were fumigated simultaneously under the same conditions with air containing no sulfur dioxide. All the determinations of the Selby Commission were made on barley, as this was supposed to be the most sensitive of all the crops.

The department of smoke investigations for the American Smelting and Refining Company in Utah, under the direction of Mr. P. J. O'Gara and Mr. E. P. Fleming, has continued the work that was started by the Selby Commission, and, through many elaborate series of careful and detailed investigations, has obtained a vast amount of reliable and definite data on the smoke problem, especially that phase of the problem concerned with sulfur dioxide. As far as the data obtained by the Selby Commission went, they were checked quite closely by those obtained by later tests. However, the work of the A. S. & R. Co. was carried out on a much larger scale, and the experiments covered so much greater range in the number of crops treated, and in regard to variety of atmospheric conditions, that comparison cannot be carried very far.

In conducting these investigations, the smoke department of the A. S. & R. Co. has endeavored to determine if damage was being done in the vicinity of the smelters by the smoke, if so, how it was done and to what extent the damage was of economic importance. These investigations were carried further to determine what steps were necessary to prevent such damage. As soon as it was evident that such inves-

tigations were producing reliable and tangible data, and were answering in a definite manner many questions concerning the smoke problem, other companies followed their example, and at the present time companies in different parts of the country are carrying on similar studies, though on a much more modest scale. Wherever it is evident that there is no effort or desire to conceal data or twist them to suit convenient theories, it is the aim of the Bureau of Mines to co-operate and help in investigations as far as practicable.

The method used by the A. S. & R. Co. for determining the effect of sulfur dioxide on plant life was practically the same as that devised by the Selby Smelter Commission, improvement having been made in the method of introducing the air into the cabinet. In the experiments of the A. S. & R. Co., the experimental plots were 6 ft. by 6 ft. in area and cabinets were 4 ft. high. The fan delivered approximately 10 cubic meters of air per minute into the cabinet, this volume being sufficient to keep the temperature and relative humidity of the air in the cabinet similar to those of the outside air. In every experiment two plots were fumigated simultaneously, one with the sulfur dioxide mixture, the other with air free from sulfur dioxide, the latter being the check plot. The determinations were made on a great number of crops, including potatoes, tomatoes, sugar beets, cereals, alfalfa, red clover and garden truck. In 1915 and 1916 there were, in all, nearly 3000 experimental plots.

Besides the work in the field, experiments were made in which the gases were drawn from the top of the stack, these gases diluted to concentrations desired, and the mixture blown over plants that were grown in boxes under conditions similar to those in the field.

In order to determine to what extent visible bleaching affected the yield or whether an economic loss could be sustained by the crops without visible injury, it was necessary to harvest the experimental plots very carefully. Records were kept of the total yield of vegetable matter, and in the case of grains, the weight of grain, weight of kernels, number of kernels per head and percentage of germination. The A. S. & R. Co. have made complete analyses for protein, carbohydrates, fat, sulfur and crude fiber.

To summarize briefly, the fumigation tests have demonstrated these facts:

(1) Under certain atmospheric conditions, bleaching of crops, especially grain crops, can be produced by very small concentrations of sulfur dioxide, even as low as one part sulfur dioxide per million parts air, if the time of application is sufficiently long. The A. S. & R. Co. tests have demonstrated that other crops are much more resistant to sulfur dioxide than are the cereals, but that in all cases the concentrations required are low if the other factors are favorable for injury.

(2) A visible bleaching on grain and many other crops, if endured during the early stage of growth, does not necessarily affect the ultimate yield.

(3) A very small amount of bleaching can be sustained at all stages by the plants without serious effect on the yield greatly. In fact, in the latter part of the season, it was found that in order to increase the yield an even small

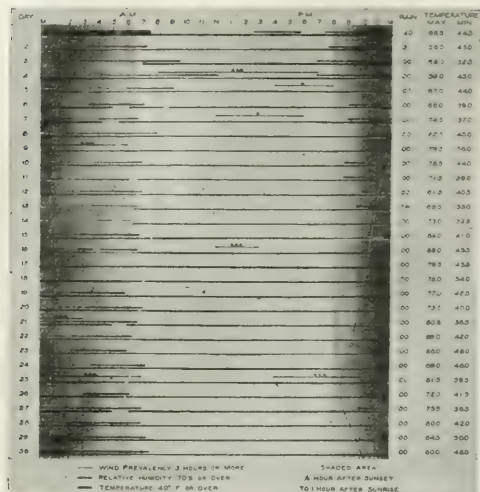


FIG. 1. COINCIDENCE OF LIGHT, RELATIVE HUMIDITY, WIND PREVALENCY AND TEMPERATURE, JUNE 1915

it was necessary to keep the plants very severely bleached during the entire growing season.

(4) There was no "invisible injury," that is to say, there was no economic loss in yield without there being a certain amount of visible bleaching. In fact it was found that in many of the fumigated plots that were treated daily with concentrations below the point of actual foliar markings, there was an actual increase in yield. Fumigated plots, even those considerably marked, as well as those treated daily without producing bleaching, showed an increase of protein above the check plots.

DETERMINATIONS OF BLEACHING CONDITIONS

The determination as to whether visible markings on crops produce economic loss has not been considered the most important phase of these investigations, although it has been necessary. The most important phase has been to determine the maximum amount of sulfur dioxide that can be present in the air without producing any bleaching under the atmospheric conditions most favorable for producing a bleach. Having determined that, it then becomes necessary so to regulate the height of discharge, concentration and temperature of the gases at the stack that the sulfur dioxide concentration in the air is less than that amount, and no injury will result.

It was established that sulfur dioxide in any such concentration as may be found in the vicinity of smelters can act on the plant only by being absorbed through the growing and functioning leaves. No action, unless it is a beneficial one, was found to take place through the soil. The beneficial effect of sulfur or sulfuric acid on soils will be discussed later in this paper. The epidermis of the plants is practically impervious to gases. It is only through the very minute breathing pores, or stomata, that all gases, including sulfur dioxide,

can pass into or out of the palisade cells and sponge-like tissue of the leaf where, under the action of light, plant food is manufactured. The opening and closing of these breathing pores or stomata are controlled by guard cells. As the walls of the guard cells, like the epidermis of the plant cells, are very impervious to gases, sulfur dioxide not excepted, whenever the breathing pores are closed by the guard cells, no gases can be absorbed by the plant, excepting under extremely high concentrations, far above those encountered under any imaginable conditions. Even carbon dioxide, which is an essential plant food and which is found normally at 300 p. p. m. in the air, is not absorbed by the plants when the stomata are closed. Thus, whenever the guard cells are closed, this generally taking place at night, the plants are much more resistant to sulfur dioxide than when the cells are open.

Furthermore, carbon assimilation does not take place at night, but only during hours of daylight, all other factors being favorable. It is believed that the nascent oxygen given off when carbon is assimilated is effective in oxidizing any sulfur dioxide in the cells to sulfuric acid, and this produces the injury to the plants. Thus at night, when no nascent oxygen is present in the cells, there would be less chance for injury by sulfur dioxide even if the cells were only partially closed.

LIGHT AND HUMIDITY conditions have a very marked effect upon the opening and closing of the breathing pores. For the most part the tendency is for plants to close their stomata during the night and open them during the day. It was found that in Salt Lake Valley, in the case of alfalfa and various other plants, nearly complete closure of the stomata is the normal condition at night, opening beginning an hour or more after sunrise and closure again taking place, on a normal day, during the evening. Closure may take place as early as 11 A.M. if the humidity is especially low. Low humidity is very effective in producing a collapse of the guard cells and thus closure of the stomata.

A great deal of study has been given to the examination of the effect of different intensities of light and degrees of humidity on the susceptibility of crops to sulfur dioxide. It was found, in the investigations of the A. S. & R. Co., that plants in complete darkness were from 5 to 6 times as resistant to sulfur dioxide as were plants in the light. Plants began to show resistance whenever the light value was as low as 2 per cent, but there was no difference between 8 per cent and 60 per cent values. It was determined, both in the work of the Selby Commission and in the work of the A. S. & R. Co., that humidity is of very great importance as affecting the susceptibility of crops to sulfur dioxide. In the Salt Lake Valley it was found that 70 per cent was about the critical humidity; above that point plants were much more susceptible to sulfur dioxide than below.

It may be stated that in any locality with a definite concentration of sulfur dioxide in the air, four factors must be in coincidence before injury will take place, namely temperature, light, relative humidity and wind prevalence, the latter determining the time of application of the sulfur dioxide. For example, in order that

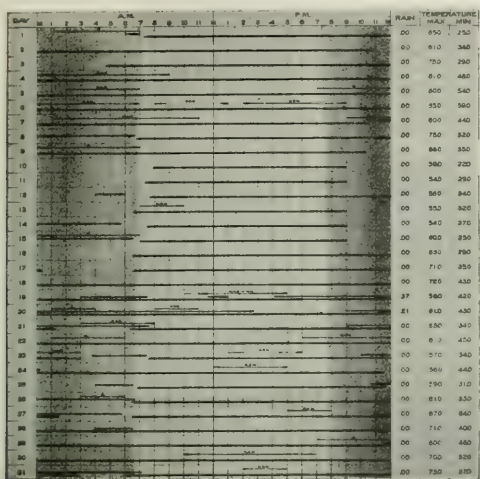


FIG. II—Coincidence of Light, Relative Humidity, Wind Prevalency and Temperature, May 1916

a concentration of one part sulfur dioxide in a million parts of air should produce bleaching on the most susceptible plants, *e. g.*, barley, oats, alfalfa, etc., it is necessary that this concentration exist around the plant for three hours and that the humidity shall be 70 per cent or more, the temperature above 40°, and that the fumigation should be made in the daylight. Under the same external conditions, greater concentrations would require shorter time of application. Under lower humidity conditions, higher concentrations or longer times of application were necessary to produce the same bleaching.

INFLUENCE OF WEATHER CONDITIONS

Thus, in order to know the possibilities of injury to vegetation in the region of smelters, one must determine not only the average and maximum values for the sulfur dioxide in the smoke stream, but also the weather conditions, that is, wind prevalence, relative humidity, temperature and light conditions. A knowledge is necessary of the number and duration of the critical periods, that is to say, the periods when all factors favorable for the bleaching of crops with small concentrations of sulfur dioxide are coincident. If these periods occur frequently or are of long duration, then the amount of sulfur dioxide that can be discharged into the air without doing injury must necessarily be lower than under more favorable conditions.

For the determination of the weather conditions, a complete installation of standard weather instruments is essential. This equipment must consist of wind vane, anemometer, thermometer, hygrometer, maximum and minimum thermometer, rotating psychrometer, sunshine bulb and rain gauge. The wind direction and velocity, sunshine and precipitation and relative humidity should be automatically recorded.

The American Smelting and Refining Co. during the last three years have kept a very accurate and clear record of the weather conditions around their plant

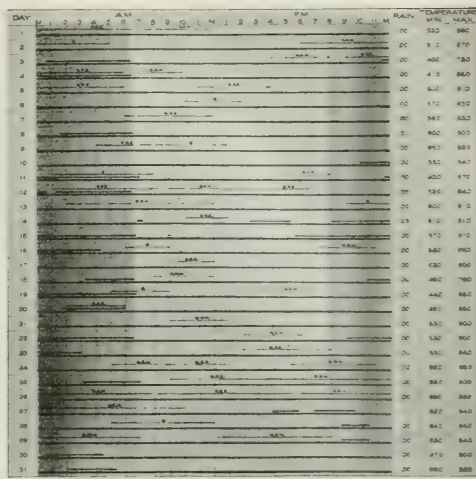


FIG. III—Coincidence of Light, Relative Humidity, Wind Prevalency and Temperature, July 1916

in Murray, Utah, and with their consent I will describe briefly their method of plotting the weather data so that the critical periods during the months can be seen readily. This method will surely be of value to those who are called upon to do similar work in other places.

It was found that in the Murray smoke zone, the sulfur dioxide concentrations in the air under the conditions existing in 1915-1916 were such that the critical weather conditions were: (1) temperature above 40° F.; (2) relative humidity above 70 per cent; (3) wind prevalence 3 hours or more; (4) daylight.

In Fig. I, the weather data for June 1915 are plotted to bring out the time of coincident factors. The shaded portion of the figure shows approximately the hours of darkness per day during which the stomata of the plants were normally closed and during which time very little gas was taken through the breathing pores of foliage. During hours included in the light portion, it may be assumed that the breathing pores were open. The lowest line shown in the space representing each day indicates the time during which the temperature was above 40° F. The line next above shows the hours during which the humidity was above 70 per cent, and the highest line, wherever it is present, shows that for at least 3 hrs. there was a prevalent wind. It is to be noted that on June 4 between 8 o'clock in the morning and 11 o'clock noon there was a lull in a hours when there was a steady south-southwest wind and humidity was above 70 and temperature above 40° F. The average sulfur dioxide concentration in the air in a southeast direction about the Murray plant during this time was above the value for these conditions and there was produced a well defined zone of bleaching in vegetation used as a test having the form of an elongated ellipse, pointing in a southeasterly direction from the plant. The Fig. 14 shows (theoretical) the May weather. On May 10, dark, another period of coincident weather conditions but on May 14 the wind shifted to the southwest and the temperature

weather observer at the Murray Smelter and the sulfur dioxide output was curtailed during that period, which lowered the concentration in the air. As a result no injury occurred.

At night, coincidences of three factors, *i. e.*, temperature, humidity and wind prevalence, frequently

by all the smelting companies for the determination of the sulfur dioxide condition of the atmosphere, is one that was devised originally by Mr. J. R. Marston, Chief Chemist at the Selby Smelter, and which was developed to its present high degree of accuracy, speed and ease of manipulation by the chemists of the Selby

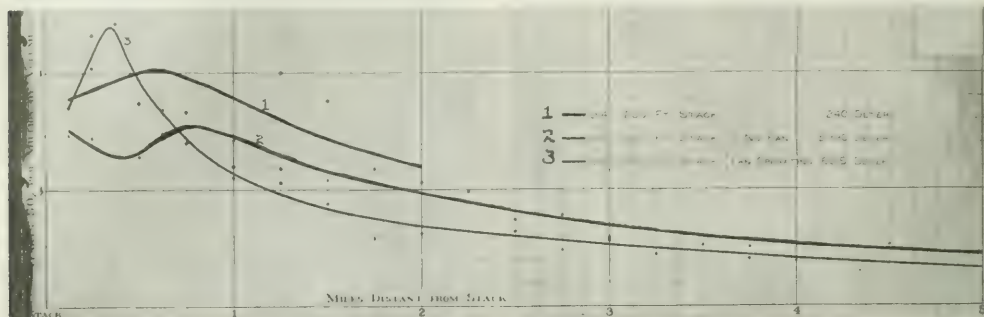


FIG. IV—MURRAY GAS STREAM: AVERAGE CONCENTRATIONS OF SO_2 IN 5-MI. ZONE

occur and for long periods of time. In July 1916, many long periods of these three coincident factors were found (Fig. III). However, no bleaching has been done at night, even though the sulfur dioxide output from the smelter remained high. This fact checks the observations which were made in experimental work on the fumigated plots, showing that at night, when the breathing pores of the plants are closed and carbon assimilation is at a standstill, the plants are very resistant to sulfur dioxide.

Having determined the concentration of sulfur dioxide necessary to produce markings upon vegetation under the various field atmospheric conditions, and also having obtained complete data concerning the atmospheric conditions that may exist, it is then necessary to know whether or not sulfur dioxide is present in sufficient strength in the field to do damage under the existing operating conditions of the plant.

Smelter Commission. By this method a sample of the atmosphere can be taken in a few seconds time and analysis made in less than 5 minutes. In fact the field men are supposed to make from 10 to 13 determinations per hour.

Concentrations as low as 0.1 part sulfur dioxide per million parts of air are determinable. Laboratories supplied with aspirators and vacuum pumps, titration bottles and reagents, are equipped on automobiles, in which the investigators can follow up the smoke stream or change from one part of the stream to the other. In most cases these "smoke cars" are also supplied with wind vanes and anemometers. By the use of several machines, it is possible to obtain many thousand determinations in a season, these being taken at all parts of the smoke stream and under all conditions of temperature, humidity, wind velocity and prevalence.

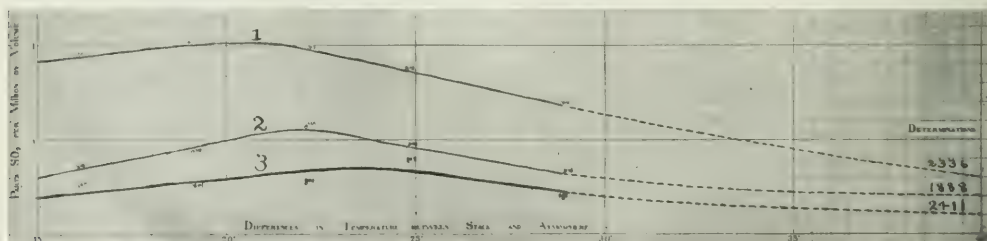


FIG. V—MURRAY GAS STREAM: DILUTER FAN OPERATING

SEGREGATION OF SO_2 DETERMINATION ACCORDING TO DIFFERENCES IN TEMPERATURE BETWEEN STACK AND ATMOSPHERE
Observations Made: (1) Inside of 1-mi. Zone, (2) Between 1- and 2-mi. Zones, (3) Outside of 2-mi. Zone and Mainly Inside of 4-mi. Zone

If such is found to be the case, it is then necessary to determine how the sulfur dioxide concentration in the smoke zone can be lowered without actually reducing the sulfur dioxide output from the smelter.

DETERMINATION OF SULFUR DIOXIDE IN AIR

The method that is now being used quite generally

DATA FURNISHED BY AMERICAN SMELTING AND REFINING COMPANY

With the consent of the A. S. & R. Co., the air data that have been obtained in the Murray Gas stream during the last three years under three conditions of operation of the plant are shown in the curves

of Fig. IV. These curves represent the average sulfur dioxide concentrations that were found in the air with different heights of discharge and temperatures of the gas at the stack. Such curves give a very clear idea of the sulfur dioxide content of the smoke stream under the three conditions, and aid toward making estimates as to the best method for improving the conditions. From these curves it is apparent that by increasing the height of discharge of the smoke, the dilution of the sulfur dioxide into the atmosphere is very greatly benefited. (Compare 1 and 2, Fig. IV.) The point at which the maximum average concentration of sulfur dioxide was found with a 200-foot stack was about one-half mile from the stack. With a stack 300 feet high, the point of maximum average concentration had moved out to the three-quarter mile zone. However, the concentration found in the three-quarter mile zone with the higher stack was much less than the concentration from the half-mile zone with the shorter stack. The high concentrations in Curve 2, at a dis-

mile zone, but outside of that three-quarter mile zone the concentrations were less.

The effect of increasing the difference in temperature between the stack gases and the outside air is shown even more clearly in the curves given in Fig. V. It is to be noted that, as the difference in temperature of the stack gases and air was increased, the point at which the gas currents met the ground extended further out from the stack. However, the further out the point of maximum concentration, the less was the actual concentration found.

The maintenance of a considerable difference in temperature between stack gases and atmosphere is of the greatest importance. It has been found in one instance that putting the furnace gas through a bag house, which procedure of course necessitated reducing the temperature of the gases to that at which a bag house could be operated, resulted in the sulfur dioxide gas doing considerable bleaching to the surrounding vegetation, whereas in former years, when the gases

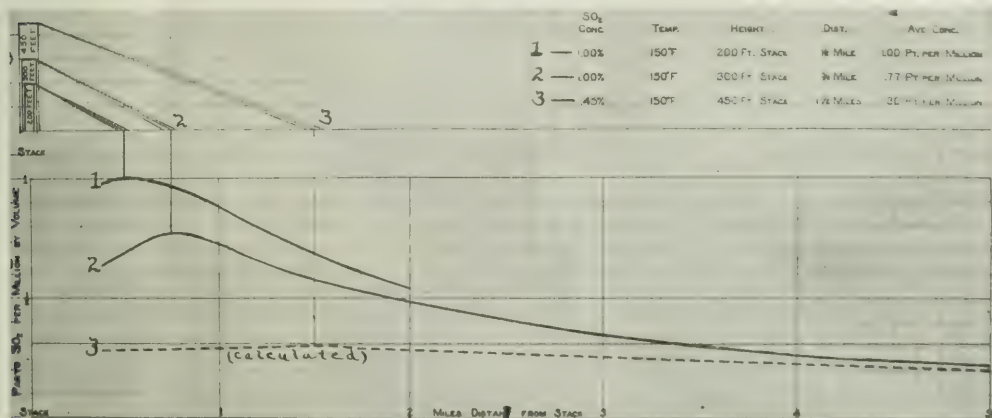


FIG. VI. MURRAY GAS STREAM ZONES OF MAXIMUM CONCENTRATION

tance of about $\frac{1}{4}$ mile from the plant, were not due to stack gases but to low gases leaking from the furnaces, etc. The curve for the stack gases begins at the $\frac{3}{8}$ -mile zone.

The dilution of the sulfur dioxide in the stack itself by the introduction of cold air may be carried to too great an extent, for the cooler gases will settle closer to the stack, and even though the concentration in the stack is lower, yet the actual concentration of the sulfur dioxide coming in contact with vegetation in the near vicinity of the stack may be higher. This fact is shown by Curve 3 in Fig. IV. It is to be noted that when the gases were diluted from 0.7% to 0.45% per cent SO₂, and at the same time cooled to nearly the atmospheric temperature by the introduction of outside cold air by a diluter fan, the point of maximum average concentration was about $\frac{1}{4}$ of a mile from the plant, and that the concentration at that point was higher than under either of the two previous conditions. The effect of diluting gases in the stack was to increase the concentration within the three-quarter

went into the atmosphere unfiltered, but at a higher temperature, there was practically no sulfur dioxide injury. It has been concluded by those who are investigating these problems, that in cases where the smelter must discharge large quantities of sulfur dioxide into the atmosphere, especially one located immediately adjacent to agricultural districts, it is much better to remove the solids at as high a temperature as is practicable. A bag house, although it gives the most perfect clearance of solids, is not always desirable for these conditions, as the use of a bag house may necessitate reducing the temperature to too low a point. An electrical precipitation apparatus may not give perfect clearance of the solids, but in such cases is much preferable. The higher the temperature of the gases in the stack, of course, the greater the amount of arsenic and sulfuric acid mist that will escape, and in cases where large quantities of these are present, there is a maximum safety of temperature at which precipitation should be effected.

The amount of sulfuric acid mist that is condensed

would escape under the conditions of high temperature electrical precipitation treatment, would do no harm to the surrounding vegetation; at the worst would produce only a slight spotting of the vegetation. It can be stated that at many lead, copper and zinc smelting plants where a recovery of the dust and fume is desirable, it would be much better for the smoke conditions in the immediate vicinity of the plant if only partial clearness of dust and metallic fumes were obtained, that is to say, 85 or 95 per cent, at a temperature which would still leave the gases much higher in temperature than the atmosphere, rather than to obtain perfect clearness, if, in order to obtain complete recovery of the dust and fume, it would be necessary to put the gases through a bag house and consequently allow them to escape into the atmosphere at a low temperature.

In Fig. VI are shown again the curves which represent the average concentration of sulfur dioxide in the air around the Murray plant with a 200- and 300-ft. stack. There is plotted also the calculated probable average sulfur dioxide concentration under the condition of a 450-foot stack and a gas concentration of 0.45 per cent, the temperature remaining about 150° F.

If this last condition were attained, the possibility of injury to vegetation in the vicinity of the Murray plant would be so remote as to be negligible, and this is the aim of the A. S. & R. Co.

CONDITIONS IN ZINC PLANTS

At the zinc plants in the natural gas belt, in southeastern Kansas and Oklahoma, it is found that the roaster stack temperatures are very high, around 350 to 400° C. Where the temperatures are lower, that is, around 150 to 200° C., the gas concentrations are also very low, that is, less than 0.3 per cent sulfur dioxide. Thus, even though the stacks are low, varying in height between 100 and 130 ft., the conditions are favorable for a rapid diffusion of the sulfur dioxide into the atmosphere. This fact probably accounts for the fact that very little, if any, sulfur dioxide injury has been noted in the vicinity of the plants in that district. In cases where the sulfur dioxide may be doing damage, it will be necessary to determine the critical atmospheric conditions for that district, and how often or for how long these critical conditions may occur. If they occur only occasionally it may be the most economical procedure to curtail the sulfur dioxide output during those critical times, rather than build higher stacks, especially at those plants which are of only a temporary nature.

At the zinc plants, as at the lead or copper smelters, wherever it is possible to dispose commercially of the acid or any sulfur product, it is highly desirable that such products be manufactured. If acid or other products cannot be disposed of commercially, then the best method for wasting the sulfur dioxide is to discharge the gases through a high stack and at as high temperature as is practicable.

BENEFICIAL EFFECTS OF SULFUR AND SULFURIC ACID ON SOIL

In regard to market for the sulfur or the acid, it is important to note that in the last several years there

has been developed a new outlet which promises to be of great importance, especially to those smelters in the west. This outlet is made through the use of sulfur and sulfuric acid for agricultural purposes as a fertilizer and as an agent for reclaiming vast areas of now useless lands. Within recent years a number of the U. S. Department of Agriculture Experiment Stations, especially those in Wisconsin, Oregon and California, have made some very remarkable discoveries concerning the beneficial effect of sulfuric acid on soils.

Among the most important and recent of the investigations along this line were those of Dr. C. B. Lipman and L. T. Sharp at the University of California,¹ and those made by the smoke department of the American Smelter and Refining Co. in Utah. Dr. Lipman's earlier experiments were made in pots, but later were made in field plots, using sulfuric acid. The A. S. & R. Co. experiments were made in field plots, using solid elemental sulfur, gaseous sulfur dioxide and liquid sulfuric acid. The beneficial results obtained have been astonishing. On the fifteen kinds of crops experimented with in 1916, all plots that were treated with sulfur or acid gave a big increase in yield over the checked untreated plots—in many cases over 100 per cent, and in some, over 150 per cent increase.

These results have been checked by other experimenters. In fact even more astonishing results have been obtained on certain crops at agricultural experiment stations. The value of sulfur or sulfuric acid as a very important fertilizer is no longer doubted.

Quoting Dr. C. B. Lipman,² "If the smelters will only produce the acid cheaply enough, as they now seem inclined to do, we should be able to banish much costly litigation, let the smelter industry develop untrammelled, give the smelter companies compensation for oxidizing the SO₂ and last, but not least, put a large acreage of barren land into good crop-producing condition."

U. S. BUREAU OF MINES
WASHINGTON, D. C.

THE NATURE OF CEMENT MILL POTASH

By R. J. NESTELL AND E. ANDERSON

Received May 31, 1917

Of the many sources of potash which have been suggested, exploited or developed since the supply of German material was shut off by the war, one that holds many interesting features and potential possibilities is the escaping dust and fume from cement mills.

Up to a comparatively short time ago, this material, belched forth from the stacks of cement plants to the amount, in some cases, of 10 tons or more per kiln per day, constituted only a very serious problem as a nuisance to be abated in populous districts, or an unavoidable but negligible feature of plant operation in localities where a question of nuisance needed no consideration.

Where it has been necessary to provide some means of catching this escaping dust, several different meth-

¹ Univ. Cal. Publ. Agri. Sci., 1, 275.

² *Ibid.*, No. 13, 1, 557.

ods of collection have been employed, among which may be mentioned simple settling chambers of large capacity, bag houses, water sprays, and electrical precipitation. The latter is, however, the only one that has received any extended application.

Originally installed for the purpose of preventing the escape of objectionable quantities of dust, and thus to remove the cause of complaint and litigation on the part of adjacent residents or land owners, the electrical precipitators or "treaters" began the collection of large quantities of mineral dust and fume.

With the increasing value of crude potash salts, due to decreased or entirely eliminated imports of the foreign material, the possibility and practicability of utilizing this cement dust as a source of potash were soon recognized.

This dust, collected from cement kiln gases, consists of partly calcined raw material and ash from the fuel which have been mechanically carried over by the draught, and also of volatilized alkali compounds.

These latter are principally in the form of sulfates. Presumably these alkalis are volatilized as oxides which then combine with products of combustion and calcination to form salts. Since practically all fuel used for cement burning contains sulfur, there are present in the kiln gases, besides carbon dioxide and water, also sulfur compounds, the latter probably largely in the form of sulfur dioxide. Consequently there exists the possibility of the alkalis combining either as carbonates, hydroxides or sulfites, and, due to the possible oxidation or reduction of the latter, as sulfates or sulfides.

ANALYSES OF VARIOUS DUSTS

An analysis taken at random from the many which have been made of treater dust from a plant where oil is used as fuel, shows the following percentage composition:

SiO ₂	8.41%	K ₂ O (Total).....	8.91%	SO ₃	14.98%
(FeAl) ₂ O ₃	7.02	K ₂ O (Water-soluble).....	7.65	CO ₂	13.80
CaO.....	39.23	Na ₂ O.....	3.65	H ₂ O and undetermined.....	3.40
MgO.....	0.60				

This sample is slightly below the average in K₂O content, which usually runs about 10 or 11 per cent. Of this, approximately 86 per cent is water-soluble, and, as fertilizing material is sold by law upon its water-soluble content, it would show this dust, with a present average value of \$3.50 per unit K₂O, to be worth about \$27.00 per ton.

The soluble K₂O is present entirely as K₂SO₄, while the insoluble portion is largely made up of such inert silicate from the raw mix.

This analysis represents the composition of the collected material, when no attempt is made to separate the heavy mechanically-carried-over calcined part from the true volatilized compounds. In some of the Cottrell installations, however, the construction is such that the collected dust may be separated thus obtaining a separation of these two mentioned fractions. An analysis of the lighter portion, which is precipitated but in such an installation, and which carries the greater part of the volatilized constituents, is as follows:

SiO ₂	1.61%
(FeAl) ₂ O ₃	0.63
CaO.....	7.78
MgO.....	0.74
K ₂ O (Total).....	28.96
K ₂ O (Water-soluble).....	28.40
Na ₂ O.....	1.58
SO ₃	41.64
CO ₂	2.76
H ₂ O and undetermined.....	3.34

LIME AND ALKALIES PROBABLY COMBINED AS

K ₂ SO ₄	52.50%
Na ₂ SO ₄	28.71
CaSO ₄	3.43
CaCO ₃	6.27
CaO.....	3.31
K ₂ O as silicates.....	0.56

This sample is typical of the material obtained where oil is used as fuel, and all the sulfur compounds have been oxidized to sulfates.

From this analysis it is evident that the volatilized alkalis have combined with the sulfur compounds rather than with the carbon dioxide, in spite of the great preponderance of the latter in the kiln gases. With fuel carrying about 1 per cent sulfur, this ratio of sulfur dioxide to carbon dioxide, in ordinary kiln practice, is about 1 : 300.

While the analyses just cited are representative of material collected from oil-fired kilns, it has been found that *where coal is used as fuel* a product of somewhat different character is obtained.

The following is an analysis of dust collected from a plant where powdered coal carrying about 1.5 per cent sulfur is the fuel:

SiO ₂	17.68%	SO ₃	9.94%	K ₂ O (Total).....	1.33%
(FeAl) ₂ O ₃	11.56	Sulfur in sulfides and sulfates.....	1.63	K ₂ O (Water-sol.).....	6.74
CaO.....	32.28	Na ₂ O.....	1.48	H ₂ O.....	0.46
MgO.....	1.52	CO ₂	10.04		

The composition of a sample of dust from which the greater part of the heavier portions have been removed by previous precipitation, is shown by the following analysis:

SiO ₂	11.90%
(FeAl) ₂ O ₃	10.94
CaO.....	21.85
MgO.....	1.19
Total S as SO ₃	17.47
K ₂ O (Total).....	20.60
K ₂ O (Water-soluble).....	16.04
Na ₂ O.....	1.14
CO ₂	10.90
C.....	1.03
H ₂ O and undetermined.....	2.98

LIME AND ALKALIES PROBABLY COMBINED AS

K ₂ SO ₄	50.68%
Na ₂ SO ₄	7.76
CaSO ₄	4.40
CaCO ₃	14.40
CaO.....	6.27
K ₂ O as silicate.....	3.88

The most important differences in the potash material from coal-fired and oil-fired kilns, as shown by the analyses given, lie in the relative amounts of soluble and insoluble K₂O, and in the wide variation in potash concentration in the lighter fractions of dust obtained from kilns using these two different forms of fuel.

Thus when oil is used as fuel, the soluble potash in the heavy dust was 86 per cent of the total, and in the lighter material, 98 per cent, while the corresponding figures for dust from the coal-fired kiln were 50 and 70 per cent, respectively. Similarly, in the case of oil-fired kilns, the ratio of the total potash content of the heavier to the lighter fraction was 4.75 to 1, while the corresponding ratio in the dust where coal was used as fuel was 1.5 to 1.

Since, as has been stated, the lighter fraction contains a greater percentage of volatilized constituents, the results of these analyses would show that the dust light upon the reason for the difference in potash solubility and concentration above mentioned.

This is the case from oil-fired kilns, where the total potash content was relatively low, and with a high percentage of insolubles. The amount of the soluble potash and the ratio of the total to the insoluble potash content were much lower in the dust from coal-fired kilns.

was used, and the total potash content was high and practically all soluble, the sum of the silica, alumina and iron oxides was only 2.24 per cent.

An appreciable difference is also noted in the sulfur content in the two cases, since with oil fuel the amount of sulfur in the dust is higher than where coal is used. In the latter case the sulfur is also frequently present in large part as sulfide and sulfite.

Experiments on coal-fired kilns have proved that increasing the sulfur content of the fuel, and maintaining a less reducing atmosphere in the kiln, both tend to produce a potash product of a higher degree of solubility. But even with a large excess of sulfur over that required to combine with all the volatilized alkalis, the per cent of insoluble potash in the collected material was still considerable.

In the two cases cited, all the soluble K_2O has been in the form of sulfate, but the following analysis of dust collected from an oil-fired kiln using the wet process, shows that soluble potash compounds, other than the sulfate, may exist in such dust. The fuel used in this plant does not contain sufficient sulfur to combine with all the volatilized potash, so that some of the potash must appear as carbonate, due to the large excess of CO_2 in the kiln gases:

ANALYSIS OF DUST		LIME AND ALKALIES PROBABLY COMBINED AS	
CaO	37.70%	K_2SO_4	29.70%
K_2O (Total).....	19.57	K_2CO_3	2.91
K_2O (Water-soluble).....	18.08	Na_2CO_3	1.66
Na_2O	0.97	CaO	29.96
SiO_2	13.60	$CaCO_3$	13.82
CO_2	7.70	K_2O in silicates.....	1.49

Since an excess of sulfur does not always prevent the formation of insoluble potash compounds, and a deficiency of sulfur does not necessarily result in the formation thereof, it follows that a reason for the existence of such compounds must be sought for elsewhere.

In the dust from the oil-fired and coal-fired kilns previously referred to, where in the first case the per cent of insoluble K_2O was 0.56 per cent, and in the second case was 4.55 per cent, it seems safe to assume that the amount of mechanically carried over raw material was practically the same. Consequently the difference noted in the amount of silicious material shown cannot be due to a greater proportion of calcined raw mix in one case. The only other source of silicious material is the ash from the coal used as fuel. Ordinarily this coal carries 8 to 12 per cent ash, of which 35 to 40 per cent is SiO_2 and 40 to 50 per cent R_2O_3 ; and since this ash, coming as it does from finely powdered coal, must be in a state of extremely fine subdivision, approaching that of a true fume, it is reasonable to suppose that part of this ash would be collected among the lighter portions of the dust.

Since approximately 9 lbs. of coal ash are introduced into the kiln per barrel of clinker burned, if only one-half this amount is carried out with the gases, it would still be sufficient to affect appreciably the composition of the collected dust, as the amount of dust caught per barrel of clinker produced is only about 20 lbs. Consequently it is probable that the considerable amount of insoluble potash shown to be present

in the dust from coal-fired kilns is in reality due to a combination of the volatilized potash with the finely divided, incandescent particles of silicious coal ash.

On account of the practical impossibility of separating the insoluble potash compound from the other constituents of the dust, its exact identification has not been effected.

The so-called "insoluble" potash is completely soluble in dilute HCl , and, as will be shown later, also in boiling water on sufficiently long continued treatment. This latter property was taken advantage of in an attempt to throw some light upon the nature of the compound in question.

A sample of the dust was first treated with boiling water according to the official method for water-soluble potash. The residue was then boiled with water under a reflux condenser for several hours, and the resulting solutions, numbered 1 and 2, in each case analyzed. These analyses, with hypothetical combination, are given below:

ANALYSES OF DUST			HYPOTHETICAL COMBINATION		
Solution	1	2	Solution	1	2
SiO_2	0.05%	0.08%	K_2SO_4	11.28%	0.00%
R_2O_3	0.71	0.71	K_2O	0.0(a)	1.66(a)
CaO	8.49	0.91	Na_2SO_4	1.99	0.0
MgO	0.13	0.13	Na_2O	0.0	0.25
K_2O	6.10	0.66	$CaSO_4$	1.97	1.04
Na_2O	0.87	0.25	CaS (including		
SO_3	7.46	0.61	$CaSO_4$).....	1.57	0.0
S in sulfides and			CaO	6.46	0.48
sulfites.....	0.70	0.00	MgO	0.13	0.0
Alkalinity as OH	3.78	1.22	Al_2O_3	0.0	0.71

(a) As silicates.

The slowly soluble potash, which, in the above hypothetical combination, is given as silicate, appeared, of course, in solution as hydroxide, due to hydrolysis, which decomposition may be influenced to a certain extent by the presence of lime in the solution.

Other investigators¹ have shown that when a feldspar is boiled in presence of lime, the potash is brought into solution in the same form. Hence it is reasonable to suppose that the original potash compounds in the two cases were similar in nature, and that, therefore, this slowly soluble material is a type of recombined silicate which, as previously pointed out, was formed through the union of the silicious ash particles and the potash vapor.

If, also, as seems reasonable, such a compound is of greater specific gravity than that formed from the potash vapor and the sulfur gases, this would explain the difference in potash concentration already noted.

The possibility of such a silicious combination has long been recognized, and a method for overcoming the effects thereof on the solubility of collected potash, has been patented by Haff and Cheeseman.

WATER-SOLUBLE POTASH CONTENT OF DUSTS

The chief use of this treater dust being as a fertilizer, and as its value for such purpose is based upon its content of water-soluble potash, the question of solubility is of prime importance.

In order to determine not only the ready solubility of the potash in water, but also to gain some knowledge of the degree of solubility which it might show when subjected to conditions similar to those existing

¹ W. H. ROSS, THIS JOURNAL, 9 (1917), 467.

in its practical application as a fertilizing material, a series of tests was made to determine these facts. A description and the results thereof follow.

Wherever figures for "water-soluble" potash are given herein, they have been obtained by the Official Method of the A. O. A. C., which consists of washing 2.5 g. of the material, contained in a 12.5 cm. filter, with 200 cc. boiling water, and determining the K_2O in the resulting solution. The older method for this determination, and which is still used by some fertilizer chemists, is to boil the material with water under a reflux condenser for one-half hour.

One of the reasons for the adoption of the new method by the A. O. A. C., was that it was found, in certain cases, that the older method gave results somewhat below the true value, and tests we have made in connection with this work show this to be so.

Analysis of the dust used for these solubility experiments showed the following K_2O content:

TOTAL K_2O	10.91 per cent	Per cent of Total
Water-soluble.....	5.84	53.5
Soluble in 5% HCl.....	10.03	91.9

In order to show the effect of continued treatment with hot water, 10 g. of dust with 100 cc. water were boiled under a reflux condenser for varying periods of time, and the amount of K_2O then in solution determined, with the results shown in Table I:

TIME HOURS	PER CENT K_2O DISSOLVED	PER CENT OF TOTAL K_2O DISSOLVED
1/2.....	5.49	50.3
2.....	6.65	60.9
4.....	7.68	70.4
6.....	8.51	78.0
8.....	9.13	83.7
10.....	9.95	91.2
12.....	10.12	92.8
14.....	10.35	94.9
16.....	10.45	95.8
20.....	10.55	96.7
24.....	10.56	96.8

This table shows very strikingly the ultimate solubility of practically all the potash under the conditions of the treatment given. It also emphasizes the importance of accurately stating conditions of treatment when reporting "soluble potash" and indicates that the criticism of the old method for obtaining soluble potash was justified. Thus, according to the new method, there was 5.84 per cent soluble K_2O , while with one-half hour boiling, only 5.49 per cent was found.

The reason for this difference is probably due to a primary combination between the potash and the silica to form a slowly soluble silicate which is, however again broken down by continued treatment with the hot alkaline solution. Further evidence bearing on this point will be found in some of the following experiments.

To illustrate the effect of continued cold water treatment, 10 grams of dust with 100 cc. water were placed in 16-oz. bottles, tightly stoppered, and subjected to continuous agitation in a revolving container. The percentage of extraction obtained is shown in Table II. A parallel run was made with similar conditions except that the extraction water was separated from the dust each day, and fresh solvent added. The results obtained in this series appear in Table III.

TIME HRS.	PER CENT K_2O DISSOLVED	PER CENT OF TOTAL
1.....	5.59	51.2
24.....	5.92	54.3
72.....	6.06	55.5
168.....	6.24	57.2
336.....	6.38	58.5
672.....	8.00	73.3
840.....	8.25	75.6

TIME HRS.	PER CENT K_2O DISSOLVED	PER CENT OF TOTAL
168.....	6.62	60.6
336.....	6.86	62.8
504.....	7.20	66.0
672.....	7.34	67.3
840.....	7.40	67.8
1008.....	7.46	68.3

In order to simulate, to a certain extent, conditions of leaching which obtain when fertilizing material is applied to the land, an apparatus was arranged for carrying on continuous percolation of the treater dust with measured amounts of cold water. This apparatus was designed by H. V. Welch, and is shown in Fig. I. The dust to be leached was placed in 16-oz. bottles from which the bottoms had been removed and replaced by a couple of layers of filter paper held in position with a disc of wire screen. These bottles

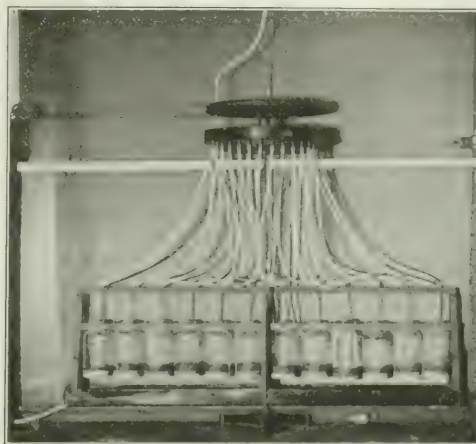


FIG. I

are supported in a wooden frame over a drain pan, and the water supplied to the tops of the bottles by means of the rubber tubes which terminate in openings arranged around the periphery of a circular pan below the distributor. The latter is a large wooden pulley through which passes a tube connected with the water supply. This pulley is revolved by means of belting from a small electric motor. By this means each bottle receives the same amount of water, which may be controlled by regulating the size of the opening in the water supply tube, and measured by collecting the water delivered by any one of the tubes.

Fifty grams of the dust were used, and the amount of water passing through was equal to 100 cc. daily. At the end of the specified time, the bottles were dried and analyzed for K_2O . The loss in weight of the dust, due to the removal of water taken therefrom, is the basis for the calculation for the loss in weight of the dust, due to the removal of water taken therefrom. The results are shown in Table IV.

TIME	PER CENT K_2O DISSOLVED	PER CENT OF TOTAL
1.....	5.59	51.2
24.....	5.92	54.3
72.....	6.06	55.5
168.....	6.24	57.2
336.....	6.38	58.5
672.....	8.00	73.3
840.....	8.25	75.6

Considering Tables III and IV, which show the amounts of potash dissolved when the soluble salts are removed from the sphere of action, it is seen that the potash compounds are brought into solution by the action of cold water at a well defined, though slow rate. Comparing Tables III and IV with Table II shows that ultimately more potash is dissolved when the soluble constituents of the material are allowed to remain in the solvent. In all probability this is due to the action of the lime present, since, as previously stated, this has a marked solvent action on such silicious material. This action is shown more clearly where the solvent was used at boiling temperature, for, in this case, where the dissolved products, a large proportion of which is lime, were allowed to remain with the solvent, the rate of solution was 22 per cent greater than in a similar test where fresh solution was used from time to time.

While the rate of solution in cold water is very much slower than in hot, it is, nevertheless, considerable, and it is safe to assume that the greater part of such slowly soluble potash material from cement kiln gases, would be rendered available in the course of a season.

As is known, ground feldspar is often used as a potash fertilizer. Compared with the recombined silicious potash of cement kiln dust, this potash material is much more slowly soluble, which is evident from the fact that a feldspar-lime mixture, containing practically the same percentage of lime as the treater dust, yielded, on boiling with water for 16 hours, only 1.7 per cent of the total K_2O , while the treater dust, from which all of the readily soluble potash had been removed, under parallel conditions gave 35 per cent of its remaining, slowly soluble K_2O .

EFFECT OF SOIL ADMIXTURE

Some tests were made to determine the effect of an admixture of soil upon these potash compounds. It is, of course, known that soluble potash salts, when mixed with some soils, tend to become, in part, soluble. Our tests show that with treater dust this action is also quite rapid, so that in a comparatively short time a large part of the originally soluble potash becomes so attached to the soil that it cannot be extracted when treated according to the Official Method for water-soluble potash. At the same time, however, the originally slowly soluble potash compounds are being rendered soluble. The ultimate result of such action of soil on a mixture of the two types of compounds existing in this treater dust, as shown by the following tests, is to yield a larger relative percentage of readily soluble potash than is the case where the original material consisted entirely of perfectly soluble salts.

In the first set of these tests, a hot water extraction of the original dust was made, and aliquot parts of the resulting solution poured upon samples of soil contained in beakers. These were then allowed to stand for varying periods of time, when the residual water-soluble potash content was determined. At the end of two weeks, this water-soluble potash had decreased 13.6 per cent, and at the end of four weeks, 38.7 per cent.

The dust remaining, after the water-soluble part

was removed by washing, was also mixed with soil and allowed to stand. At the end of two weeks, 12 per cent of the slowly soluble potash had become soluble, and at the end of four weeks, this solubility had increased to 17 per cent.

From these results it is evident that the effect of the soil upon the readily soluble potash is more pronounced than that upon the slowly soluble, so that the net result would be to decrease the total amount of readily soluble potash in such a mixture.

The following test confirms the above assumption: The original dust was mixed with soil, moistened with water, and allowed to stand as in the previous cases. At the end of three weeks, the soluble potash had decreased 2.45 per cent of its original value. At the end of six weeks, the decrease was 4.9 per cent, and at the end of ten weeks, was 9.95 per cent.

As was shown above, with the soluble part of this dust similar to the soluble potash salts of the ordinary fertilizer, this decrease, in only four weeks, was 38.7 per cent. It is possible that this recombination between the soluble potash and the soil is analogous to the one pointed out in connection with the solubility of the dust in boiling water. As was stated then, a half-hour boiling showed a soluble potash content of 5.49 per cent, while the Official Method gave 5.84 or a decrease, caused by boiling, of 6 per cent of the total soluble potash present. When the silicious material in the mixture is largely increased by the addition of soil to the dust, it is to be expected that the recombination, under similar treatment, would be more marked. Tests made by boiling such mixtures confirm this view. Thus a mixture of 10 per cent dust and 90 per cent soil, which showed by the Official Method 0.66 per cent soluble potash, on boiling one-half hour, gave only 0.47 per cent, a decrease of 29 per cent.

It appears evident, from the data presented, that the Official Method for determining soluble potash in fertilizer does not necessarily give a true indication of the potash value of all such material. As to the ultimate availability for plant use of the potash in a fertilizer, it would seem that such slowly soluble potash compounds as have been shown to be present in dust from cement kilns, more nearly approach the ideal form of a plant food than do the more readily soluble potash salts, since these slowly soluble compounds undoubtedly can be assimilated by the plants in the course of a season, and are not to such a large extent apt to be leached out by rains and irrigation.

The United States Bureau of Soils has under way a series of experiments on leaching this dust with water under conditions of high pressure and temperature, a complete report of which will undoubtedly be published in the near future. The results of some of their early experiments would indicate that the rate of solution of the slowly soluble potash compounds is enormously increased by this treatment.

SUMMARY

I—Dust from cement kiln gases may be composed of mechanically carried over raw material and solid

residues from fuel combustion, together with volatilized alkalis.

II—Such dust contains considerable amounts of potash present both in readily and slowly soluble form.

III—The readily soluble potash usually occurs as sulfate, due to a combination of this base with the sulfur of the fuel and where there is a deficiency of sulfur, partly as carbonate.

IV—The slowly soluble potash is probably of a silicious nature, largely formed by the union of potash vapor with incandescent ash particles.

V—This silicious potash becomes soluble on boiling with water for a few hours, and on treatment with cold water for longer periods.

VI—The presence of lime accelerates the solution.

VII—Slowly soluble potash compounds are also formed by the interaction of potash salts in solution with silicious material, this recombination being greatly accelerated by heat.

VIII—The action of moist soil promotes the availability of the slowly soluble potash.

IX—In view of the gradual and continued solution of the potash in cement kiln dust, it should be of particular value as fertilizer material.

Acknowledgments are due to Mr. R. C. Haff and associates, of the Security Cement & Lime Company, and to Mr. H. V. Welch, of this laboratory, for assistance and suggestions.

LABORATORIES OF THE WESTERN PRECIPITATION COMPANY
LOS ANGELES, CALIFORNIA

SOME RELATIONS OF THE EFFECT OF OVERHEATING TO CERTAIN PHYSICAL AND CHEMICAL PROPERTIES OF ASPHALTS¹

By A. W. HINSON AND HAROLD E. HANDS

The use of carbon tetrachloride as a solvent in differentiating bitumens was first suggested by Richardson and Forrest² in 1906. They found that true asphaltic hydrocarbons were soluble to the same extent in it as in carbon bisulfide. In residual pitches which were carelessly refined, they found that the bitumen soluble in carbon tetrachloride was less than in carbon bisulfide. To the hydrocarbons soluble in carbon bisulfide but insoluble in carbon tetrachloride, Richardson later applied the term "Carbenes."³ It was suggested that these were the result of weathering in true asphalts. In the case of residual pitches it was thought to be the result of overheating during the industrial processes used in production.

Kirschbraun⁴ took up Richardson's suggestion and performed a series of experiments on the effect of overheating on refined Bermudez asphalt and on fluxed Bermudez asphalt. He found that carbenes were formed at high temperatures (600-650° F.) and suggested that they were the result of either cracking at high temperature or concentration—probably both.

In 1910 Mackenzie¹ took up the subject in the endeavor to determine the cause of certain discrepancies in the results of carbene determinations in the same samples made in the New York Testing Laboratory and another laboratory on the Pacific Coast. He found that in the same sample of bitumen there was an increase of carbenes when the carbon tetrachloride solution was allowed to stand in the light. He therefore called those carbenes which were precipitated completely from a tetrachloride solution on standing in the dark for 12 hrs., "true carbenes." To those which were then precipitated on allowing the filtrate from this determination to stand in the light he applied the name "pseudo-carbenes." He concluded: "That light acting upon a solution of bitumen in tetrachloride causes the bitumen to decompose, the tetrachloride giving hydrochloric acid, which in turn combines with unsaturated hydrocarbons and precipitates them. But only certain bitumens (namely, those which have been more or less overheated) can bring about this phenomenon." Similar results and conclusions were the result of practically a simultaneous work by Alexander.²

As far as can be ascertained, no systematic work has been published which has to do with the effect of overheating, and the presence of carbenes caused by this overheating, upon the physical and chemical properties of asphalts. This investigation was therefore undertaken with the object of determining to what extent an asphalt could be heated and still retain those properties desirable for a durable pavement. If carbenes are a result of overheating, then what is their effect upon an asphalt; is the effect due simply to the heating or do they alter markedly the properties of asphalt by their presence? It was hoped to arrive at a conclusion as to the value of the carbene specification for asphaltic materials to be used in road construction.

It was noticed that, using the same asphalt, Mackenzie was unable to check the results obtained by Kirschbraun either concerning the carbene content, or certain other properties, *e. g.*, bitumen soluble in carbon bisulfide. This is not to be wondered at since neither investigator gave details of the methods of analysis used. It is a well-known fact that in asphalt analysis two investigators have difficulty in checking each other even when the same methods are used. The errors due to technique are too well known to be recounted here. Needless to say, it is therefore impossible for any later investigators to check their results quantitatively. In this work no effort was made to check the results of either Mackenzie or Kirschbraun.

PURIFICATION OF REAGENTS

In order to be absolutely sure of the results it was thought necessary carefully to purify the carbon tetrachloride and the carbon bisulfide to be used.

The technique was first worked with benzene and it was found that it was applicable to *cc.* This removed any impurities which might be present as impurities.

¹ Presented at the 34th Meeting of the American Chemical Society, Kansas City, April 19 to 24, 1917.

² Richardson and Forrest, *J. Soc. Chem. Ind.*, **24**, 411.

³ The Modern Asphalt Presentation, 3rd Ed., pp. 118-120.

⁴ *Municipal Engineer*, **30**, 1908, 449.

ties. To insure the complete removal of any hydrogen sulfide the bisulfide was placed in a distilling flask, covered with one inch of a water solution of lead acetate and distilled over a water bath. The distillate was then fractionated using a Glinsky 4-bulb distilling head. That fraction with a boiling point of 46.3° was saved. This was water-white with a pleasant ethereal odor and gave no residue when 20 cc. of it were allowed to evaporate spontaneously on a watch glass. It was then dried over lime, placed in glass-stoppered, brown bottles, and kept in a cool, dark place.

The carbon tetrachloride was freed from carbon bisulfide by adding a quantity of alcoholic potassium hydroxide solution. It was then heated to 60° C. for one-half hour and the potassium xanthate formed was precipitated by adding water. The liquid was repeatedly washed with water until free from alcohol and potassium hydroxide. It was then fractionated, using a Glinsky 4-bulb distilling head. Fractions with a boiling point of 76.6 to 76.8° C. were kept dried over calcium chloride and stored in the same manner as the bisulfide.

In using both solvents, the wash bottles were completely covered with black paper to prevent any decomposition by light.

METHODS OF ANALYSIS

DETERMINATION OF BITUMEN SOLUBLE IN CARBON BISULFIDE (TOTAL BITUMEN)—The method proposed by the Committee on standard tests for road materials of the American Society for Testing Materials was tried. In the case of Trinidad asphalt, where the mineral matter is high, the results were very unsatisfactory. Filtration proceeded very slowly and much of the fine mineral matter went through the filter. It was also found difficult to prepare two asbestos pads for the Gooch crucible which would retain the same amount of mineral matter. For this reason great difficulty was experienced in obtaining concordant results. When very dense pads were used it was still found difficult to check the results. Moreover, when carbon tetrachloride was used as a solvent, it required several days for filtration, and in one case over a week. Obviously, this would not do, for, as Alexander and Mackenzie found, the longer the time taken to filter a tetrachloride solution of bitumen, the greater the amount of bitumen insoluble, due probably to the action of light. So the following method was used:

One gram of the asphalt (if the mineral content be low, more can be taken) was weighed into a tared 200-cc. Erlenmeyer flask and treated with 100 cc. of carbon bisulfide. The flask was then loosely stoppered and was shaken from time to time until solution was complete. This usually required about 30 minutes. The solution was then centrifuged at high speed for 30 minutes. Two C. Schleicher and Schüll No. 589 Blue Ribbon filter papers, which had been previously extracted with carbon bisulfide, were then weighed and onto these the supernatant liquid was carefully decanted. A double filter was used to insure the collection of even the finest mineral matter. The residue in the

bottom of the centrifuge flasks was then washed with bisulfide and ultimately all was brought upon the filters. The residue was washed with bisulfide until the washings were colorless. Suction was applied when necessary. All flasks and the filters were then dried at 100° C. and weighed. The filter papers containing the residue were then ignited to determine the amount of "organic matter insoluble" and ash. In this manner the ratio of "organic matter insoluble" to ash was found. If any insoluble matter remained in the flasks this ratio was applied to it and the ash and "organic matter insoluble" thus found were added to that found on ignition of the filter papers. The reason for this is obvious when one considers that the insoluble mineral matter in the flasks will have absorbed or adsorbed a certain amount of bituminous material. It was found that the ash determined in the fixed carbon test was slightly greater (about 1.35 per cent in the case of Trinidad asphalt) than that obtained by filtration. The reason for this is unknown. Richardson¹ is authority for the statement that the solution containing this shows, under the ultra-microscope, the characteristic Brownian movement of colloids and that it is due to colloidal clay and other mineral matter. But might not this difference be caused by a solution of slight amounts of mineral salts in the solvent? These salts might be salts of mineral acids or mineral salts of organic acids of high complexity. This might be expected, especially if the solvents were not completely water-free—a condition hard to secure.

If the mineral is colloidal then it will probably have bitumen adsorbed on its surface. In this work it was assumed to be colloidal and therefore a correction was applied to the mineral matter found on filtration. In making this correction the same ratio between ash and "organic matter insoluble" was used as that found on ignition of the filter residue. In order to determine if the long standing, as specified in the method of the American Society for Testing Materials, was of value before centrifuging, experiments were carried out in which the asphalt stood in contact with the solvent for different lengths of time. In each case one gram of refined Trinidad asphalt was shaken with 100 cc. of carbon bisulfide. The results, given in Table I, showed that long standing was not necessary when the centrifuge was used.

TABLE I		30 mins.	24 hrs.	48 hrs.	70 hrs.	48 hrs.(a)
TIME OF STANDING						
Bitumen soluble in CS ₂	58.02	58.00	58.65	59.77	57.41	
Mineral matter insoluble.....	30.00	33.31	32.66	30.04	33.48	
"Organic matter insoluble"....	7.98	8.69	8.69	7.19	9.11	

(a) Stood 24 hours, was decanted and 100 cc. fresh solvent added; then stood 24 hours longer.

The following points then led to the adoption of the above method of separation:

1—The time element was cut to a minimum, it being possible to complete filtration, even from a tetrachloride solution which formerly took several days, in a few hours. This is very important in making the carbene determination.

2—Results could be made to check closely.

3—By the use of filter paper, instead of an asbestos

¹ J. Phys. Chem., 19, 245.

padded Gooch crucible, it was possible to control more evenly the size of the openings and therefore the amount of mineral matter retained.

BITUMEN SOLUBLE IN CARBON TETRACHLORIDE—The same method was used as in determining the bitumen soluble in carbon bisulfide, using instead 100 cc. of carbon tetrachloride.

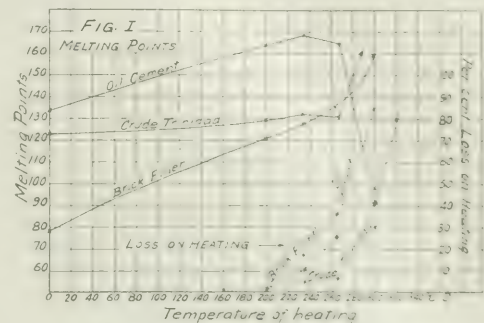
CARBENES—No attempt was made to determine the pseudo-carbenes described by Mackenzie. The bitumen soluble in carbon bisulfide but insoluble in carbon tetrachloride, when the determinations were made as described above, was taken as the carbene value.

FLOW TEST—This test was performed according to the directions given by Richardson.¹ The test was made at the melting points of the asphalts and the flow in millimeters during 5 minutes was taken. An electric oven was used.

All other tests were performed according to the directions given in The Office of Public Roads, *Bulletin 38*, on "Methods for the Examination of Bituminous Road Materials."

In making the melting-point test, the oil bath was heated at the rate of 5° per minute. All penetration

black homogeneous substance which was quite soft and sticky. The oil asphalt was a dull black homogeneous substance which was also quite soft and sticky. However, it could easily be cut with a knife.



PROPERTIES AFTER HEATING

In the case of each asphalt there was an increase in the melting point after heating to 200° C., more marked possibly in the case of the brick filler (Fig. I).

TABLE II—TESTS MADE AT DIFFERENT TEMPERATURES																			
Temperature of Heating	CRUDE TRINIDAD ASPHALT					BRICK FILLER					OIL ASPHALTIC CEMENT								
	163°	200°	235°	265°	300°	163°	200°	235°	265°	300°	163°	200°	235°	265°	300°	350°			
Bitumen Soluble:																			
in CS ₂	54.90	53.77	51.62	50.39	30.70	99.26	98.48	98.94	98.70	97.80	98.18	97.27	97.36	96.88	81.32	...			
in CCl ₄	52.78	53.63	52.27	53.13	27.64	99.26	98.48	97.21	97.51	85.50	97.93	97.52	96.14	96.58	73.38	...			
Carbenes.....	2.12	0.14	-0.65	-2.74	3.06	None	None	1.73	1.19	12.30	0.24	-0.25	1.22	0.30	7.94	...			
Matter Insoluble:																			
Organic.....	9.45	10.58	10.87	12.00	18.29	None	0.78	0.17	0.17	0.78	1.55	2.48	2.34	2.76	16.44	1.18			
Mineral.....	35.65	35.65	37.21	37.61	51.01	0.74	0.74	0.89	1.13	1.42	0.27	0.25	0.30	0.36	1.34	...			
Fixed Carbon:																			
Determined.....	8.71	10.70	8.73	8.45	18.98	13.49	15.96	16.93	18.46	26.18	14.38	15.33	15.03	14.97	31.13	58.83			
Corrected.....	8.71	10.70	8.30	8.02	13.26	13.49	15.96	14.07	12.09	13.64	14.38	15.33	13.82	11.24	4.83	13.46			
Loss on Heat-																			
ing.....			1.0	4.95	5.21	30.11	0.23	1.0	16.85	34.51	47.88	0.40	1.0	10.00	25.00	84.48	77.12		
M. P. (° C.).	113	129.5	133.0	130.5	Doesn't flow	78	121	128.3	136	159	113	16.4	167.5	164.5	81.3	...			
Penetration.....	40.5	4.0	4.0	4.0	4.0	1.0	65.7	53.0	21.5	16.3	8.4	6.4	42.0	30.5	27.5	24.5	25.0	81.6	
Flow at M. P.	10.5	123.5	120	90	0	32.5	50.5	185	47.5	3.0	185	13.5	8.0	8.0	1.0	...			

tests were made under a load of 100 g. for 5 seconds at a temperature of 38° C., except in the case of the oil cement, where the load was 50 g. The New York Testing Laboratory Penetrometer was used.

MATERIALS USED

1—Crude Trinidad asphalt which had been finely powdered and air-dried before testing.

2—A brick filler which consisted of a natural asphalt fluxed with 70 per cent of asphaltic oil residuum.

3—An oil asphaltic cement of unknown origin.

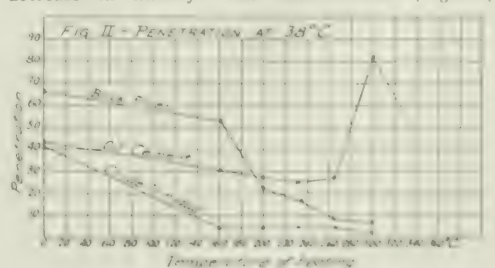
METHOD OF HEATING—About 100 g. of the asphalt were placed in a large crucible-shaped porcelain dish and heated to the desired temperature in an air oven over a period of five hours. At the end of this time it was poured out, allowed to cool, and if hard enough was ground to powder and sampled. Tests were made at the different temperatures as given in Table II.

The nature of the change on heating may perhaps be followed better by considering the change at each temperature.

ORIGINAL PROPERTIES

The crude Trinidad asphalt when pulverized had a dry earthy appearance. The brick filler was a

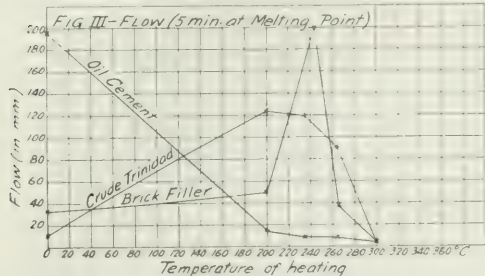
black homogeneous substance which was quite soft and sticky. The oil asphalt was a dull black homogeneous substance which was also quite soft and sticky. However, it could easily be cut with a knife.



showed a slight increase, and was to be expected. Of special interest is the decrease of carbon content (Fig. IV) in the Trinidad asphalt. A corresponding decrease was found in the oil cement, in fact, the bitumen was even more soluble in carbon tetrachloride than in carbon bisulfide.

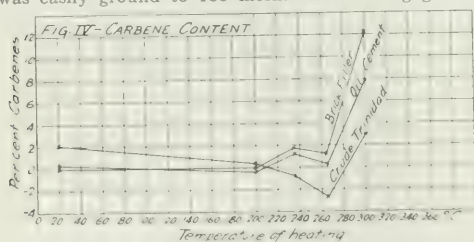
¹ "The Modern Asphalt Pavement," 1st Ed., p. 437.

Changes in the nature of the asphalts were quite noticeable after heating to 235° C. The melting points continued to rise in all cases. The asphalts became harder. The Trinidad became so hard that it was easily crushed and ground in a coffee mill. The brick filler broke with a conchoidal fracture when hit a quick, hard blow. The oil cement continued to be fairly soft. The flow tests showed that the Trinidad asphalt and oil cement became slightly more viscous, while the brick filler showed its max-



imum fluidity at this point, it being so fluid that it flowed off the end of the plate. While the oil cement and brick filler both showed an increase in carbenes at this temperature, the decrease was still greater in the case of the Trinidad asphalt, which now became more soluble in carbon tetrachloride than in carbon bisulfide; there also appeared a decrease in the fixed carbon content! After heating to 265° a break was noticed in all the curves depicting the various properties. In the case of the Trinidad asphalt and oil cement, there was a lowering of the melting point, the fluidity, and the fixed carbon, while in all three there was a decrease in the carbenes. The Trinidad became more markedly soluble in carbon tetrachloride than in carbon bisulfide!

Upon heating to 300° a very decided change took place. The Trinidad asphalt became so hard that it was easily ground to 100 mesh. After being ground

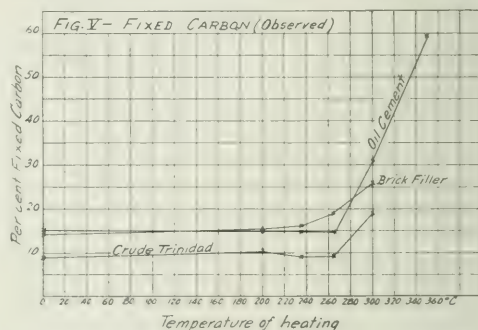


it would not fuse together again, so it was impossible in this manner to make a cube for the melting-point determination. Fortunately, a large lump was at hand, which was then molded into shape and the test performed. However, the asphalt would not flow even after heating to 300° C. The brick filler was ground in the mill and the oil cement became very soft, mealy and lost its stickiness. While the penetration of the other samples became suddenly less, the penetration of the oil cement became decidedly

greater. Its melting point became lower and it refused to flow on the flow plate. In each case a decided increase in fixed carbon and carbenes was noticed. Each asphalt seemed to lose its fluidity.

In centrifuging the carbon bisulfide and carbon tetrachloride solutions of these samples an interesting observation was made. In the case of the former, all the insoluble matter went to the bottom of the flasks. However, in the carbon tetrachloride solution there was a separation—there being a layer of shiny bituminous substance at the top. If this top layer consisted of the carbenes it indicates that their density lies between that of the bisulfide (1.270) and tetrachloride (1.604). This may afford an effective means for their separation.

In reviewing the changes in properties, the question naturally arose as to the cause of the Trinidad asphalt becoming more soluble in tetrachloride after heating to 235° and 265°, and why the carbene content of the other two became less at 265° than at 235°. There seemed to be a corresponding change in other properties during this range of temperature. Evidently there was a decided change in the nature of the hydrocarbons themselves. Just what this change is can at



present only be surmised. The fixed carbon content may be of assistance in explaining this. If this is calculated back to the basis of the weight before heating, it may offer a suggestion. If there is no change in the nature of the hydrocarbons, and the process is simply one of distillation, we should get a straight line curve when the values are plotted. Accordingly this was done using the formula

$$F.C._{\text{original}} = F.C._{\text{observed}} \times \frac{100 - \text{Loss on Heating}}{100}$$

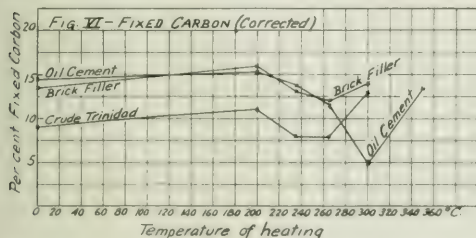
and the values so obtained were plotted in Fig. VI. It is noticed that in all cases there is a drop at 235 to 265°. The brick filler and Trinidad curves then turn upward at 300°. However, the oil-cement curve continued to fall at this temperature. Evidently then, there was some change in the nature of the hydrocarbons themselves and this may give a clue as to the nature of the carbenes.

Richardson¹ has found that paraffin hydrocarbons of the series C_nH_{2n-2} yield no fixed carbon on ignition and that the amount left increased as the propor-

tions of carbon to hydrogen increased. In Grahamite, when the ratio is 8 to 1, there is as high as 50 per cent of fixed carbon. If this is true for asphaltic hydrocarbons, the general nature of the change may be followed.

By consulting Fig. VI it is seen that up to 200° the process was probably one of distillation of lighter hydrocarbons. This was confirmed by an increase in melting points and decrease in the penetration. In the case of the natural asphalts the hydrocarbons left were more mobile when melted. In the case of oil cement, when the hydrocarbons are chiefly of the paraffin series,¹ they are less mobile when heated, due to higher hydrocarbons. Upon heating to 235°–265° the curve would indicate that the proportion of carbon to hydrogen is less. This may be due simply to a distillation of low boiling point hydrocarbons rich in carbon. Those hydrocarbons left in case of natural asphalt, though very hard, show the maximum fluidity when heated to their melting point. They are also more soluble in carbon tetrachloride than in carbon bisulfide. Just what hydrocarbons are formed offers an interesting field for research.

Upon heating to 300° the natural asphalts show an upward turn in the curve, indicating that the proportion of carbon to hydrogen has again increased. This may be due to a cracking process in which either unsaturated hydrocarbons or those of the naphthene



type are formed—either of which are stable at high temperatures. Carbenes now put in a marked appearance. Mackenzie suggests that the carbenes are unsaturated hydrocarbons, but might they not be both? To determine whether a large amount of unsaturated compounds appeared, the iodine numbers were run upon the brick filler and Trinidad. The method used was that of Hubl-Waller described by Holde.³ The values are given in Table III. In neither case was there a marked increase due to the presence of carbenes.

TABLE III.—IODINE NUMBERS

	Original	Heated to 300°
Crude Trinidad	90.11	89.16
Brick Filler	15.11	19.36

In the case of the oil cement a still further decrease in the fixed carbon was observed at even 400°. Since oil residuums consist mainly of saturated paraffin hydrocarbons, it would seem that distillation of the lighter hydrocarbons proceeds even at this temperature. If such is the case, further heat should crack them into unsaturated hydrocarbons and naphthenes.

Accordingly, a sample was heated to 350° C. for 5 hours. The fixed carbon was found to increase as was expected. Evidently, then, the so-called carbenes may consist of either unsaturated hydrocarbons or saturated naphthenes, or both. Much further work is necessary, however, before their nature can be definitely established.

CONCLUSIONS

I—The results of this work seem to show that carbenes are probably the result of the cracking of paraffin and asphaltic hydrocarbons into both naphthenes and unsaturated hydrocarbons.

II—Moderate heating may so change the nature of the hydrocarbons as to render them more soluble in carbon tetrachloride than in carbon bisulfide.

III—Overheating causes marked changes in both natural and oil asphalts which render them unfit for paving purposes. Whether natural asphalt which has been heated over 235° C. is still suitable for durable pavements can be determined only by actual experience, but certainly a temperature limit is important.

IV—It is believed that the fixed carbon curve when corrected to the original weight of material before heating offers a means of tracing the changes in the molecular structure of the hydrocarbons when they are subjected to the influence of heat.

V—There is a close relation between the carbene value and the physical properties of asphaltic materials. Although the physical specifications may be so made that a high carbene content will be excluded, it would seem wise to keep the carbene specification as a safeguard until further information on the subject can be obtained.

INDUSTRIAL CHEMISTRY LABORATORY
STATE UNIVERSITY OF IOWA, IOWA CITY

OBSERVATIONS ON THE ACTION OF SULFUR MONOCHLORIDE ON BITUMINOUS AND TARRY SUBSTANCES AND HYDROCARBON OILS

By JOSEPH V. MEIGS

Received March 22, 1917

It was the writer's original intention to work out an analytical method for examining bituminous substances on the basis of the amount of hydrogen sulfide evolved per unit weight of bitumen on heating the latter with sulfur. This idea was soon abandoned, however, on account of the inconvenience and undesirability, for analytical purposes, of maintaining a uniform elevated temperature (approx. 135° C.). To see whether sulfur and bitumen would react in solution, varying amounts of both were dissolved together in carbon disulfide and allowed to stand, but no sensible reaction was observed.

On evaporating the carbon disulfide, black sulfur crystals were obtained which, examined under the microscope in polarized light, had a somewhat the appearance of a solid solution of bitumen in sulfur.

The advantage of sulfur monochloride as a form of sulfur more active in the cold, than the element, then presented themselves. The effect of this reagent (1% (w/v) solution in carbon tetrachloride) on bitumen

¹ The Modern Asphalt Pavement, 3rd ed., p. 105.

² Examination of Hydrocarbon Oils, Holde-Mueller, p. 430.

was found to be a very distinct one, not only as a reagent but also as a solvent.

A residual oil asphalt, which we will designate as "asphalt B," with a penetration of 12° (100 g., 5 sec., 25° C.), containing 99.6 per cent pure bitumen, was found, qualitatively, to be soluble in sulfur monochloride at room temperature to the extent of leaving no sticky residue on filtration of the solution. Several liquid bitumens were found to be similarly soluble.

Moreover, on treating a solution of "asphalt B" in carbon disulfide with a solution of sulfur monochloride in carbon disulfide, the writer found, by testing with filter paper moistened with ammonia, and comparison with a blank test on a solution containing no bitumen, that hydrochloric acid gas was evolved, slowly, but in considerable amount. This was the only external evidence of a chemical reaction.

More pronounced, however, were the effects, when a tar product used for paving purposes, which we will designate as "tar binder B," was so treated. In addition to a much larger evolution of hydrochloric acid gas than in the case of the asphalt, a marked change took place, in the course of 15 minutes, in the character of the solution; *i. e.*, much of the material in solution was removed, as evidenced by the precipitation of a black, friable powder, insoluble in carbon disulfide, and by a color change, from black and opaque, to deep red and transparent. It is interesting to note that when sulfur monochloride was added, full strength, to "tar binder B," in the proportion by volume of one to two, a violent reaction ensued. Vigorous ebullition and frothing took place, and a degree of heat was developed, much the same as when strong sulfuric acid and water were mixed in the same proportion (one to two). This effect is to be contrasted with the externally quiet, solvent action of strong sulfur monochloride (undiluted with carbon disulfide) on "asphalt B." Indeed, one of the most noticeable effects of the strong sulfur monochloride on "tar binder B" was to increase its viscosity to such an extent that, in the course of 10 minutes, the originally liquid material became changed to a hard, brittle mass. "Tar binder B" yielded the following fractions on distillation:

PERCENTAGES	By Volume	By Weight
Water.....	1.1	0.6
First oils to 110° C.....	1.3	0.9
Second oils to 170° C.....	2.4	1.9
Heavy oils to 270° C.....	28.8	25.4
Heavy oils to 315° C.....	14.1	12.9
Pitch.....	52.3	58.2

In order to prove that the evolution of hydrochloric acid gas in the cases cited was not due to the presence of water in the substances themselves, or in the reagents, as well as to study the action of the sulfur monochloride, an apparatus was devised to measure accurately the ratio of the amount of hydrochloric acid gas evolved to the amount of bituminous substance acted upon by the sulfur monochloride.

The method employed in conjunction with the apparatus, which is seen in diagrammatic form in Fig. 1, consisted in dissolving the bitumen in carbon disulfide, then adding the sulfur chloride reagent in a closed tube, aerating this solution with dry air, and

sucking the dry air, mixed with hydrochloric acid gas and a certain quantity of sulfur monochloride vapor, *first*, through a Pennsylvania Railroad tube (*R'*), containing carbon bisulfide, in order to dissolve and remove the vapor of sulfur monochloride, *second* through water,¹

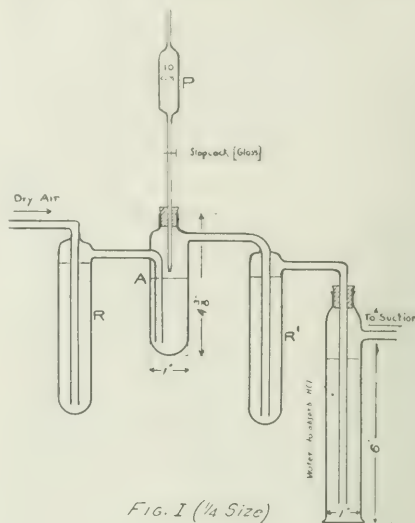


FIG. 1 (1/4 Size)

to absorb the hydrochloric acid gas. This was then determined by titrating an aliquot portion of the water with *N*/20 sodium hydroxide, using methyl orange as indicator. Before entering the reacting solution, the air was saturated with carbon bisulfide vapor in a second Pennsylvania Railroad tube (*R*, Fig. 1) to prevent evaporation of carbon bisulfide from the reacting solution.

The air used for aerating the reacting solution (by means of aspiration) was dried and freed from carbon dioxide by passing through two drying towers, 15 inches high, filled with fused calcium chloride, then through a soda lime tube, four gas-washing bottles containing strong sulfuric acid (sp. gr. 1.84), and finally, through a drying tower 12 inches high containing alternately placed layers of glass wool and phosphoric anhydride.

The Pennsylvania Railroad tubes (*R* and *R'*, Fig. 1) and the reaction tube *A* were heated to 130° C. and cooled in a vacuum desiccator over strong sulfuric acid (sp. gr. 1.84) before use. The sulfur monochloride reagent finally adopted was made by dissolving 50 g. of Kahlbaum's "Schwefelchlorür" in 470 g. of carbon disulfide, which had been previously dried by shaking with and standing over anhydrous sodium sulfate and phosphoric anhydride, respectively. This solution was kept in a glass-stoppered bottle in a desiccator over concentrated sulfuric acid in which 20 per cent by weight of phosphoric anhydride was dissolved. All the carbon disulfide used was dehydrated and pre-

¹ It is not possible to use NaOH solution as absorbent, since carbon bisulfide is carried over into the absorbing solution, and would react with the latter, as the writer found.

served in the same manner. The asphalt, in order to remove traces of water, was kept for ten minutes with stirring, at 130° C., cooled and preserved in a desiccator containing the drying agent mentioned ($\text{H}_2\text{SO}_4 + \text{P}_2\text{O}_5$). The "tar binder B" used was dehydrated by keeping at 110° C., with stirring, for 5 minutes, then cooled and preserved as in the case of the asphalt.

It is to be emphasized that the action of the sulfur monochloride on the substances examined was found to be distinctly a time reaction. Indeed, in the case of the hydrocarbon oils to be mentioned, bubbles of hydrochloric acid gas were seen coming off and shown to be such, even after the lapse of 16 hours. The action in the case of the asphalts and tar examined was much more rapid, but nevertheless, time-consuming, especially as regards the asphalt.

Blank determinations on the apparatus, using a solution of sulfur monochloride without any bitumen, checked closely, and in the standard length of time employed for reaction and aeration (4 hours), and with the standard rate of passage of gas (one bubble per second through the Pennsylvania Railroad tubes), there was imparted to the water used as absorbent of the hydrochloric acid gas, an average acidity equivalent to only 0.043 mg. of hydrogen --C-- 0.84 cc. of 0.050 *N* sodium hydroxide. The pipette *P* (Fig. 1), used for adding the sulfur monochloride reagent, passed into the reaction tube *A* through a cork stopper, made gas-tight by soaking in paraffin. This pipette was heated to drive off adsorbed moisture, immediately before use.

The results are expressed in what the writer proposes to call a "hydrogen number," namely $100 \times$ milligrams of hydrogen removed from organic combination and evolved as hydrochloric acid gas by the oxidizing action of sulfur monochloride, on one gram of the substance examined. Expressed in terms of sodium hydroxide solution, we have the following formula for the "hydrogen number," *vis.*:

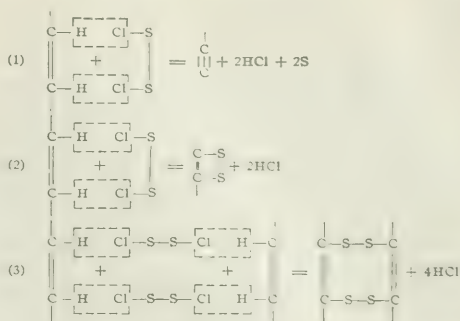
$$\frac{\text{cc. NaOH Solution} \times N}{\text{weight of sample}} \times 100,$$

where *N* = normality of the sodium hydroxide, preferably *N*/20 or *N*/50. The writer used from 0.2 to 0.5 g. of bituminous or tarry matter and 10 cc. of the sulfur monochloride reagent described above. The sample was first dissolved in 15 cc. of carbon bisulfide and the sulfur monochloride then added.

The method gave results concordant to 1 per cent. The following hydrogen numbers were determined.

"Oil asphalt B"	26.5	11	(penetration = 100)
Bermudez asphalt (refined)	1.6	11	(penetration = 14)
"Tar binder B"	184	184	

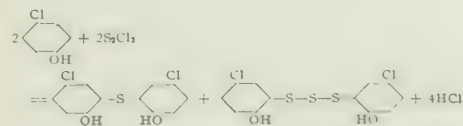
The mechanism of the reaction between sulfur monochloride and the substances examined remains to be elucidated by further work, which the writer hopes to carry on. At this time, however, it appears not unlikely that the reaction takes place between unsaturated hydrocarbons and the sulfur chloride, perhaps in one of the following ways:



Whereas the first reaction produces further unsaturation in the already unsaturated hydrocarbon, the second reaction gives rise to ring formation.

The third reaction expresses a combined ring formation and polymerization phenomenon, and is of the general type ascribed by various writers, notably Lange,¹ to express the reaction between sulfur chloride and phenols, as well as aromatic amines.

In the case of *p*-chlorophenol, Richter has shown² that sulfur monochloride acts as follows:



This reaction and Equation (3), above, are of the same general type, so far as condensation is concerned.

It is known³ that the natural asphalts from the Trinidad and Bermudez deposits contain a larger percentage of unsaturated hydrocarbons than the residuals prepared from Mexican, California and Texas oils. If the sulfur chloride reaction, as described by the writer, be due to unsaturated hydrocarbons, then the large difference between the "hydrogen numbers" of "oil asphalt B" and refined Bermudez asphalt, noted above, is accounted for.

It should be stated that the acid gas evolved as described was shown to be hydrochloric acid by the test with ammonia, as well as by precipitating silver chloride from the solution of the gas in water. No hydrogen sulfide or other sulfur-containing gases were detected in any of the reactions.

Whether the sulfur monochloride also adds itself, as such, to unsaturated hydrocarbons, contained in bitumens, remains to be determined, possibly by means of an analytical method, which the writer has worked out, and which consists in pipetting out a portion of the reacting solution, determining the excess sulfur monochloride in this aliquot portion by shaking with water, and comparing, not with a blank, but with the corresponding "hydrogen number" determined in the same previous method.

¹ *Journal of the American Chemical Society*, 1912, 34, 1131.

² *Journal of the American Chemical Society*, 1912, 34, 1131.

³ *Journal of the American Chemical Society*, 1912, 34, 1131.

ACTION OF SULFUR MONOCHLORIDE ON GAS ENGINE OILS

In testing several gas engine oils with sulfur monochloride, the procedure was adopted of adding 1 cc. of sulfur monochloride to 5 cc. of the oil in a test-tube, mixing thoroughly, allowing to stand in the cold for 15 minutes, and then comparing the results with those obtained on an oil of known refinement.

Several gas engine oils found on the market were tested and it was found that the specially refined oils showed but a slight wine-colored tinge, whereas those not so carefully selected and refined changed to a deep wine color in some cases, and almost black in others. In the latter cases, the evolution of small bubbles of hydrochloric acid gas was clearly visible after half an hour, and these were shown to be such by testing with ammonia and comparing with a blank test. That is to say, the reaction in the case of the oils was found to be evidently identical, as to the evolution of hydrochloric acid gas, with the reaction in the case of the bituminous and tarry matter. It was also found that the more rapid the development of color in the case of the oils, the more vigorous the evolution of hydrochloric acid gas. Finally, if the gas engine oils were arranged in order, beginning with those that showed least color change in the same time interval, and proceeding to those that developed the darkest color, it was found that this order was the same as that in which the oils were placed by Gill's gumming test¹ beginning with those showing least gum formation and proceeding to those showing the most gum, or tar.

Since hydrogen is removed from the hydrocarbon molecule by the action of the sulfur monochloride and, since, as is well known, the removal of hydrogen (as water vapor or steam by the agencies of heat and atmospheric oxygen) constitutes a large part of the process of carbonization of lubricating oils, it would seem that sulfur monochloride might be used to measure the relative "sensitiveness" of the hydrogen in hydrocarbon oils, that is to say, as a measure of the relative stabilities of those oils.

The matter is being further studied, in order to show, if possible, whether the action of sulfur chloride on bituminous matter, tarry substances and paraffin oils, is due, as appears very likely, to the presence of unsaturated hydrocarbons.

SUMMARY

I—It has been shown that sulfur chloride acts on bituminous matter, tarry substances and hydrocarbon oils, giving hydrochloric acid gas as one product of the reaction.

II—Sulfur monochloride, undiluted, is proposed as a reagent for testing the comparative stabilities of transparent lubricating oils.

III—Sulfur monochloride in carbon disulfide is proposed as a reagent for investigating the nature of bitumens and hydrocarbon oils.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY, BOSTON

¹ Gill, "Handbook of Oil Analysis," 7th Ed., p. 43.

THE PHYSICAL TESTING OF PAPER AS AFFECTED BY HUMIDITY

By ROSS CAMPBELL

Received April 23, 1917

As a result of reading the article on the "Influence of Humidity on the Physical Constants of Paper" by Kress and Silverstein, in *THIS JOURNAL*, 9 (1917), 277, it was decided to contribute the data on the same subject which was collected in this laboratory by E. J. Goldstein during the summer of 1916.

APPARATUS

Unfortunately, we were not blessed with the excellent equipment described in the above-mentioned article. We had no method of temperature control and were forced to control the humidity by regulating a Comins Sectional Humidifier head by hand. The humidity was determined by means of a recording wet and dry bulb thermometer and a sling psychrometer. Even with this very crude control, it was found that the relative humidity did not vary more than two or three points, at most, nor the temperature more than 1°.

The tensile strengths of the specimens were determined by means of a hand-operated Schopper tensile-strength test machine. The test strips were 180 mm. long.

Resistances to folding were determined by means of a motor-driven Schopper folding machine.

Times of penetration were determined by floating the samples on an ink bath.

PROCEDURE

About 8.00 A.M. the test room was closed and the humidifier started. The sheets of paper to be tested had been hung in the test room the night previous. It was found that the humidity could be brought to the desired point by 1.00 P.M. and that, owing to the gradual increase of the humidity, the weight of the sheets to be tested was constant at about the same time. The testing was then begun. All the tests of a given kind, on a given sample were, of course, run on the same day.

OBJECT OF TESTS

The object of the tests which form the subject of this article was to determine how closely it would be necessary to control the humidity in order to have physical tests comparable from day to day. In addition it was desired to see whether the different grades, as fines, bonds, etc., varied in the same way.

PAPERS TESTED

The papers tested were the company's regular commercial output. They varied, as is shown in the table, from high-grade, loft-dried bond and ledger, to a relatively low-grade, machine-dried, fine.

Sample	Kind	FURNISH (PERCENTAGES) Rag	Soda	Sulfite	THICKNESS in	FOLIO Wt. in Lbs. per 500 sheets
A	Bond	25	Few	75	0.00384	20
B	Ledger	85	..	15	0.00385	20
C	Bond	90	..	10	0.00360	20
D	Bond	50	..	50	0.00320	20
E	Envelope	Trace	0.00362	24
F	Bond	15	..	80	0.00338	20
G	Envelope	Few	0.00410	28
H	Bond	15	10	75	0.00405	20
J	Blueprint	50	..	50	0.00406	16
K	Bond	60	..	40	0.00492	19
L	Blueprint	50	..	50	0.00509	24

RESULTS OF PHYSICAL TESTING OF PAPER WITH VARYING HUMIDITY

Av. Rel. Humidity	A	B	C	D	E	F	G	H	J	K	L
PENETRATION (NEW STANDARD): SECS.											
54	862	686	387	222	1320	810	902	438	99	316	
61											
64	544	318	251	447	726	500	496	343	206	48	179
65	882	544	379	556	1326	846	996	403	89	367	
70	733	402	269	446	1079	555	820	554	307	79	288
75	81	615	398	278	423	974	569	760	558	292	74
86	830	664	387	556	1362	826	1062	401	91	326	
90											
92	462	215	412	729	549	613	356	227	63	171	
98											

MULLEN: LBS.

54	26.1	43.5	35.8	23.5	19.1	20.6	10.2	28.6	22.9	25.8
61											
64	27.2	43.9	37.2	23.1	18.9	20.4	9.9	28.5	22.6	23.8	33.6
65											
70	26.1	43.5	36.3	22.4	18.1	18.6	10.1	29.1	22.8	23.8	35.0
75	26.6	41.6	36.2	21.9	18.0	19.5	10.5	26.6	22.3	24.3	32.8
81	26.3	41.4	38.2	21.2	19.1	18.9	9.5	26.9	30.8	24.0	31.3
86	23.3	38.0	33.4	19.8	15.8	16.2	8.8	24.8	21.3	21.7	27.6
90	20.6	34.3	28.4	18.6	12.5	14.3	7.7	21.9	20.3	20.3	
92								18.6		25.6	
98	18.1	27.8	22.7	14.9	9.1	12.6	6.2	16.8	20.9	14.6

FOLDING, CROSS, DOUBLE FOLDS

54	89	402	555	44	11	25	7	111	95	262	...
61											
64	114	460	620	42	13	23	6	84	71	193	342
65											
70	82	372	887	37	8	22	5	134	60	212	249
75	64	557	407	37	10	23	6	67	56	189	217
81	104	355	737	34	21	25	6	76	57	168	296
86	62	361	533	27	6	21	6	68	60	172	188
90	64	358	583	29	6	15	5	49	53	167
92									51	185	
98	54	222	377	17	4	11	3	55	249	62

FOLDING MACHINE, DOUBLE FOLDS

54	38	811	554	61	13	28	4	76	139	360
61											
64	58	1260	754	77	15	24	5	75	195	388	292
65											
70	55	2090	899	72	9	31	5	161	161	485	426
75	109	2124	1028	71	13	33	5	147	148	586	676
81	92	2457	1318	94	27	39	6	211	207	483	329
86	88	3580	1430	78	11	29	6	163	171	534	451
90	76	4160	1980	64	12	32	5	155	292	542
92									156	411	
98	47	3328	2110	46	9	35	4	142	379	279

RESULTS OF PHYSICAL TESTING OF PAPER WITH VARYING HUMIDITY

Av. Rel. Humidity	A	B	C	D	E	F	G	H	J	K	L
TENSILE STRENGTH, CROSS KO.											
54	4.21	4.62	4.46	3.28	3.25	3.06	2.89	4.21	3.42	3.53
61											
64	4.02	4.23	4.66	2.96	3.14	2.99	2.69	4.00	3.26	3.57	4.73
65											
70	3.83	4.09	4.03	2.85	2.86	2.63	2.57	3.59	2.89	3.05	4.69
75	3.80	4.03	4.32	2.90	2.76	2.55	2.35	3.62	2.96	3.20	4.34
81	3.71	3.83	3.69	2.61	2.58	2.45	2.45	3.31	2.78	2.97	4.21
86	3.22	3.67	3.35	2.43	2.33	2.39	2.25	3.29	2.61	2.93	3.89
90	2.65	2.46	2.59	1.74	1.84	1.78	1.58	2.37	1.93	2.02
92									2.12	3.34
98	1.86	2.19	2.67	1.93	1.78	1.54	1.66	1.72	2.60	1.99

TENSILE STRENGTH, MACHINE, KO.

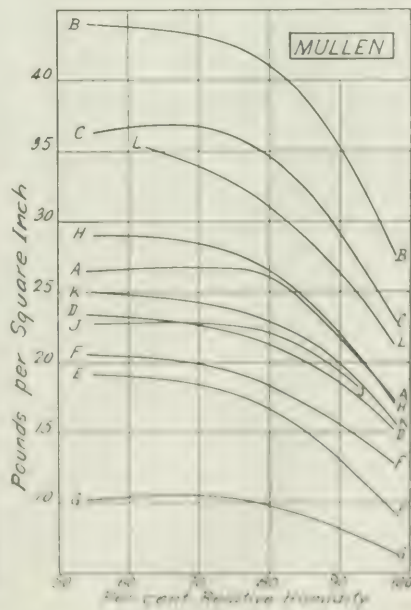
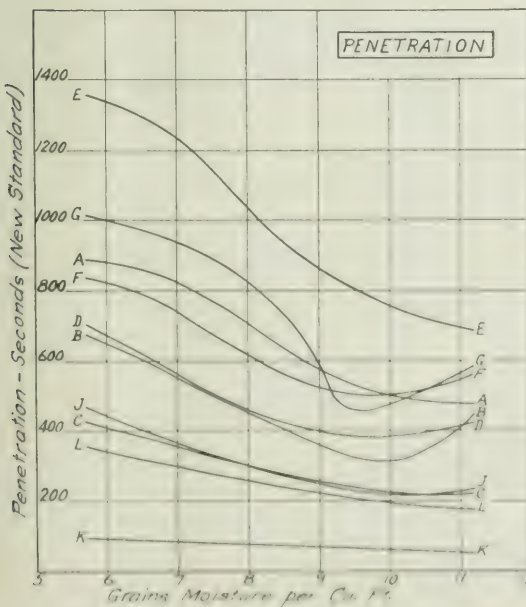
54	6.70	8.69	7.78	5.78	6.27	6.09	4.03	7.35	6.14	6.54
61											
64	6.91	8.65	7.94	5.88	6.12	5.62	3.81	7.39	5.97	6.28	7.78
65											
70	6.06	7.80	7.25	5.37	5.89	5.34	3.49	6.38	5.38	5.99	7.32
75	6.40	7.86	7.23	5.14	5.64	5.17	3.31	6.52	5.59	5.58	6.74
81	5.76	7.70	6.76	5.13	4.66	4.69	3.17	6.38	6.72	5.40	6.55
86	5.58	7.28	6.53	4.61	5.10	4.63	3.04	5.98	5.07	5.22	6.28
90	4.13	5.34	4.81	3.32	3.67	3.41	2.19	4.82	4.05	3.88
92									8	5.03	
98	3.77	4.33	4.67	3.34	3.80	2.88	2.28	3.61	4.29	3.69

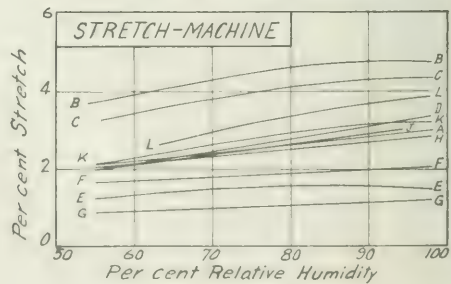
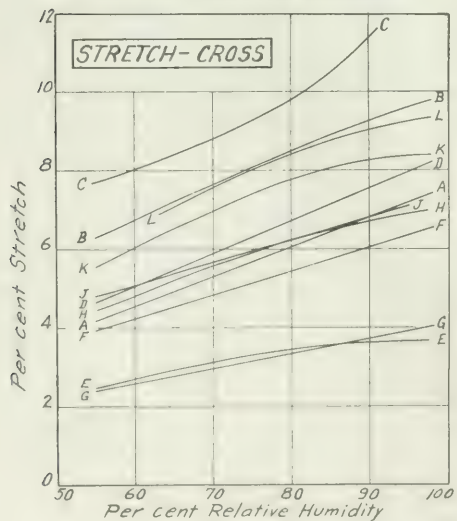
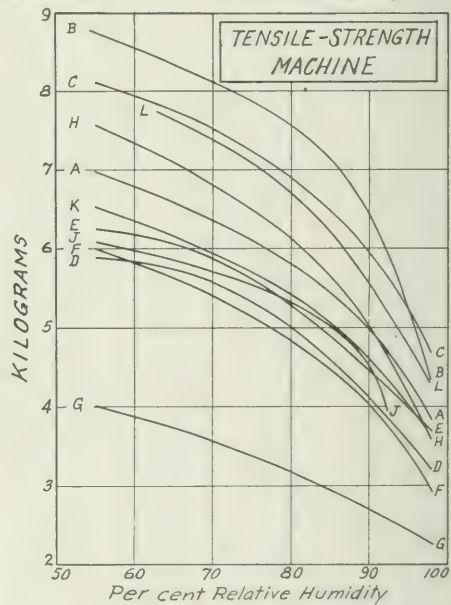
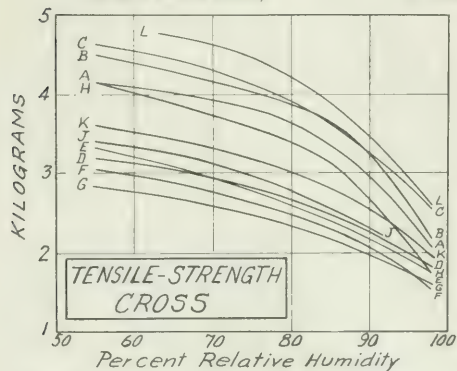
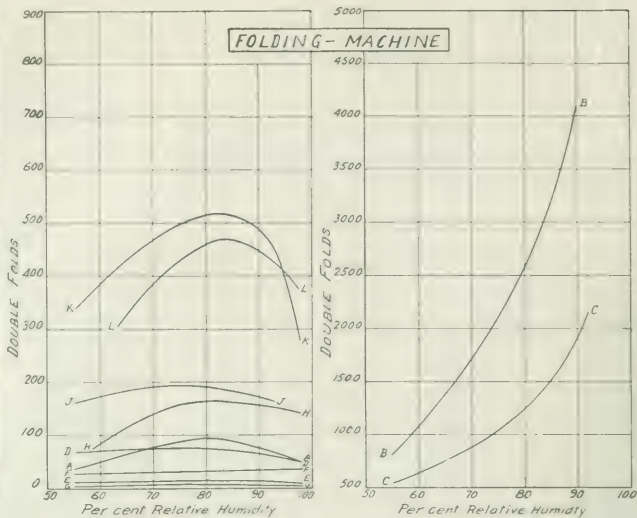
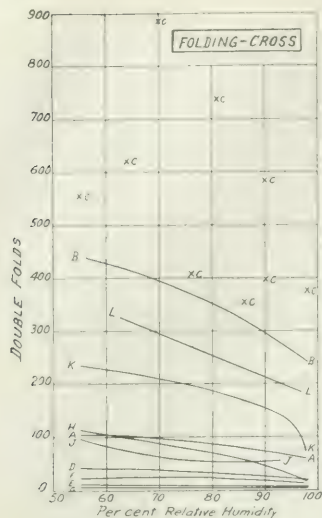
STRETCH, CROSS, PER CENT

54	4.4	6.6	7.9	4.8	2.6	4.0	2.4	3.8	4.8	5.0	...
61											
64	4.2	6.5	8.0	5.1	3.1	4.8	2.8	5.0	4.2	6.0	6.3
65											
70	5.8	8.0	9.1	6.5	2.9	4.8	3.2	5.4	6.1	6.3	7.8
75	5.2	6.9	9.7	5.6	4.8	5.6	3.8	6.6	6.3	8.1	8.4
81	6.3	9.2	10.2	7.6	3.1	6.4	3.6	6.8	6.7	8.5	8.4
86	6.8	9.1	11.6	7.0	3.5	5.8	3.3	6.1	6.8	8.0
90											
92											
98	7.5	9.0	10.4	8.5	3.7	6.8	4.0	7.0	9.2	8.1	9.3

STRETCH, MACHINE, PER CENT

54	2.2	3.6	3.1	2.0	1.2	1.7	0.9	2.1	2.0	2.1	...
61											
64	2.3	4.0	3.5	2.3	1.5	1.7	1.0	2.1	2.0	2.3	2.7
65											
70	2.6	4.3	4.0	2.8	1.4	1.9	1.0	2.3	2.5	2.8	3.8
75	2.7	4.7	3.9	2.5	1.7	1.9	1.1	2.6	2.5	2.7	3.0
81	2.8	4.5	4.2	3.0	1.6	1.8	1.1	2.8	2.8	3.0	3.8
86	2.5	5.1	4.8	3.1	1.6	1.9	1.1	2.6	2.9	3.3
90											
92											
98	3.1	4.6	4.4	3.4	1.6	2.1	1.3	2.9	3.9	3.2	5.6





RESULTS

The results obtained are given in the accompanying set of tables and plots. Before making the plots, two preliminary sets were made, one using relative and the other absolute humidities. It was found that the results could be plotted against the relative humidity only, except in the case of the penetration tests, where the results yielded a curve only when plotted against the absolute humidity.

It will be noted that the results here given agree with those obtained by Kress and Silverstein in the case of the Mullen test plot only. These variations may have been due to the higher grades of paper used in our tests, but this seems rather doubtful, as no such variations were observed over the range of qualities tested here.

It was found impossible to draw a curve for "penetration" for sample "H" owing to the wide variations noted between different tests at the same humidity. In the "folding-cross" tests no curve could be drawn for "C," the points being as shown on the drawing. The "folding-machine" tests for B and C were so far beyond the range of the other samples that their curves are presented on a different scale.

SUMMARY

The magnitude of most of the tests decreased 40 to 50 per cent as the relative humidity increased from 50 to 98 per cent. The stretch in the machine direction increased about 30 per cent and in the cross direction about 40 to 50 per cent under the same circumstances.

The results of the folding tests in the machine direction tended to reach a maximum at about 80 per cent relative humidity in all except two cases. In the cases of samples "B" and "C," the curve plotted from the results of this test increased very rapidly with the increase of relative humidity and tended to become asymptotic to about the 95 per cent humidity line.

The time of ink penetration decreased 40 to 50 per cent as the absolute humidity increased from 6 grains per cubic foot of air (55 per cent relative humidity at 80° F.) to 11 grains per cubic foot (100 per cent relative humidity at 80° F.).

Special attention is called to curves "B" and "K." These samples were the same in every way except that "B" was tub sized and "K" was not. The advantages of a good tub size are very clearly shown.

RESEARCH LABORATORY, AMERICAN WRITING PAPER COMPANY
DORCHESTER, MASSACHUSETTS

THE OCCURRENCE OF GERMANIUM IN MISSOURI AND WISCONSIN BLENDES¹

By G. H. ROUSSIER

Of the fifty or more elements which we usually distinguish as rare, few are more worthy of the distinction than the element germanium. Discovered in 1886 by Winkler in a new silver mineral, argyrodite, and identified by him as the element of Mendeleev, it has dropped back into oblivion since the days of

this classic work, until to-day it is one of our least known elements. With but few exceptions our entire knowledge of the properties of the element is due to Winkler. According to Urbain,¹ the material worked over by Winkler for the preparation of germanium was a mixture of argyrodite with other minerals, and did not contain more than 0.36 per cent of argyrodite. Since the germanium content of argyrodite is 6 to 7 per cent, the germanium content of his raw material could only have been between 0.02 and 0.03 per cent. From this material Winkler obtained 80 kilos of mixed metallic sulfides which yielded 156 g. pure germanium.

Argyrodite, the richest source of the element heretofore known, has proved exceedingly rare, and during the thirty years that have elapsed since the work of Winkler only a very few additional sources of the element have been brought to light.

Krüss has reported the presence of 0.1 per cent germanium in euxenite. Its occurrence in samarskite, tantalite and niobite has been reported and denied, a disagreement which is not surprising in view of the complexity of these minerals. Two other sources have been more recently discussed. Urbain² by spectroscopic methods detected germanium in 38 out of 64 blendes from various localities. Taking 550 kilos of one of these, a Mexican blende, he obtained from it 5 g. pure germanium. Bardet,³ also by spectroscopic methods, detected traces of germanium in certain French mineral waters. Since the recovery of germanium from blendes by the method of Urbain was long and costly, he believed that the residues from these mineral waters might yield sufficient germanium to provide for the needs of scientific study. From 100 kilos of residues, representing 250,000 liters of mineral water, he obtained 60 mg. GeO_2 .

A more recent report of the occurrence of germanium is due to W. F. Hillebrand and J. A. Scherrer⁴ in a paper on "The Recovery of Gallium from Spelter in the United States," mention is made of an examination for germanium of a number of blendes, carried on at the Bureau of Standards by Dr. K. Burns. By the use of the spectroscope germanium was identified in several of these, notably in a Missouri sulfide. A short paper by the writer was published in *This Journal* in July, 1916, p. 585, relating to the identification of germanium in zinc-bearing materials. At that time it was not possible to give details as to the origin of the rich germanium-bearing material. It is the purpose of the present paper to discuss the nature of this material, which now appears to be the richest source of the element known.

During the summer of 1917 there was brought to the writer⁵ attention an article in the *Black Hills* newspaper, printed from spelter mined in the American west. A chemical examination revealed the presence of considerable quantities of an unusual constituent, which was identified as the element germanium.

The identification with certainty is a statement of

¹ *Comptes Rendus*, 150 (1860).

² *Ann. Ch.*, 149 (1905).

³ *Comptes Rendus*, 158 (1914).

⁴ *Trans. Am. Chem. Soc.*, 38 (1916).

⁵ Presented at the 54th Annual Meeting of the American Chemical Society, Boston City, April 10 to 14, 1917.

the oxide of zinc with hydrochloric acid, a slow current of chlorine being bubbled through the solution during boiling to prevent distillation of arsenic. The strongly acid distillate was diluted and saturated with hydrogen sulfide. A voluminous white precipitate was formed which was readily soluble in alkalis and which dissolved in water, although more slowly. The sulfide was slowly re-precipitated from its aqueous solution upon addition of strong acids. The addition of hydrofluoric acid to the aqueous solution of the sulfide, followed by saturating the mixture with solid potassium chloride, produced a grayish, gelatinous precipitate, the double fluoride of potassium and germanium.

A roughly quantitative determination of the ratio $\text{GeO}_2 : \text{GeS}_2$ gave the value 0.747. The theoretical ratio, assuming 72.5 for the atomic weight of germanium, is 0.766. The sulfide precipitate was weighed without washing free from precipitated sulfur, since the usual alcohol-carbon bisulfide washing caused the precipitate to run through the asbestos Gooch. The presence of sulfur in the precipitate when weighed would, of course, lower the ratio. Bearing this in mind, the agreement between calculated and observed values is fairly close.

By distilling weighed samples of the oxide of zinc with chlorine and hydrochloric acid, and precipitating and weighing the sulfide, the value $\text{GeO}_2 = 0.25$ per cent was obtained.

A sample of the oxide of the element, prepared by ignition of the sulfide and treatment of the residue with nitric acid, was examined at the Bureau of Standards with the spectroscope and was reported, "Germanium, principal constituent."

As has been stated, the oxide of zinc in which this considerable amount of germanium was detected was prepared from spelter residues. The attempt was now made to locate geographically the source of the element.

The residues in question were mixed residues from Joplin and Wisconsin ores. An examination of a number of oxides of zinc prepared from ores from various localities, including those made from Missouri and Wisconsin ores, was now undertaken. For this work a delicate test for the presence of germanium was required. The following procedure was applied with success to a large number of samples; the details are those which were found necessary with this class of material. The essential details of the method are due to A. A. Noyes:

Weigh a 100-g. sample of the oxide of zinc into a liter distilling flask connected with a water-cooled condenser, and add 200 cc. concentrated hydrochloric acid. Pass chlorine into the mixture until the gas appears in the receiver of the condenser, and then heat the mixture to boiling and distil to about half volume, continuing the passage of a slow current of chlorine. Dilute the distillate with an equal volume of water and pass hydrogen sulfide into it for at least 30 minutes. If no precipitate is formed (other than the usual opalescence due to sulfur), germanium is absent. If

a precipitate is formed, filter it off on a small paper and wash it with a very little cold water.

Place the paper containing the precipitate in a flask with about 150 cc. water, boil for 15 minutes, and filter. To the filtrate add 50 cc. concentrated hydrochloric acid, cool and treat with hydrogen sulfide as before. A white flocculent precipitate indicates the possible presence of germanium.

Filter on a small paper and wash once with a little cold water. Pour ammonia through the filter, receiving the solution and washings in a platinum dish. Evaporate to dryness. Moisten the residue with concentrated nitric acid and evaporate to dryness again. When dry, ignite for a few minutes.

To the residue add a very little water and a few drops of hydrofluoric acid, saturate with solid potassium chloride and allow to stand in the cold for 15 minutes. If germanium is present a grayish, gelatinous precipitate is formed, soluble on heating or diluting the solution.

The presence of germanium is not reported unless this last confirmation test is obtained.

With this procedure positive results were obtained with both Joplin and Wisconsin Separator ores. Positive results were also obtained from Mineral Point "Special Leaded Oxide of Zinc," from an oxide made from a Mexican ore (La Bufa), and from one or two others. Negative results were had from two other Mexican ores, from ore from Austinville, Va., from Mineral Point "Prime Oxide of Zinc," and from New Jersey ores ("XX Oxides"). In all cases where positive results were obtained the amounts detected were very much less than were met with in the oxide made from spelter residues, probably not one-tenth as much. It is probable that the procedure described would detect as little as 0.01 per cent germanium in an oxide of zinc.

It is evident from these results that the germanium content of the residuum may have been derived from either the Wisconsin or the Missouri ore, or from both of them, and that it has been greatly concentrated during the metallurgical treatments which it has undergone. The treatment in the spelter retorts and in the oxide fires has carried on this concentration on an enormous scale and we have, as a result, an abundance of a material much richer in germanium than the original ores.

The properties of the substance as given in the literature explain the nature of this concentration. The metal is said to be readily obtained by reduction of the oxide with carbon at a red heat, so that under the conditions prevailing in the spelter retort the germanium must be present in the elementary state. It is not markedly volatile at 1350°C . Accordingly, while the zinc was distilling off into the condenser, the germanium for the most part remained behind, and was discharged with the residues. The qualification seems necessary, since Uhler has detected traces of germanium in the leady residues from the redistillation of low-grade metal.¹ In the zinc oxide furnaces the ger-

¹ Browning, "Introduction to the Rarer Elements," 4th edition, p. 84.

manium burned to oxide and passed off with the zinc smoke into the bags.

It is possible to obtain a rough approximation of the amount of germanium in the original ore by assuming a zinc oxide content of 10 per cent for the residues, and of 50 per cent for the original ore. Assuming in all cases complete recoveries, the GeO_2 content of the residues would have been one-tenth that of the oxide of zinc, or 0.025 per cent, and that of the original ore would have been approximately 0.01 per cent.

The work reported in the preceding paragraphs was carried on by the writer in the Research Laboratory of The New Jersey Zinc Company, at Palmerton, Pennsylvania, to the officials of which company the writer is under obligations for permission to publish these results. Through the kind offices of Mr. George C. Stone, of the New Jersey Zinc Company, a supply of the germaniferous oxide of zinc has been furnished the Massachusetts Institute of Technology for study. This work has already been begun.

MASSACHUSETTS INSTITUTE OF TECHNOLOGY
CAMBRIDGE, MASSACHUSETTS

PHOSPHOR-TIN AND A VOLUMETRIC METHOD FOR ITS ANALYSIS

By RICHARD EDWIN LEE, W. H. FEELEY AND FRANK H. REICHEL

Received February 19, 1917

The paper presented here traces its origin to a request forwarded to this laboratory for a method for the rapid and accurate analysis of an alloy of phosphorus and tin, known commercially as "phosphor-tin." This material is purchased according to specifications. Analysis of each shipment, therefore, is desirable. Furthermore, since the correct proportions of the material to be used in the various processes can be determined only from a knowledge of its composition such an analysis is practically necessary. It is obvious, therefore, that a method corresponding to the description in the request should be available. No such method, however, was found in the literature.

In this connection it may be contended that inasmuch as the tin in the alloy can be readily determined by some standard method, such as the sulfide method, and the percentage of phosphorus estimated by the "method of difference," that the problem presented was not one difficult of solution. It should be noted, however, that the presence of any impurities in the alloy would cause a corresponding error in the calculation of the phosphorus content. This of course would render the procedure valueless. Obviously the problem requires for its solution the formulation of methods for the determination of both phosphorus and tin.

PROPERTIES AND USE OF PHOSPHOR-TIN

The phosphorus in phosphor-tin alloys varies as a rule from 0.1 to 3 or 6 per cent. According to Desch,¹ phosphor-tin is grouped with the so-called "brittle alloys," which are described by him as "alloys produced commercially for the purpose of facilitating the addition of small amounts of elements to molten metals. Thus aluminum and phosphorus as such are now seldom added to metals, rich alloys of these substances

with iron, copper, or tin being usually employed. These rich alloys are composed principally of inter-metallic compounds, as silicides and phosphides."

Phosphor-tin is manufactured on the large scale by melting tin and phosphorus in large furnaces which are frequently provided with apparatus for the partial exclusion of air. The alloy has a crystalline structure and is very hard and brittle. In color it resembles tin.

This alloy is used instead of tin in the manufacture of various tin alloys for the purpose of either preventing the formation of oxide or enhancing certain mechanical qualities of the alloy into which it enters. For example, in the manufacture of certain bronzes, if phosphorus is added in small amounts, it apparently does not produce, as was originally suspected, a new alloy known as phosphor-bronze. It serves simply as a deoxidizing agent in the molten metal, the resulting phosphoric oxide passing into the slag or scum on the surface.¹ When the metals entering into the composition of the alloy are melted in the absence of phosphorus the alloy is more or less seriously contaminated with oxides. It is obvious, therefore, that if the quantity of added phosphorus be carefully adjusted, the resulting product is merely a purified alloy. However, if a larger quantity of phosphorus is introduced than is required when it is to function simply as a reducing agent the product is an alloy with properties distinctly different from those of the merely purified alloy.

In the manufacture of bronze, according to Desch, "if the quantity of phosphorus introduced through the medium of phosphor-tin exceeds that required for complete deoxidation by more than about 0.1 per cent, it will cause brittleness owing to the separation of hard particles of the phosphide, Cu_3P . Such a mixture is sometimes very incorrectly called phosphor-bronze. If the alloys are to be employed in the manufacture of gear wheels, bearings, etc., the quantities of tin and phosphorus present vary from 6 to 15 per cent and 0.7 to 1.5 per cent, respectively. These alloys are very hard and better able to resist friction. The hardness is due in part to the presence of the hard particles of copper phosphide. The presence of these hard masses in the comparatively soft matrix of lead produces the combination of great hardness with a limited but distinct plasticity which is required for such purposes."

It is not desirable, however, to enter into a detailed account in this paper of investigations in this field of ternary alloys; nor is this necessary to make it perfectly obvious that methods for the rapid and accurate chemical analysis of alloys similar to phosphor-tin are of immediate need in control work.

PRELIMINARY EXPERIMENTS SHOWING THE NERBATIVE OF THE ALLOY IN CERTAIN REACTIONS

At the very suggestion of the investigation it was concluded that it would be necessary to devote part of the work to determine whether the phosphorus in the alloy is stable in the chemically combined or the combined form although it seemed rather improbable

that it should exist in the latter form. Subsequent work indicated that the metalloid is present in the alloy in the form of a definite compound.

The early part of the experimental work was devoted, therefore, to a study of the effect of various solvents on suitably prepared samples of the alloy with the following results:

Sulfuric acid (5 *N*) failed to dissolve the sample, but sulfuric acid (sp. gr. 1.84) effected its immediate solution. *Hydrochloric acid* (sp. gr. 1.20) readily dissolved the alloy, but 5 *N* acid apparently had little effect on it. *Nitric acid* (sp. gr. 1.42) decomposed the sample, leaving a white residue. When *aqua regia* was added to the alloy the authors were very much perplexed to find at first that the sample apparently ignited and burned with a blue flame. It may be noted here that it was this rather unexpected behavior which later suggested the proposed method for the solution of our problem.

Having ascertained how to effect the solution of the alloy it was decided to attempt quantitative determinations of tin and phosphorus, using sulfuric acid (sp. gr. 1.84) as a solvent, with a view to determining whether all of the phosphorus was liberated as phosphine, or whether it was partially oxidized to phosphoric acid.

One-half gram of the sample was dissolved in 10 cc. of sulfuric acid (sp. gr. 1.84) and evaporated to 7 cc. The solution was then diluted with 150 cc. of water and saturated with hydrogen sulfide. The precipitate of tin sulfide was filtered on a weighed Gooch crucible, dried, and finally ignited to the oxide and weighed. The phosphoric acid in the filtrate was then determined. As the sulfuric acid would eventually act as an interfering substance, it was precipitated as barium sulfate, using barium nitrate as the precipitant. The barium sulfate was filtered off, washed, and rejected. To the filtrate, heated to 85°, 50 cc. of ammonium molybdate solution were added. The precipitate of ammonium-phosphomolybdate was filtered on a weighed Gooch crucible, dried at 110° and weighed. From the weight of this precipitate the percentage of phosphorus was calculated. The determinations of the tin by the method outlined checked within satisfactory limits, but the results obtained from the phosphorus determinations were not concordant, the conclusion being that varying portions of the phosphorus were oxidized during the process of solution. Concentrated sulfuric acid was, therefore, abandoned as a solvent for the alloy.

Solution of the sample in hydrochloric acid proved to be the real starting point of the method presented in this paper. A 0.5-gram sample of the alloy was treated with hydrochloric acid (sp. gr. 1.20). It dissolved rapidly with the evolution of phosphine. The solution was evaporated to 10 cc., diluted with 100 cc. of water and saturated with hydrogen sulfide. The precipitate of tin sulfide was filtered out on a weighed Gooch crucible, washed, ignited, weighed as the oxide and the tin calculated as before. The series of results obtained checked very closely with those obtained when sulfuric acid was used as a solvent. This

standard procedure for determining tin was used in the early stages of the work to check the determinations of tin by the proposed method. Further confirmation of these results was secured later by the electrolytic method.

The filtrate from the tin sulfide was heated to remove hydrogen sulfide, then neutralized with ammonium hydroxide and magnesia mixture added. Six separate tests failed to show evidence of the presence of phosphoric acid, even after 24 hrs.

With the evidence at hand indicating that the phosphorus is evolved quantitatively in the form of phosphine when the alloy is dissolved in hydrochloric acid, the solution of one phase of the problem, namely, the determination of the phosphorus content, was anticipated if a method could be formulated by which the gas might be absorbed and oxidized to phosphoric acid.

DEVELOPMENT OF METHOD FOR DETERMINING PHOSPHORUS

A variety of solutions have been employed in gasometric methods for absorbing phosphine quantitatively. Only two of those suggested, however, were found suitable, owing to the nature of the procedure involved. These two were bromine water and a solution of potassium permanganate.

The apparatus used consisted of a Florence flask of 500 cc. capacity fitted with a 3-holed rubber stopper through which a 100-cc. tap-funnel and two pieces of glass tubing bent at right angles were inserted. For the absorption train, three Erlenmeyer flasks of 150 cc. capacity were connected in series with the Florence flask.

AQUEOUS SOLUTION OF BROMINE—To each of the Erlenmeyer flasks 100 cc. of bromine water were added. The train was connected to the evolution flask in which a 0.5-g. sample of the alloy was placed. Hydrochloric acid (sp. gr. 1.20) was added to decompose the alloy. The greater part of the bromine in the first absorption flask disappeared before that in the second flask was attacked, owing to the rapid absorption and oxidation of the phosphine. The evolution flask was finally freed from phosphine by sweeping out the system with natural gas or carbon dioxide. By this latter procedure most of the remaining bromine was displaced from the water solution and escaped into the laboratory. Owing to the well-known irritating action of bromine vapors on the respiratory passages it was thought that the use of bromine water as an absorbent might not be regarded as entirely satisfactory for routine analytical work. Nevertheless, four analyses were made. The phosphoric acid in each flask was determined separately to be sure that no phosphine escaped the last flask in the train, it having been shown that none remained in the hydrochloric acid solution in the evolution flask.

The contents of the three flasks in which the respective delivery tubes had been rinsed were transferred to beakers marked Nos. 1, 2 and 3, corresponding to the positions in which the flasks were located in the train. The phosphoric acid present in each flask was

determined by a standard procedure with the results given in Table I.

TABLE I—RETENTION OF PHOSPHINE BY AQUEOUS SOLUTIONS OF BROMINE

Flask No.	Per cent Phosphorus Found			
	1	2	3	TOTAL
Experiment 1.....	2.69	0.32	0.00	3.01
Experiment 2.....	2.91	0.07	0.00	2.98
Experiment 3.....	2.87	0.16	0.00	3.03
Experiment 4.....	2.51	0.50	0.00	3.01

The absence of phosphorus in the third absorbing-flask indicates that no phosphine escaped.

Although it appears that bromine water may be used for routine work with satisfactory results if operations are conducted in a hood, or if a trap is provided to prevent the escape of bromine vapor, it was abandoned as an absorbent for one which proved more suitable. This was a solution of potassium permanganate.

AQUEOUS SOLUTION OF POTASSIUM PERMANGANATE—

The use of a solution of potassium permanganate as an absorbent of phosphine with its ultimate oxidation to phosphoric acid, H_3PO_4 , immediately suggested the attractive procedure of determining the phosphorus by titration of the excess of a known quantity of a standard solution of the substance. Unforeseen difficulties were encountered, however, when an effort was made to conduct the analysis according to the foregoing scheme.

The hydrochloric acid which is used as the solvent for the alloy tended to pass over into the absorbing flasks where it decomposed the permanganate. This fact made it necessary to search for another absorbent which would trap the hydrochloric acid, but not the phosphine. Water and aqueous solutions of sodium hydroxide, sodium carbonate, and ammonium hydroxide were tested separately with respect to the property of absorbing the two gases. All of these substances were found to absorb hydrochloric acid gas as fast as it was evolved; but unfortunately, they absorbed phosphine also. This was shown by adding bromine to the solutions to oxidize the phosphine to phosphoric acid, and then precipitating the latter. Sodium hydroxide dissolved the most phosphine and water the least. In all cases, however, enough was dissolved to make the results valueless. Other solutions were tested in similar respects but the results obtained were no more encouraging. Finally the search for an absorbent which would prevent the passage of the hydrochloric acid into the permanganate solution and at the same time be inert as regards its action toward phosphine was abandoned. This meant, of course, the relinquishing of the scheme whereby the excess or unused portion of permanganate was to be titrated and the substituting of a procedure providing for the precipitation of the phosphoric acid from the absorbing solution of potassium permanganate.

With the adoption of the method of the ultimate precipitation of the phosphorus as phosphoric acid the next problem that presented itself was the determination of that concentration of the absorbing solution which would prove most efficient. It was thought advisable, however, to employ a solution of such concentration that all of the phosphine would be absorbed in the solutions in the first two of the three absorbing

flasks as this would provide for a relatively large margin of safety when analyzing new alloys.

The best concentration of permanganate to be used in the analysis of alloys containing a given percentage of phosphorus was determined by a series of experiments in which a moderately concentrated solution was used at first, followed by the gradual reduction of the concentration of the solution in each succeeding experiment until phosphoric acid was found in the absorbent in the third flask. In each of the determinations in the series reported in Table II, using sample No. 1 of the alloy, 90 cc. of potassium permanganate solution of known concentration were introduced into each of the three Erlenmeyer absorption flasks, after which the experiment was conducted in the same manner as when an aqueous solution of bromine was employed as the absorbing agent.

TABLE II—RETENTION OF PHOSPHINE BY AN AQUEOUS SOLUTION OF $KMnO_4$

No.	Grams $KMnO_4$ in 270 cc. of absorbing solution	PER CENT PHOSPHORUS FOUND			TOTAL
		Flask No. 1	2	3	
1.....	3.0000	3.01	0.02	3.03
2.....	2.5000	2.98	0.02	2.99
3.....	2.0000	2.76	0.25	3.01
4.....	1.5000	2.73	0.28	3.01
5.....	1.0000	2.74	0.29	3.03
6.....	0.5000	2.61	0.39	3.00
7.....	0.2500	1.87	1.01	0.16	3.04

From the data in Table II, it was concluded that a concentration of 0.5 g. of potassium permanganate in 270 cc. was necessary for the complete absorption of the phosphine in the first two flasks. But since the percentage of phosphorus in different samples varies ordinarily from 2 to 6 per cent it was thought advisable to employ a solution containing 1 g. in 270 cc.

EFFECT OF THE PRESENCE OF NITRIC ACID IN THE PERMANGANATE SOLUTION—Following the absorption of the phosphine by the potassium permanganate solution and its ultimate oxidation to phosphoric acid, about 30 cc. of nitric acid (sp. gr. 1.42) were added to the 270 cc. of solution preparatory to the precipitation of the phosphoric acid. It occurred to the authors that if the nitric acid were added to the absorbing solution before the phosphine was introduced, it might be possible to use an absorbing solution with a smaller concentration of potassium permanganate. The series of experiments reported in Table III show how well the suspicion was founded.

TABLE III—RETENTION OF PHOSPHINE BY A SOLUTION OF $KMnO_4$ AND HNO_3

No.	Gms $KMnO_4$ in 270 cc. of absorbing solution containing 50 cc. HNO_3	PERCENTAGES PHOSPHORUS FOUND			TOTAL
		Flask No. 1	2	3	
1.....	0.5000	3.00	0.03	3.03
2.....	0.4500	2.96	0.04	2.99
3.....	0.4000	2.90	0.04	2.98
4.....	0.3500	2.80	0.19	2.99
5.....	0.3000	2.71	0.18	2.99
6.....	0.2500	2.64	0.35	2.99
7.....	0.2000	2.02	0.87	0.12	3.01

The increase in the absorbing and oxidizing power of this solution over the potassium permanganate solution is probably not due solely to the oxidizing action of the nitric acid but to reactions into which it enters or effects. For example, nascent chlorine is introduced into the system by the action of the nitric acid on the hydrochloric acid which distills over from the acid in the evolution flask. Other reactions probably occur also. At least three strong oxidizing

agents, potassium permanganate, nitric acid and nascent chlorine are acting together under the conditions of the procedure.

PROCEDURE USED IN CHECKING PROPOSED METHOD FOR DETERMINING PHOSPHORUS

The authors have attempted so far to show experimentally that the phosphorus present in phosphor-tin is probably in the form of a phosphide, that on solution of the alloy in hydrochloric acid it is liberated quantitatively as phosphine, and that this latter substance may be entirely absorbed and oxidized in certain solutions and later determined as phosphoric acid. At this stage of the work, with a view to determining the accuracy of the proposed method for determining phosphorus, a portion of Sample 1 was analyzed by the long and rather tedious but well-known procedure, commonly known as the cyanide method. This method is sometimes employed in the determination of phosphorus in the phosphor-bronzes when accuracy is the chief consideration. The liberation of hydrocyanic gas at one stage of the method also contributes to its lack of popularity. The results obtained by use of the cyanide method were slightly but uniformly lower than those obtained by the rapid method proposed in this paper. This has been attributed to the large number of filtrations required by the older method.

CYANIDE METHOD—The procedure used by the authors in making the analyses of the alloy by the cyanide method was as follows: To 0.5 g. alloy in a 200 cc. beaker, 25 cc. nitric acid of sp. gr. 1.42, were added. The beaker was covered with a watch glass, and after the first violent action had ceased, it was placed on a water bath and heated until the alloy was completely decomposed and the residue was entirely white. All the phosphoric acid remains with the tin as stannic phosphate.

The nitric acid solution of the alloy was diluted and the stannic oxide containing the phosphoric acid was filtered off, washed several times and dried. The precipitate was transferred to a crucible, and mixed with three times its weight of potassium cyanide. The crucible was covered and the mass fused a few minutes at red heat. On cooling, the fused mass was extracted with hot water, filtered and the paper washed with hot water.

The hydrocyanic and cyanic acids were expelled from the filtrate by boiling with concentrated hydrochloric acid. The solution was evaporated to dryness to dehydrate the silicic acid which had been dissolved from the porcelain crucible. The dry residue was dissolved in a little hydrochloric acid, and hydrogen sulfide passed through the solution to precipitate small amounts of tin likely to be present. The precipitate was filtered off and washed and the hydrogen sulfide destroyed in the filtrate by adding bromine water and boiling. The phosphoric acid was then precipitated, ignited, and weighed as the pyrophosphate.

Twelve phosphorus determinations were made by this method. The results of these determinations are given in Table V.

DEVELOPMENT OF THE METHOD FOR DETERMINING TIN

A survey of the methods proposed for the determination of tin in alloys will reveal the fact that the majority of those possessing accuracy require considerable time for their execution. Even the sulfide method is regarded as being comparatively long and tedious when considered from the standpoint of the analyst doing routine work. It was recognized, therefore, at the very beginning of the work that the attractiveness of any proposed method would be greatly enhanced if it provided for a rapid and accurate determination of tin in the alloy.

In considering the problem at this stage of the work the authors were led naturally to an investigation of the solution of the alloy from which the phosphorus had been liberated as phosphine with a view to ascertaining if it could be used in determining the tin either gravimetrically or volumetrically.

It is well known that tin dissolves in hydrochloric acid in the absence of oxidizing agents with the formation of stannous chloride. It was this reaction which suggested the point of attack, namely, the problem of dissolving the sample of alloy used in the phosphorus determination in such a manner that the tin should be left in the hydrochloric acid solution (in the generating flask) in the "ous" condition. If this could be accomplished the solution of the problem was indicated, for all that would then be required to complete the determination would be the titration of this stannous chloride solution with a suitable standard oxidizing solution.

As the result of the experimental work following the lines of inquiry suggested in the previous paragraph, it was found that if the system of apparatus used in the phosphorus determination was swept free from air before and after the liberation of phosphine by the use of illuminating gas, carbon dioxide, or any other gas inert as regards the stannous chloride, (1) the phosphor-tin dissolved in hydrochloric acid with the quantitative formation of phosphine and stannous chloride; and (2) it was possible to determine the amount of tin present by adding to the solution a slight excess of pure ferric chloride and determining the amount of reduction by titrating with a solution of potassium dichromate.

Using this procedure a number of series of determinations of tin in Sample 1 were made. The results were in close agreement with those obtained in the preliminary experiments when the sulfide method was used to determine the tin content of the different samples of the alloy. The results given in Table IV indicate the relative accuracy of the method.

	1	2	3	4	5	Average
Sulfide Method	96.30	96.38	96.34	96.39	96.37	96.36
Proposed Method	96.35	96.42	96.37	96.41	96.43	96.40

Although the foregoing data indicated that the proposed method possessed an accuracy comparable to that of the sulfide method it was deemed advisable to secure further confirmation of the probable tin content of the alloy. With this in view an electrolytic method was used in the final series of test experiments

to check results obtained by the method proposed in this paper for the determination of tin.

PROCEDURE USED IN CHECKING PROPOSED METHOD FOR DETERMINING TIN

According to Smith,¹ tin may be deposited electrolytically from a stannous or stannic ammonium chloride solution containing an excess of a hot saturated solution of ammonium oxalate. Therefore, instead of titrating the hydrochloric acid solution of stannous chloride in the evolution flask it was cooled at this point and then neutralized with ammonium hydroxide. The precipitate which formed was dissolved with hydrochloric acid, and 100 cc. of a hot saturated solution of ammonium oxalate were added. This solution was then electrolyzed, using a rotating anode and a tared platinum dish (previously coated with silver or copper) as the cathode. A current of N.D. 100 = 5 amperes and 9 volts was applied for one and one-half hours.

The results obtained by the procedure just described confirmed those given by both the sulfide method and the proposed method. These results are tabulated in Table V.

SOLUTIONS USED FOR DETERMINING TIN STANDARD POTASSIUM DICHROMATE SOLUTION—4.1248 g. of C. P. crystals dried at 105° were dissolved in water and the solution made up to one liter. The solution was standardized by means of pure ferrous ammonium sulfate: 1 cc. of this solution was found to be equivalent to 0.005 g. of tin.

INDICATOR—The potassium ferricyanide solution used for determining the end-point in the titration with the dichromate solution was prepared just prior to use. A crystal of potassium ferricyanide about the size of a pea was dissolved in about 75 cc. of distilled water. When a drop of this solution was mixed with a drop of ferric chloride only a light brown color was produced.

SOLUTIONS USED FOR DETERMINING PHOSPHORUS

Absorbing Solution of Potassium Permanganate: Two g. of the pure salt in one liter.

Ammonium Molybdate: This solution was prepared by one of the well-known standard procedures.²

Wash Solution of Acid Ammonium Sulfate: To one liter of water, 16 cc. of ammonium hydroxide (sp. gr. 0.90) and 25 cc. of sulfuric acid (sp. gr. 1.84) were added.

Standard N/10 Solution of Potassium Permanganate: 3.163 g. of C. P. potassium permanganate were dissolved in water and the solution made up to one liter. It was standardized by means of pure ferrous ammonium sulfate, 1 cc. of this solution was equivalent to 0.000885 g. of phosphorus.

PROCEDURE FOR ANALYSIS OF ALLOY

Sawings were taken from the material to be analyzed. Any iron introduced by abrasion of the saw blade was removed by drawing a magnet over the sawings spread in a thin layer. Sawings are to be prepared

to drillings as the latter are quite coarse owing to the brittleness of the alloy.

A 0.5-g. sample of the alloy was put into the Florence flask. Any fine particles of the phosphor-tin adhering to the walls of the flask were rinsed down with a jet of water. The rubber stopper, through which the two tubes bent at right angles and the tap-funnel are inserted, were fitted tightly into the mouth of the Florence flask.

To each of the three absorption flasks assembled as a train, 90 cc. of the potassium permanganate solution and 10 cc. of nitric acid (sp. gr. 1.42) were added. The train was connected with the Florence flask with a short piece of rubber tubing. Carbon dioxide or illuminating gas was then directed through the system for 3 minutes to sweep out the air, and the inlet then closed with a pinchcock: 30 cc. of hydrochloric acid (sp. gr. 1.20) were transferred to the tap-funnel, the stopcock was opened and the hydrochloric acid allowed to run into the flask. The stopcock was immediately closed and heat applied to the flask. The boiling point should be reached in about 5 minutes and maintained until the alloy is completely decomposed. When the alloy was dissolved the Bunsen burner was removed and carbon dioxide or illuminating gas was again forced through the system for 3 minutes so that any traces of phosphine in the Florence flask would be swept into the permanganate solution. Without stopping the flow of gas the absorption train was disconnected from the Florence flask. The tin remains as stannous chloride in the Florence flask and the phosphorus is found as phosphoric acid in the absorption flasks.

One or two grams of ferric chloride which gave no test for ferrous iron were added immediately to the contents of the generating flask, and the solution was titrated at once with potassium dichromate, using potassium ferricyanide as an external indicator. By determining the amount of ferric iron reduced by the stannous chloride the amount of tin present was easily ascertained (1 cc. of the potassium dichromate solution as prepared was equivalent to 1 per cent of tin when a half-gram sample was used).

The contents of the three absorption flasks were then transferred to a 500 cc. Florence flask. The permanganate solution was boiled one minute. It was then removed from the hot plate and potassium nitrite was added in small portions until the excess permanganate was reduced and the solution was colorless. It was then boiled one minute to expel any nitrous acid that might be present since it acts as an interfering substance later on in the procedure.

The solution was removed from the hot plate and cooled to about 40° by placing in a cooling bath, after which it was made slightly alkaline with ammonium hydroxide. When the neutral point was reached, a heavy precipitate of ammonium phosphomolybdate which served as an indicator of the point. This precipitate was not dissolved with water and up to 1.40 and 0.10 cc. were added to excess. The solution was heated to a temperature of 85° and as the standard potassium molybdate were added the

¹ Edgar E. Smith, *Electro-Analysis*, 1911, 191.

² Blue, *Chemical Analysis of Iron*, 1913, 99.

temperature must not exceed 85°, because of the possibility of molybdic acid being precipitated. The contents of the flask were vigorously stirred for 5 minutes. The yellow precipitate of ammonium phosphomolybdate was filtered off and washed with acid ammonium sulfate solution until 2 or 3 cc. of the wash water did not give a brown coloration on the addition of a drop of ammonium sulfide: 7 cc. of ammonium hydroxide of sp. gr. 0.90 and 15 cc. of water were poured into the flask in which the precipitate was formed, to dissolve any adhering precipitate: the solution was then poured on the precipitate in the filter. The filtrate containing the ammonium molybdate and ammonium phosphate was next prepared for the Jones reductor. The filter was washed with water until the filtrate had a volume of about 60 cc.: 10 cc. of sulfuric acid (sp. gr. 1.84) were added. (If a precipitate forms on the addition of the sulfuric acid, it should be redissolved with ammonium hydroxide and the same amount of sulfuric acid added a second time.)

The solution was then passed through a Jones reductor charged with amalgamated zinc. It was passed through a second time after the addition of 2 cc. more of sulfuric acid. This was followed with 200 cc. of water. The solution collected from the reductor was titrated at once with *N*/10 potassium permanganate.

TEST EXPERIMENTS

In order to show the relative accuracy of the proposed method, two different samples of phosphor-tin were used in making the following series of determinations of tin and phosphorus: Twelve different portions of Sample I were analyzed for phosphorus and tin, six by the recommended procedure and six by standard procedures described in the body of this paper. This series was then followed by a similar series of analyses in which Sample II was used.

TABLE V—RESULTS OF ANALYSES OF PHOSPHOR-TIN

Sample No.	No.	PERCENTAGES TIN FOUND		PERCENTAGES PHOSPHORUS FOUND	
		Electrolytic Method	Proposed Volumetric Method	Cyanide Method	Proposed Evolution Method
I	1	96.32	96.38	2.97	3.03
	2	96.34	96.40	2.98	3.02
	3	96.38	96.35	2.98	2.99
	4	96.38	96.36	2.96	3.04
	5	96.36	96.40	2.99	3.01
	6	96.40	96.35	2.95	3.02
II	1	96.50	96.45	3.10	3.12
	2	96.46	96.52	3.07	3.11
	3	96.52	96.50	3.09	3.11
	4	96.44	96.48	3.06	3.10
	5	96.50	96.45	3.08	3.13
	6	96.48	96.50	3.07	3.12

SUMMARY

The need of a method formulated specifically for the analysis of the alloy, phosphor-tin, has been shown, and attention has been called to the fact that the related literature apparently does not contain such a method.

A volumetric method has been developed and is proposed in the foregoing discussion. The tests to which this method has been subjected indicate that it is not only easy of execution but that it is also rapid and accurate.

The method provides for the carrying out of the determinations in a train of flasks. The alloy is dissolved in hydrochloric acid in the first flask, from which

all air is excluded by means of a current of illuminating gas or carbon dioxide. The tin dissolves as stannous chloride and the phosphorus is liberated as phosphine which is absorbed by solutions in the train of three flasks. The tin is titrated at once with an oxidizing solution. The phosphine is converted into phosphoric acid by the absorbing solutions from which the acid is precipitated as phosphomolybdate which is then reduced in a reductor and finally titrated.

The time required for making the two determinations, after the sample is weighed, need not exceed 45 minutes. Other methods, adapted to phosphor-tin analysis and giving the same order of accuracy, required hours for their execution.

The proposed method provides for the detection of impurities in the alloy. It is, therefore, as well adapted for careful assay work as for "control" analyses.

As a result of the study of various absorbing agents it has been shown that potassium permanganate solutions are satisfactory absorbents for phosphine. And furthermore, it appears that the oxidizing and absorbing power of the reagent is increased in a marked degree by the addition of nitric acid.

CARNEGIE HALL OF CHEMISTRY
ALLEGHENY COLLEGE
MEADVILLE, PENNSYLVANIA

THE ELECTROMETRIC TITRATION OF ZINC¹

By F. RUSSELL V. BICHOWSKY

Of all the troubles to which the zinc chemist is heir, none perhaps is more vexatious than the trickiness and general unreliability of even the better methods of zinc analysis. Mr. Keith's² report discloses, for instance, that analyses of the same sample made by some of the best known zinc chemists of the country, all using the same method of analysis (the "Beale"), varied among themselves by as much as 4 per cent of the total zinc content. Of course such variations are far beyond the errors of the personal equation and can be accounted for only as being due either to loss of zinc in the processes leading to the final titration (such as for example might be due to absorption on the Fe-Mn precipitate), or to the interference of the various substances with the end-point of the ferrocyanide titration. Of these two sources of error the last is undoubtedly the most serious, as, at least in the author's experience, the loss of zinc in any of the better known commercial methods is very slight.

Assume, therefore, that we have carried through the preliminary more or less complete separation of SiO₂, Fe, Mn, Cd, etc., according to any of the regular methods. We will then have left a solution containing besides all our zinc (hoffentlich) more or less free chlorine, bromine, nitric acid, hydrochloric acid, manganese, copper, lead, iron and cadmium, and no one knows what else, all in amounts depending enormously on even the slightest variation in our procedure. Our problem is now to find the best way of determining

¹ Presented at the Symposium on the Chemistry and Metallurgy of Zinc, 54th Meeting American Chemical Society, Kansas City, April 10 to 14, 1917.

² Keith, "Zinc Ore Analysis," Leadville Publishing and Printing Co., Leadville, Colo.

the zinc in this mixture. Unfortunately, there is, with the possible exception of Hg_2SCN , no specific reagent which will precipitate zinc without at the same time precipitating traces at least of most of the other elements. The best substitute for a specific reagent is undoubtedly potassium ferrocyanide, but unfortunately this reagent, besides precipitating almost any of the heavy metals, has the added disadvantage that it is a reducing agent, and thus will react with whatever bromine, chlorine, or nitric acid is present, and so will give too high results unless extreme care is taken in the preliminary elimination of all oxidizing agents, heavy metals and, especially, manganese. Besides this the end-point of the ordinary ferrocyanide titration obtained either by the use of uranium, molybdenum or iron, is always uncertain, especially in the poor light of the ordinary laboratory, and, moreover, the whole titration is tedious and uncertain, due to the large blank correction necessary. It is thus, perhaps, no wonder that zinc analyses vary so conspicuously among themselves.¹

The most rational way to correct this state of affairs is not so much to improve the methods of preparation of the zinc solution (though undoubtedly precautions, such as the addition of SO_2 , should be taken to remove any free oxidizing agents) as to change the conditions of the ferrocyanide precipitation by carrying it out in solutions containing from 10 to 20 per cent hydrochloric acid. In these solutions zinc-ferrocyanide is only slightly soluble, but lead, manganese, iron and copper are very soluble and even cadmium is fairly soluble. At this concentration of acid, however, the ordinary indicators are comparatively useless, as would be indeed almost any chemical indicator. For this reason electrometric methods similar to those used with so much success in the analysis of iron, vanadium, chromium, etc., immediately suggest themselves:

First, because outside of their being almost the only ones possible under these conditions, they are, under any conditions, the most convenient and accurate methods available. One does not have to depend on the time-consuming and always inaccurate outside indicator, nor on the inaccurate and, in my experience, unreliable internal indicator, such as ferrous iron. One simply notes the point of sudden deflection of a galvanometer needle, a point which can be determined, but with little care, to a fraction of a drop.

Second, this method is also the quickest and most certain. There is no danger of overrunning and the titration can be finished in less than one-third the time of the older methods.

Third, the electrometric end-point is not affected by the color of the solution, by the lighting of the room, by the presence of acid or neutral salts present, and, in fact, at least in 10 per cent acid, is not affected by iron, lead, manganese (up to 50 mg.), or small amounts of copper and cadmium, all of which (except lead) have marked effects, especially on the uranium end-point.

The method as finally worked out requires no complicated apparatus: a cheap galvanometer, a slide wire resistant, some sort of standard electrode such as a calomel electrode (made from a bottle, a cork and a piece of bent tubing, a sodium chloride solution, and a few g. of mercury and calomel), a piece of platinum wire (for the platinum electrode), some copper wire for connections, and a couple of dry cells complete the needed extra equipment, though a voltmeter is a great convenience. If this apparatus seems too complicated to make, it can be purchased already made up for the determination of chromium, iron, vanadium, etc. A detailed description of the apparatus, the theory of it and the general methods of using it will be found in the *Journal of the American Chemical Society* in several places.¹

Having the apparatus set up, the operation is simplicity itself. The two electrodes are dipped in the beaker containing the solution to be analyzed (which solution should be hot, should contain at least 10 per cent strong hydrochloric acid, but no free oxidizing agents nor more than a trace of cadmium); by adjusting the slider of the resistance the pointer of the galvanometer should be brought to zero and the titration begun. As the ferrocyanide is slowly added with constant stirring the pointer will swing slowly until the end-point is almost reached; at the end-point the direction of the swing will be reversed. From this point on the ferrocyanide is added drop by drop until one drop causes a sudden very large but permanent deflection. This is the end-point. Or, if one has a voltmeter in the set-up, one can simply set the slider so that the voltmeter reads 0.24 volt and titrate until the galvanometer indicates zero current. This end-point is accurate, even with 20 per cent (strong) hydrochloric acid, to 0.1 cc. of the usual ferrocyanide solution.

Using this method, the preliminary operations for the purification of the ore lose their customary importance. Almost any of the best known methods can be used. My own method is to dissolve the ore in the minimum strong hydrochloric acid, add a pinch of KClO_4 , add quickly 100 cc. dilute NH_4OH , make up to 250 cc., filter an aliquot, and acidify. Add 10 per cent excess hydrochloric acid, add SO_2 until saturated, boil out the SO_2 with heat and a stream of air (or add test lead) and titrate. In ordinarily pure ores simple solution in strong hydrochloric acid and the addition of the test lead and aluminum works very nicely. Of course, if extreme accuracy is desired or if the ore contains large amounts of cadmium, some standard method such as Bayer's is to be preferred for the preliminary operations. The electrometric end-point method, however, replaces Bayer's as Mn, vanadium and points out some difficulties in such tests as accuracy and convenience for small amounts of the element in 100 zinc solutions free from cadmium, manganese, etc., to analyze smaller acid concentrations should be employed.

¹ My attention was called to the need of an electrometric method for the titration of zinc by Mr. Hyman Gfrober at the Bureau of Standards.

¹ *Journal of the American Chemical Society*, 35 (1913), 100; 35 (1913), 101; 35 (1913), 102; 35 (1913), 103; 35 (1913), 104; 35 (1913), 105; 35 (1913), 106; 35 (1913), 107; 35 (1913), 108; 35 (1913), 109; 35 (1913), 110; 35 (1913), 111; 35 (1913), 112; 35 (1913), 113; 35 (1913), 114; 35 (1913), 115; 35 (1913), 116; 35 (1913), 117; 35 (1913), 118; 35 (1913), 119; 35 (1913), 120; 35 (1913), 121; 35 (1913), 122; 35 (1913), 123; 35 (1913), 124; 35 (1913), 125; 35 (1913), 126; 35 (1913), 127; 35 (1913), 128; 35 (1913), 129; 35 (1913), 130; 35 (1913), 131; 35 (1913), 132; 35 (1913), 133; 35 (1913), 134; 35 (1913), 135; 35 (1913), 136; 35 (1913), 137; 35 (1913), 138; 35 (1913), 139; 35 (1913), 140; 35 (1913), 141; 35 (1913), 142; 35 (1913), 143; 35 (1913), 144; 35 (1913), 145; 35 (1913), 146; 35 (1913), 147; 35 (1913), 148; 35 (1913), 149; 35 (1913), 150; 35 (1913), 151; 35 (1913), 152; 35 (1913), 153; 35 (1913), 154; 35 (1913), 155; 35 (1913), 156; 35 (1913), 157; 35 (1913), 158; 35 (1913), 159; 35 (1913), 160; 35 (1913), 161; 35 (1913), 162; 35 (1913), 163; 35 (1913), 164; 35 (1913), 165; 35 (1913), 166; 35 (1913), 167; 35 (1913), 168; 35 (1913), 169; 35 (1913), 170; 35 (1913), 171; 35 (1913), 172; 35 (1913), 173; 35 (1913), 174; 35 (1913), 175; 35 (1913), 176; 35 (1913), 177; 35 (1913), 178; 35 (1913), 179; 35 (1913), 180; 35 (1913), 181; 35 (1913), 182; 35 (1913), 183; 35 (1913), 184; 35 (1913), 185; 35 (1913), 186; 35 (1913), 187; 35 (1913), 188; 35 (1913), 189; 35 (1913), 190; 35 (1913), 191; 35 (1913), 192; 35 (1913), 193; 35 (1913), 194; 35 (1913), 195; 35 (1913), 196; 35 (1913), 197; 35 (1913), 198; 35 (1913), 199; 35 (1913), 200; 35 (1913), 201; 35 (1913), 202; 35 (1913), 203; 35 (1913), 204; 35 (1913), 205; 35 (1913), 206; 35 (1913), 207; 35 (1913), 208; 35 (1913), 209; 35 (1913), 210; 35 (1913), 211; 35 (1913), 212; 35 (1913), 213; 35 (1913), 214; 35 (1913), 215; 35 (1913), 216; 35 (1913), 217; 35 (1913), 218; 35 (1913), 219; 35 (1913), 220; 35 (1913), 221; 35 (1913), 222; 35 (1913), 223; 35 (1913), 224; 35 (1913), 225; 35 (1913), 226; 35 (1913), 227; 35 (1913), 228; 35 (1913), 229; 35 (1913), 230; 35 (1913), 231; 35 (1913), 232; 35 (1913), 233; 35 (1913), 234; 35 (1913), 235; 35 (1913), 236; 35 (1913), 237; 35 (1913), 238; 35 (1913), 239; 35 (1913), 240; 35 (1913), 241; 35 (1913), 242; 35 (1913), 243; 35 (1913), 244; 35 (1913), 245; 35 (1913), 246; 35 (1913), 247; 35 (1913), 248; 35 (1913), 249; 35 (1913), 250; 35 (1913), 251; 35 (1913), 252; 35 (1913), 253; 35 (1913), 254; 35 (1913), 255; 35 (1913), 256; 35 (1913), 257; 35 (1913), 258; 35 (1913), 259; 35 (1913), 260; 35 (1913), 261; 35 (1913), 262; 35 (1913), 263; 35 (1913), 264; 35 (1913), 265; 35 (1913), 266; 35 (1913), 267; 35 (1913), 268; 35 (1913), 269; 35 (1913), 270; 35 (1913), 271; 35 (1913), 272; 35 (1913), 273; 35 (1913), 274; 35 (1913), 275; 35 (1913), 276; 35 (1913), 277; 35 (1913), 278; 35 (1913), 279; 35 (1913), 280; 35 (1913), 281; 35 (1913), 282; 35 (1913), 283; 35 (1913), 284; 35 (1913), 285; 35 (1913), 286; 35 (1913), 287; 35 (1913), 288; 35 (1913), 289; 35 (1913), 290; 35 (1913), 291; 35 (1913), 292; 35 (1913), 293; 35 (1913), 294; 35 (1913), 295; 35 (1913), 296; 35 (1913), 297; 35 (1913), 298; 35 (1913), 299; 35 (1913), 300; 35 (1913), 301; 35 (1913), 302; 35 (1913), 303; 35 (1913), 304; 35 (1913), 305; 35 (1913), 306; 35 (1913), 307; 35 (1913), 308; 35 (1913), 309; 35 (1913), 310; 35 (1913), 311; 35 (1913), 312; 35 (1913), 313; 35 (1913), 314; 35 (1913), 315; 35 (1913), 316; 35 (1913), 317; 35 (1913), 318; 35 (1913), 319; 35 (1913), 320; 35 (1913), 321; 35 (1913), 322; 35 (1913), 323; 35 (1913), 324; 35 (1913), 325; 35 (1913), 326; 35 (1913), 327; 35 (1913), 328; 35 (1913), 329; 35 (1913), 330; 35 (1913), 331; 35 (1913), 332; 35 (1913), 333; 35 (1913), 334; 35 (1913), 335; 35 (1913), 336; 35 (1913), 337; 35 (1913), 338; 35 (1913), 339; 35 (1913), 340; 35 (1913), 341; 35 (1913), 342; 35 (1913), 343; 35 (1913), 344; 35 (1913), 345; 35 (1913), 346; 35 (1913), 347; 35 (1913), 348; 35 (1913), 349; 35 (1913), 350; 35 (1913), 351; 35 (1913), 352; 35 (1913), 353; 35 (1913), 354; 35 (1913), 355; 35 (1913), 356; 35 (1913), 357; 35 (1913), 358; 35 (1913), 359; 35 (1913), 360; 35 (1913), 361; 35 (1913), 362; 35 (1913), 363; 35 (1913), 364; 35 (1913), 365; 35 (1913), 366; 35 (1913), 367; 35 (1913), 368; 35 (1913), 369; 35 (1913), 370; 35 (1913), 371; 35 (1913), 372; 35 (1913), 373; 35 (1913), 374; 35 (1913), 375; 35 (1913), 376; 35 (1913), 377; 35 (1913), 378; 35 (1913), 379; 35 (1913), 380; 35 (1913), 381; 35 (1913), 382; 35 (1913), 383; 35 (1913), 384; 35 (1913), 385; 35 (1913), 386; 35 (1913), 387; 35 (1913), 388; 35 (1913), 389; 35 (1913), 390; 35 (1913), 391; 35 (1913), 392; 35 (1913), 393; 35 (1913), 394; 35 (1913), 395; 35 (1913), 396; 35 (1913), 397; 35 (1913), 398; 35 (1913), 399; 35 (1913), 400; 35 (1913), 401; 35 (1913), 402; 35 (1913), 403; 35 (1913), 404; 35 (1913), 405; 35 (1913), 406; 35 (1913), 407; 35 (1913), 408; 35 (1913), 409; 35 (1913), 410; 35 (1913), 411; 35 (1913), 412; 35 (1913), 413; 35 (1913), 414; 35 (1913), 415; 35 (1913), 416; 35 (1913), 417; 35 (1913), 418; 35 (1913), 419; 35 (1913), 420; 35 (1913), 421; 35 (1913), 422; 35 (1913), 423; 35 (1913), 424; 35 (1913), 425; 35 (1913), 426; 35 (1913), 427; 35 (1913), 428; 35 (1913), 429; 35 (1913), 430; 35 (1913), 431; 35 (1913), 432; 35 (1913), 433; 35 (1913), 434; 35 (1913), 435; 35 (1913), 436; 35 (1913), 437; 35 (1913), 438; 35 (1913), 439; 35 (1913), 440; 35 (1913), 441; 35 (1913), 442; 35 (1913), 443; 35 (1913), 444; 35 (1913), 445; 35 (1913), 446; 35 (1913), 447; 35 (1913), 448; 35 (1913), 449; 35 (1913), 450; 35 (1913), 451; 35 (1913), 452; 35 (1913), 453; 35 (1913), 454; 35 (1913), 455; 35 (1913), 456; 35 (1913), 457; 35 (1913), 458; 35 (1913), 459; 35 (1913), 460; 35 (1913), 461; 35 (1913), 462; 35 (1913), 463; 35 (1913), 464; 35 (1913), 465; 35 (1913), 466; 35 (1913), 467; 35 (1913), 468; 35 (1913), 469; 35 (1913), 470; 35 (1913), 471; 35 (1913), 472; 35 (1913), 473; 35 (1913), 474; 35 (1913), 475; 35 (1913), 476; 35 (1913), 477; 35 (1913), 478; 35 (1913), 479; 35 (1913), 480; 35 (1913), 481; 35 (1913), 482; 35 (1913), 483; 35 (1913), 484; 35 (1913), 485; 35 (1913), 486; 35 (1913), 487; 35 (1913), 488; 35 (1913), 489; 35 (1913), 490; 35 (1913), 491; 35 (1913), 492; 35 (1913), 493; 35 (1913), 494; 35 (1913), 495; 35 (1913), 496; 35 (1913), 497; 35 (1913), 498; 35 (1913), 499; 35 (1913), 500; 35 (1913), 501; 35 (1913), 502; 35 (1913), 503; 35 (1913), 504; 35 (1913), 505; 35 (1913), 506; 35 (1913), 507; 35 (1913), 508; 35 (1913), 509; 35 (1913), 510; 35 (1913), 511; 35 (1913), 512; 35 (1913), 513; 35 (1913), 514; 35 (1913), 515; 35 (1913), 516; 35 (1913), 517; 35 (1913), 518; 35 (1913), 519; 35 (1913), 520; 35 (1913), 521; 35 (1913), 522; 35 (1913), 523; 35 (1913), 524; 35 (1913), 525; 35 (1913), 526; 35 (1913), 527; 35 (1913), 528; 35 (1913), 529; 35 (1913), 530; 35 (1913), 531; 35 (1913), 532; 35 (1913), 533; 35 (1913), 534; 35 (1913), 535; 35 (1913), 536; 35 (1913), 537; 35 (1913), 538; 35 (1913), 539; 35 (1913), 540; 35 (1913), 541; 35 (1913), 542; 35 (1913), 543; 35 (1913), 544; 35 (1913), 545; 35 (1913), 546; 35 (1913), 547; 35 (1913), 548; 35 (1913), 549; 35 (1913), 550; 35 (1913), 551; 35 (1913), 552; 35 (1913), 553; 35 (1913), 554; 35 (1913), 555; 35 (1913), 556; 35 (1913), 557; 35 (1913), 558; 35 (1913), 559; 35 (1913), 560; 35 (1913), 561; 35 (1913), 562; 35 (1913), 563; 35 (1913), 564; 35 (1913), 565; 35 (1913), 566; 35 (1913), 567; 35 (1913), 568; 35 (1913), 569; 35 (1913), 570; 35 (1913), 571; 35 (1913), 572; 35 (1913), 573; 35 (1913), 574; 35 (1913), 575; 35 (1913), 576; 35 (1913), 577; 35 (1913), 578; 35 (1913), 579; 35 (1913), 580; 35 (1913), 581; 35 (1913), 582; 35 (1913), 583; 35 (1913), 584; 35 (1913), 585; 35 (1913), 586; 35 (1913), 587; 35 (1913), 588; 35 (1913), 589; 35 (1913), 590; 35 (1913), 591; 35 (1913), 592; 35 (1913), 593; 35 (1913), 594; 35 (1913), 595; 35 (1913), 596; 35 (1913), 597; 35 (1913), 598; 35 (1913), 599; 35 (1913), 600; 35 (1913), 601; 35 (1913), 602; 35 (1913), 603; 35 (1913), 604; 35 (1913), 605; 35 (1913), 606; 35 (1913), 607; 35 (1913), 608; 35 (1913), 609; 35 (1913), 610; 35 (1913), 611; 35 (1913), 612; 35 (1913), 613; 35 (1913), 614; 35 (1913), 615; 35 (1913), 616; 35 (1913), 617; 35 (1913), 618; 35 (1913), 619; 35 (1913), 620; 35 (1913), 621; 35 (1913), 622; 35 (1913), 623; 35 (1913), 624; 35 (1913), 625; 35 (1913), 626; 35 (1913), 627; 35 (1913), 628; 35 (1913), 629; 35 (1913), 630; 35 (1913), 631; 35 (1913), 632; 35 (1913), 633; 35 (1913), 634; 35 (1913), 635; 35 (1913), 636; 35 (1913), 637; 35 (1913), 638; 35 (1913), 639; 35 (1913), 640; 35 (1913), 641; 35 (1913), 642; 35 (1913), 643; 35 (1913), 644; 35 (1913), 645; 35 (1913), 646; 35 (1913), 647; 35 (1913), 648; 35 (1913), 649; 35 (1913), 650; 35 (1913), 651; 35 (1913), 652; 35 (1913), 653; 35 (1913), 654; 35 (1913), 655; 35 (1913), 656; 35 (1913), 657; 35 (1913), 658; 35 (1913), 659; 35 (1913), 660; 35 (1913), 661; 35 (1913), 662; 35 (1913), 663; 35 (1913), 664; 35 (1913), 665; 35 (1913), 666; 35 (1913), 667; 35 (1913), 668; 35 (1913), 669; 35 (1913), 670; 35 (1913), 671; 35 (1913), 672; 35 (1913), 673; 35 (1913), 674; 35 (1913), 675; 35 (1913), 676; 35 (1913), 677; 35 (1913), 678; 35 (1913), 679; 35 (1913), 680; 35 (1913), 681; 35 (1913), 682; 35 (1913), 683; 35 (1913), 684; 35 (1913), 685; 35 (1913), 686; 35 (1913), 687; 35 (1913), 688; 35 (1913), 689; 35 (1913), 690; 35 (1913), 691; 35 (1913), 692; 35 (1913), 693; 35 (1913), 694; 35 (1913), 695; 35 (1913), 696; 35 (1913), 697; 35 (1913), 698; 35 (1913), 699; 35 (1913), 700; 35 (1913), 701; 35 (1913), 702; 35 (1913), 703; 35 (1913), 704; 35 (1913), 705; 35 (1913), 706; 35 (1913), 707; 35 (1913), 708; 35 (1913), 709; 35 (1913), 710; 35 (1913), 711; 35 (1913), 712; 35 (1913), 713; 35 (1913), 714; 35 (1913), 715; 35 (1913), 716; 35 (1913), 717; 35 (1913), 718; 35 (1913), 719; 35 (1913), 720; 35 (1913), 721; 35 (1913), 722; 35 (1913), 723; 35 (1913), 724; 35 (1913), 725; 35 (1913), 726; 35 (1913), 727; 35 (1913), 728; 35 (1913), 729; 35 (1913), 730; 35 (1913), 731; 35 (1913), 732; 35 (1913), 733; 35 (1913), 734; 35 (1913), 735; 35 (1913), 736; 35 (1913), 737; 35 (1913), 738; 35 (1913), 739; 35 (1913), 740; 35 (1913), 741; 35 (1913), 742; 35 (1913), 743; 35 (1913), 744; 35 (1913), 745; 35 (1913), 746; 35 (1913), 747; 35 (1913), 748; 35 (1913), 749; 35 (1913), 750; 35 (1913), 751; 35 (1913), 752; 35 (1913), 753; 35 (1913), 754; 35 (1913), 755; 35 (1913), 756; 35 (1913), 757; 35 (1913), 758; 35 (1913), 759; 35 (1913), 760; 35 (1913), 761; 35 (1913), 762; 35 (1913), 763; 35 (1913), 764; 35 (1913), 765; 35 (1913), 766; 35 (1913), 767; 35 (1913), 768; 35 (1913), 769; 35 (1913), 770; 35 (1913), 771; 35 (1913), 772; 35 (1913), 773; 35 (1913), 774; 35 (1913), 775; 35 (1913), 776; 35 (1913), 777; 35 (1913), 778; 35 (1913), 779; 35 (1913), 780; 35 (1913), 781; 35 (1913), 782; 35 (1913), 783; 35 (1913), 784; 35 (1913), 785; 35 (1913), 786; 35 (1913), 787; 35 (1913), 788; 35 (1913), 789; 35 (1913), 790; 35 (1913), 791; 35 (1913), 792; 35 (1913), 793; 35 (1913), 794; 35 (1913), 795; 35 (1913), 796; 35 (1913), 797; 35 (1913), 798; 35 (1913), 799; 35 (1913), 800; 35 (1913), 801; 35 (1913), 802; 35 (1913), 803; 35 (1913), 804; 35 (1913), 805; 35 (1913), 806; 35 (1913), 807; 35 (1913), 808; 35 (1913), 809; 35 (1913), 810; 35 (1913), 811; 35 (1913), 812; 35 (1913), 813; 35 (1913), 814; 35 (1913), 815; 35 (1913), 816; 35 (1913), 817; 35 (1913), 818; 35 (1913), 819; 35 (1913), 820; 35 (1913), 821; 35 (1913), 822; 35 (1913), 823; 35 (1913), 824; 35 (1913), 825; 35 (1913), 826; 35 (1913), 827; 35 (1913), 828; 35 (1913), 829; 35 (1913), 830; 35 (1913), 831; 35 (1913), 832; 35 (1913), 833; 35 (1913), 834; 35 (1913), 835; 35 (1913), 836; 35 (1913), 837; 35 (1913), 838; 35 (1913), 839; 35 (1913), 840; 35 (1913), 841; 35 (1913), 842; 35 (1913), 843; 35 (1913), 844; 35 (1913), 845; 35 (1913), 846; 35 (1913), 847; 35 (1913), 848; 35 (1913), 849; 35 (1913), 850; 35 (1913), 851; 35 (1913), 852; 35 (1913

While no attempt to give a complete table of experimental results is made here, certain more significant results have been collected in Tables I and II:

TABLE I

Accuracy of titrations with ferrocyanide of total zinc in solutions containing various known quantities of Zn^{++} , Fe^{++} , Mn^{++} , Pb^{++} , Cu^{++} and HCl using the electrometric end-point (E. M. F.), the ferrous ferrocyanide end-point of Breyer (iron), the usual end-point with uranium nitrate as an outside indicator (uranium).

HCl (g)	CONCENTR. OF SOLUTION IN MG.					MG. OF ZINC FOUND		
	Zn	Mn	Fe	Cu	Pb	E. M. F.	Iron	Uranium
2	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.3
15	0.0	0.0	0.0	0.0	0.0	0.05	0.34	1.0
2	0.5	0.0	0.0	0.0	0.0	0.50	4.98	0.95
3	5.0	0.0	0.0	0.0	0.0	5.01	4.98	5.45
5	50.0	0.0	0.0	0.0	0.0	50.01	50.08	50.57
2	0.5	0.5	0.0	0.0	0.0	0.59	0.71	1.55
10	0.5	0.5	0.0	0.0	0.0	0.49	0.68*	0.7*
10	5.0	0.5	0.0	0.0	0.0	4.98	5.1*	5.3*
10	5.0	5.0	0.0	0.0	0.0	5.01		
10	5.0	50.0	0.0	0.0	0.0	5.05	0.0	5.7*
10	5.0	0.0	5.0	0.0	0.0	5.09	5.11	*
15	5.0	5.0	5.0	5.0	0.0	5.08	*	*
15	5.0	5.0	5.0	5.0	5.0	5.10	*	*

* End-point very uncertain.

(a) HCl content in cc. 35 per cent HCl per 100 cc. of solution.

TABLE II

Content of the same Cd-free ore by different methods showing results in per cent zinc and approximate time taken (ore contained 7 per cent Mn).

METHOD	Reference	Per cent Zinc	Time
Breyer standard	Loc. cit.	31.04	12 hrs.
"Beale"	E. M. F. end-point	31.74	8 hrs.
New Jersey Zinc Co.	See below	31.12	6 hrs.
American Zinc, Lead Smelting Co.	See below	31.32	4 hrs.
Author's long method	See text	31.10	4 hrs.
Author's short method	See text	31.6	2 hrs.

NEW JERSEY ZINC CO. METHOD (Courtesy of Mr. G. C. Stone)—

Weight out 0.5 g. of ore within 0.5 milligram. Transfer to a 250-cc. beaker. Add 15 cc. of hydrochloric acid (sp. gr. 1.20), cover and boil until all is in solution that can be dissolved by hydrochloric acid alone. If there are insoluble particles remaining, other than silica, and always with green sulfide ores, add 5 cc. of nitric acid (sp. gr. 1.42).

In case the hydrochloric acid treatment alone is necessary, boil down to about 5 cc. and remove from the hot plate.

If nitric acid is used, evaporate to dryness, leaving on the hot plate until there is no odor of acid or until a little ammonia in a beaker produces no cloud of ammonium salts when held near the assay. Remove from the plate, cool, add 5 cc. of hydrochloric acid (sp. gr. 1.20) and boil until all is in solution. If brown or green fumes are evolved it indicates that the evaporation to dryness was incomplete. In this case evaporate to dryness again with the hydrochloric acid, cool, add 5 cc. of strong hydrochloric acid as before and boil.

From this point on, the treatment is the same whether nitric acid was used in solution or not.

Wash off both sides of the cover glass and the sides of the beaker with a fine jet of cold water, using as little as possible. Be particularly careful to keep the volume down in the cases of ores carrying manganese. Add 5 g. of ammonium chloride crystals. Add saturated bromine water according to the manganese contents of the ores.

If there is no manganese, add 2 or 3 cc. to insure complete oxidation of the iron. If this is neglected the iron is incompletely precipitated by the subsequent treatment with ammonia. With small amounts of manganese, 15 to 25 cc. of bromine water are needed.

When the manganese is high, the volume of the ore solution must be less than 10 cc. Shake the bottle of bromine water violently with an excess of bromine and quickly pour 25 cc. into the ore solution before the suspended free bromine can settle.

Allow time for the ammonium chloride to dissolve completely, then add 15 cc. of ammonia water.

In the case of the high manganese ores great care is necessary on account of the excess of bromine. If the ammonia water is poured in carelessly the reaction with the free bromine which

has settled to the bottom of the beaker is very violent, and may cause loss of solution or injury to the hands of the operator. The best method of manipulation is to incline the beaker at an angle, keeping the cover glass in place and to pour the ammonia water in slowly through the lip of the beaker, allowing it to run down the side of the beaker and float as a separate layer on the ore solution. Now place the beaker on a warm (not hot) part of the plate, on two or three layers of asbestos paper if there is no gradation of heat on the plate. The ammonia will then gradually diffuse into the solution, precipitating the iron and manganese completely without any violent reaction.

Bring the contents of the beaker to a boil. Allow to boil for one minute to insure the coagulation of the precipitate. Do not allow to boil longer than one minute, or there is danger of re-solution of a part of the manganese. Wash the cover glass off with a hot jet of the wash solution when removing it from the beaker.

Filter while hot, allowing all the solution to run through the filter before commencing washing. Transfer as much of the precipitate as possible to the filter, using the jet to loosen it from the beaker, and carefully wash the entire inner surface of the beaker. Then wash the filter and precipitate thoroughly three times more with a jet of the hot wash solution, containing 50 g. of ammonium chloride and 50 cc. of ammonia water per liter.

Wash the precipitate from the filter into the beaker in which the original precipitation was carried out with a small quantity of the wash solution: add a few drops of hydrochloric acid to redissolve the iron and manganese. With high manganese ores it will be found necessary to heat to boiling before the manganese will dissolve. With these same ores, if the volume is over 10 cc. concentrate by evaporation to less than 10 cc. Precipitate the iron and manganese again as with the first precipitation except that it is unnecessary to use ammonium chloride crystals. The chloride contained in the solution used for washing the precipitate from the paper is sufficient for the small amount of zinc remaining. The bromine may also be omitted on the second precipitation, with ores free from manganese, as the iron is all in the ferric condition. Where manganese is present, bromine must be used in the second precipitation, observing all the precautions necessary with the first. Ten cc. of ammonia water are sufficient on account of the smaller quantity of free acid. Filter and wash beaker, filter and precipitate as before, combining the filtrates from the two precipitations. With ores very high in iron, manganese or alumina, at least one additional separation of these constituents must be made by the same method. Experience must be relied on to determine exactly how many separations are necessary with any given ore.

Heat the solution to boiling and test, if from a manganiferous ore, by adding a few cc. of bromine water. If more manganese comes down, throw the solution away and start a new assay, as the manganese cannot be separated quantitatively from so large a volume of solution without the expenditure of more time than would be required for a new assay. If no manganese comes down, boil gently for a few minutes to eliminate bromine.

Add hot water until the volume is a little less than 250 cc. Add 4 drops of an ammonium sulfide solution made by saturating with hydrogen sulfide a mixture of 2 parts ammonium water (sp. gr. 0.90) and 1 part water by volume. If there is much copper, more sulfide may be necessary.

Add hydrochloric acid cautiously until the precipitated zinc sulfide just dissolves, then add 10 cc. excess of the 1.20 sp. gr. acid and titrate with standard potassium ferrocyanide solution (containing 44 grams per liter), using 10 per cent uranium nitrate solution as an external indicator, on a paraffin-coated spot plate. The solution must be violently stirred while titrating.

AMERICAN ZINC, LEAD SMELTING CO. METHOD (Courtesy of Dr. John Johnston).—Weigh 0.5 gram into a flask of 200 cc. capacity. Add 10 cc. hydrochloric acid and boil nearly to dryness. Add 5 cc. nitric acid and take to dryness. Overheating or baking should be avoided. The best time to remove the flask from the hot plate is when it is stained red all over. Care should be taken to avoid spurling. Cool, and add 10 cc. hydrochloric acid and boil to half its volume. Add 50 cc. hot water and 10 cc. ammonia. If manganese is present add 20 cc. saturated solution of bromine water. Boil and filter through 11 cm. filter, which should leave about one-third of the funnel exposed, into a beaker 375 cc. capacity. Wash three times with hot water. Redissolve precipitate into original flask with hot dilute hydrochloric acid, 1 part acid to 3 parts water. Wash well with hot water. Add 10 cc. ammonia as before, and the same amount of bromine water, if manganese is present. Boil and filter through the same paper into the same beaker. Wash three times with hot water. Make the filtrate neutral with hydrochloric acid, using litmus paper as indicator, and add 6 cc. hydrochloric acid in excess. If copper is present add 20 g. test lead and boil until all copper is thrown down. Heat to 70° C. and titrate with a standard solution of potassium ferrocyanide. Run the solution in rather slowly and stir constantly. A slight color change will be noted in the beaker when the precipitation is almost complete. This should not be ignored, since if it does not occur there is a possibility of error. Use a 1 per cent solution of ammonium molybdate for outside indicator.

GEOPHYSICAL LABORATORY, WASHINGTON, D. C.

A NEW METHOD OF SEPARATING ZINC FROM CADMIUM AND THE LATTER'S DETERMINATION IODOMETRICALLY¹

By ERIC JOHN ERIKSON

Further research in the development of the writer's method for complete spelter analysis has demonstrated the possibility of separating the bulk of the remaining zinc from cadmium by crystallization as zinc sulfate. The exact composition of the latter has not yet been ascertained. In one analysis of the crystals only 15.50 per cent was found, while the formula $ZnSO_4 \cdot 7H_2O$ calls for 22.73 per cent.

Although a small trace of cadmium is entrained in the zinc sulfate or zinc-ammonium sulfate, for technical purposes only one crystallization is deemed necessary, in view of the large sample (19.2 grams) of spelter taken originally.

The procedure in spelter analysis is as follows:

Referring to earlier publications² for details for removing and determining lead, the filtrate from the latter is boiled until nearly neutral and a white precipitate appears. Then add 50 cc. dilute sulfuric acid (1:3), boil down to about 80 to 100 cc. volume and allow to stand over night. In the morning the bulk of the zinc will be found crystallized out as sulfate. Decant the clear solution and wash three times with cold water, allowing each washing to drain. Dilute the filtrate to 200 cc. and pass in hydrogen sulfide until all cadmium is precipitated; usually 1 to 20 minutes is sufficient with a fairly rapid evolution of gas. Allow the precipitated cadmium sulfide several hours time to settle before filtering off. Determine

cadmium by any of the methods mentioned in the above-mentioned papers.

Cadmium may also be determined iodometrically according to von Berg's³ method (modified), by transferring to an Erlenmeyer flask, adding about 125 cc. of distilled water, a measured excess of $N/10$ iodine solution and then 30 to 50 cc. dilute hydrochloric acid. Shake and titrate with sodium hyposulfite until slight iodine excess is indicated; then add a few cc. starch solution and finish titration until disappearance of the blue color. The difference is due to cadmium: 1 cc. $N/10$ iodine solution = 0.00562 gram cadmium.

The new zinc-cadmium separation has been applied successfully to zinc ores also. Before its introduction it was a difficult matter to detect and determine accurately the small amounts of cadmium usually occurring in these ores.

PROCEDURE.—Dissolve 5 grams ore in nitric or hydrochloric acid, according to the nature of the ore, fume off with 20 cc. sulfuric acid, add water, boil and filter. To the filtrate add an excess of ammonia, boil and precipitate iron and alumina. Dilute to 500 cc., filter and pipette off an aliquot portion representing 3 or 4 grams; evaporate to low bulk and until small white precipitate appears; then add sulfuric acid and boil down to 80–100 cc. Remove from hot plate and allow zinc to crystallize out. Decant solution and precipitate cadmium as previously directed. Redissolve on filter with hot hydrochloric acid, neutralize filtrate with ammonia and add about 10 grams trichloroacetic acid; dilute to 200 cc. and precipitate once more with hydrogen sulfide. A pure cadmium sulfide is now obtained, which may be determined by any of the methods previously described, but the most accurate is undoubtedly the gravimetric determination as sulfate.

I think that the above separation can be applied in brass analysis in detecting small amounts of cadmium. Recently, attention was called to the difficulty of detecting and determining small amounts of cadmium,⁴ and the need of more accurate methods. This applies particularly to methods of separation, since the actual determination does not offer any unusual difficulties.

C. H. LINDSEY, CHICAGO, ILL.
[RECEIVED SEPTEMBER 24, 1916]

THE CHEMICAL EXAMINATION OF NATURAL BRINES¹

By O. R. BARNES AND J. J. WILSON

The proper analysis of natural brines has always been important. They are used by chemical manufacturers to make comparisons with a view to finding decisions as to prospective losses of salt, sodium and other products. The accurate detection of the pairs of bromine from sodium is as high as 50 to 100 cc. as well as a small variation of other products derived from natural brines. The above can be used for additional purposes as they produce and a small loading of many of the brines contained (sodium, potassium and

¹Presented at the American Chemical Society, Chicago, Ill.

²Eng. Mining J., March 1, 1914, p. 101.

³Eng. Mining J., March 1, 1914, p. 101.

⁴Eng. Mining J., March 1, 1914, p. 101.

¹Presented at the American Chemical Society, Chicago, Ill., April 1916, p. 11.

²Eng. Mining J., March 1, 1914, p. 101.

³Eng. Mining J., March 1, 1914, p. 101.

development, and hitherto wasted. As a result many analyses have been made in the last three years as a basis for manufacturing consideration. Some of these were made in the laboratories of manufacturers themselves and some by consulting chemists. Analyses from both sources have come into the hands of the authors as the basis for report upon prospective manufacturing values. We, also, have had occasion to make check or confirmatory analyses.

It early became evident that there was no standard or uniform procedure being followed by the different workers. To this fact may be due a large part of the non-agreement encountered from time to time, though inexperience with this type of analysis is also a factor. Few chemists, even water analysts, are experienced in such a type of work as bromine determination in brine. This may be shown best by citing a report to its president by the laboratory of the chemical company. The letter from the president of one chemical company to another stated:

"The analysis of the two samples of brine which you sent us has been completed and it was some job. The results are as follows:

	WELL A	WELL B
Depth.....	1200 ft.	1206 ft.
Diameter.....	8 in.	4 in.
Specific Gravity of Brine.....	1.071	1.070
CaO.....	0.69 per cent	0.68 per cent
Br.....	0.42	0.22
Halides (as sodium halide).....	9.21	9.76
Iodine.....	None	None"

These samples were from a brine whose composition was well known to us. Furthermore, they were on the same property. It will be noticed that they are of the same depth and also the same specific gravity, CaO content, and halide content. Nevertheless, they are reported of different bromine content—a divergence of nearly 100 per cent. Such a divergence would be a very important matter industrially, for one of these wells would give nearly twice the yield of bromine for the same turnover of salt and calcium chloride and at the same fuel cost as the other well. Considering the difficulty of bromine determination, by the usual methods, the infrequency of demand for it and the concordance of all other determinations on these two brines one is tempted to suspect the accuracy of the bromine determinations. As a matter of fact even the lower value is over twice the bromine content of the field in question as shown by both analyses by various chemists and experience of *all* the plants operating on this particular brine.

Such situations give rise to controversy and discredit analytical chemistry. An examination of the literature for a basis for standard or uniform procedure disclosed no exact one which could be recommended. The procedures described for the examination of "mineral water" are not applicable directly. Certain modifications which our experience has introduced are recorded here. Not all of the procedures described have been exhaustively studied as yet. The purpose of this paper is to make a beginning with the hope that others, who have had experience in this work, will contribute their experiences, or will criticize these procedures. In this way a procedure may be developed which may be accepted as standard.

The object is to develop a method which will meet the needs of the manufacturing chemist rather than a method of exhaustive analysis. Brevity and speed of manipulation, with reasonable accuracy, are, therefore, the requirements.

ANALYTICAL PROCEDURES

SAMPLE—The sample when pumped from the earth will generally be clear, but on standing it becomes turbid due to the separation of a brown precipitate. This precipitate is mainly iron, but may contain silica and alumina. It is probably caused by oxidation and hydrolysis of ferrous bicarbonate. Generally by the time the sample will have reached the chemist the iron will have separated. The scheme of agitation to suspend the deposit uniformly through the liquid before taking a part for analysis is inaccurate, as experiments have shown. Furthermore, the specific gravity is changed and this will affect the entire percentage composition. Consideration of this point has led us to conclude that the best procedure would be to collect a sample of about one liter, allow it to oxidize and settle completely, determine the amount of deposit, and then make analyses on the filtered sample. The analysis would not be exactly that of the original brine, but the difference will be very slight, and, since this procedure gives more nearly the thing that the manufacturer wants, it is best to proceed in this manner.

DEPOSIT ON STANDING (AERATION)—The sample of about one liter, which will usually contain some deposit, is allowed to stand, with occasional shaking, and removing of the stopper, for two or three days, or until deposition is complete and the precipitate settles well. The height of the liquid is carefully marked on the outside of the bottle, and the entire sample is then filtered, rejecting the first 100 cc. The precipitate is well washed, ashed and ignited to constant weight. The bottle is dried and the amount of water which it contained to the mark is determined. With these data the grams per liter are calculated, using the specific gravity of the filtered sample, and the result recorded as "*Deposit on Aeration.*" The errors will not be large if percentages be calculated, using this figure. Since in the industries all natural brines are exposed to air and allowed to settle before they are further treated, this value is just what is wanted by the manufacturer. Further examination of the precipitate is not necessary. It is a question whether or not it would be fair to assume the precipitate to be iron oxide (Fe_2O_3) and calculate it to, and report it as, ferrous bicarbonate.

SPECIFIC GRAVITY—The specific gravity is obtained by the Westphal balance, and is taken at 15° C., although perhaps it would be better to use 20° C., since this is more nearly the average temperature. The specific gravity of the fresh brine will be different from that of the sample through which the precipitate is suspended, and this in turn will be different from the filtered sample. On one brine, for example, the specific gravity of the filtered sample was 1.2307, while that of the sample in which the precipitate was suspended was 1.2342. If the chemist could take

the specific gravity of the clear brine as soon as pumped from the well it would no doubt be best, from the point of view of the original brine but this will generally be impractical. Even if the specific gravity could be obtained on the fresh brine there would be some volume change after the precipitate settled and a small error would be introduced when taking a filtered sample for later analyses. For these reasons, and also because the manufacturer is interested in the settled brine, it is believed that the best procedure is to use the filtered, aerated brine, and to determine the specific gravity with a Westphal balance at $15^{\circ}\text{C}.$ (?). This value is used in calculating percentages.

TOTAL SOLIDS—Many chemists omit this determination because of its questionable accuracy, but its value in calculating total water content for "evaporation fuel" comparisons makes it important. Brines rich in CaCl_2 require a rather high temperature, above $160^{\circ}\text{C}.$, to expel the water completely. At this temperature the magnesium and calcium salts lose a part of their acid constituents, and a wide range of values will be obtained, depending on the temperature and duration of heating. The total solids can be calculated from the complete analysis, but this value should be checked by the total solids as obtained by evaporation. This point is being studied in this laboratory at the present time, and it is hoped that by a suitable arrangement the volatilized acids may be collected, titrated and then be added to the residual weight of the total solids. It may be that a weighed excess of some base may be added to retain the acid which is otherwise volatilized. The constituents likely to volatilize are chlorine, bromine, iodine (slight), sulfur trioxide and carbon dioxide (slight). The total solids are determined in the filtered sample, using 25-cc. portions and should be reported as *Total Solids by Evaporation*. This gives the manufacturer a basis for a reasonable estimation of the water to be evaporated in working the brine.

SILICA—A 25-cc. portion of the filtered brine is acidulated with 5 cc. of concentrated hydrochloric acid and is evaporated to dryness. It is then dried at $120^{\circ}\text{C}.$, or higher if necessary, for an hour. Five cc. of hydrochloric acid are then added, the vessel is warmed, 20 cc. of water are added, and, after warming, the whole is filtered and washed free from chlorides. The filtrate is evaporated and treated as just described, and the operation is repeated on the second filtrate. The combined precipitates are ignited in a platinum crucible, and weighed. The residue is treated with sulfuric and hydrofluoric acids. The loss in weight is reported as *silica*, and the residue is added to the iron and alumina.

IRON AND ALUMINUM The filtrate and washing, which should contain 5 cc. of concentrated hydrochloric acid, are treated with a few drops of nitric acid, boiled a few minutes, and then made alkaline with ammonia. It is then boiled until all the ammonia is expelled, and after standing, is filtered, washed and ignited in the crucible from which the silica was expelled. The residue is reported as *Iron and Aluminum Oxides*. A separation of the iron and aluminum is not necessary.

The results should be reported separately from the iron which separated on aeration. It should be remembered that the iron, aluminum and silica are not in solution as oxides, but as salts. For this reason there will be a slight difference between the total solids on evaporation and the calculated total solids.

Much time is saved if the iron, alumina and silica are all precipitated together, with ammonia. The amount of silica remaining in solution is very small. These constituents have no commercial value, and need not be reported separately. It should be remembered in this latter case that ammonium chloride must be added.

CALCIUM—The filtrate from the iron and aluminum is diluted to 250 cc. and 25 cc. are taken; this is diluted to 150 cc., heated to boiling and a hot 10 per cent solution of ammonium oxalate is added in excess. After standing for some time (15 minutes), it is filtered and washed with hot water. The precipitate is dissolved in warm dilute hydrochloric acid, a little ammonium oxalate solution added, and ammonia then slowly added to complete the precipitation. The precipitate is filtered out, after standing one-half hour, and is ignited to the oxide and weighed, or is dissolved in dilute sulfuric acid and titrated with permanganate. Our experience seemed to show that it was not necessary to allow the precipitate to stand 12 hours as is recommended in some of the books on water analysis. The calcium should be reported as sulfate and chloride.

MAGNESIUM—The combined filtrates and washings from the calcium are acidified with hydrochloric acid, a large excess of sodium hydrogen phosphate is added, and then ammonium hydroxide with constant stirring until the liquid smells of ammonia. Ten cc. of strong ammonia are added in excess and the whole is allowed to stand 12 hours. The precipitate is filtered out, washed with dilute ammonia and redissolved in hydrochloric acid (1 : 5). The volume is made up to 75 cc., a little sodium hydrogen phosphate added, and then ammonia, drop by drop, with constant stirring until the solution smells strongly. After 4 hours the magnesium is filtered out on an alundum or Gooch crucible, washed with 2 per cent ammonia water, dried and ignited to $\text{Mg}_3\text{P}_2\text{O}_7$. If an alundum crucible is used it should be heated within a glazed crucible. The magnesium should be calculated to the bromide and chloride.

The above procedure gave very good results. In the usual procedure the filtrate from calcium is evaporated to dryness, and the ammonium salts are volatilized. This requires great care, and much time, and did not give any better results than the procedure described. The reprecipitation must be carried out, even on very small amounts. These seem to be good authority, however, for the evaporation and ignition which we have omitted, and the point should be investigated further.¹

¹ In the discussion of this paper at the Industrial Chemistry of the Iron and Steel Institute, London, 1917, it was pointed out that the method described for the determination of iron and aluminum oxides is not a true gravimetric method, and that the results obtained are not comparable with those obtained by the gravimetric method. The method described in this paper is a true gravimetric method, and the results obtained are comparable with those obtained by the gravimetric method.

BARIUM AND STRONTIUM—If no sulfates are present, barium and strontium must be looked for. Indeed a case is on record where barium, lead and sulfuric acid were present simultaneously in a natural mineral water.¹ From work in progress in this laboratory it seems, however, that in the case of brines, where very little CO_2 is present, that sulfates preclude the presence of barium or strontium. Barium oxalate is sparingly soluble, and a strontium oxalate is insoluble in water. When these metals are present they will be partially precipitated along with the calcium. This point seems to have been overlooked hitherto. In cases where the barium and strontium amount to 0.2 per cent the error introduced cannot be neglected. The magnesium results may also be affected. It may be possible to precipitate the barium and strontium with ammonium sulfate before precipitating the calcium, but no work has been done on this phase. The fact that the barium is not completely precipitated by ammonium oxalate makes it impossible to apply a correction to the calcium precipitate. The determination of the barium and strontium in the calcium precipitate is too time-consuming to be practical for the ordinary technical analysis. When the barium and strontium content is small the error can be ignored. The procedure used was identical with the one described in the *Department of Agriculture Bull.*, 91, "Mineral Waters of the United States," by J. K. Haywood and B. H. Smith; a simpler method has not yet been found.

AMMONIA—Traces of ammonia have been reported in some brines, but the amount is generally so small as to be of no commercial importance. It may be, however, that its significance is greater than we now know, especially in brines for electrolysis. The suggestion has been made by cell operators that nitrogen chloride may be connected with the explosions which occur from time to time in electrolytic chlorine apparatus. If this should prove true the determination of ammonia will be important.

SULFURIC ACID, SODIUM AND POTASSIUM—Fifty cc. of the filtrate from the iron and alumina are diluted to 100 cc. and treated, while boiling hot, with 10 per cent BaCl_2 solution, adding it slowly and with constant stirring. The BaSO_4 is filtered off, the paper burned off in a porcelain crucible, and the precipitate dissolved in a few cc. of warm, concentrated sulfuric acid. The solution is now carefully poured into 250 cc. of water, and, after standing some time, is filtered, washed and ignited. It should be reported as calcium sulfate. This method of freeing the BaSO_4 from iron and other absorbed matter is very effective. It is essentially that taught for decades at the John Harrison Laboratory, University of Pennsylvania, Philadelphia.

The filtrate from the sulfuric acid is used for sodium and potassium. From this point, the procedure we have been using is the same as described in "Mineral Waters in the United States," *Department of Agriculture Bull.*, 91, *Loc. cit.* It is difficult, however, to determine small amounts of potassium in the presence

of large amounts of sodium chloride, and it is believed that some procedure¹ should be used which will precipitate most of the sodium first.

CHLORINE—The brine should be tested with phenolphthalein. It will usually be neutral, but if it is not, it should be made so with NaHSO_4 solution. 10 cc. of the filtered sample are diluted to a liter and 10 cc. used for titration. This is diluted to 200 cc., 2 cc. of K_2CrO_4 solution are added and the mixture is titrated to the end-point. Na_2CrO_4 would probably be a satisfactory indicator here but we have not yet proved this to be true. Take an amount of standard sodium chloride solution equivalent to the amount of silver nitrate used, dilute to 200 cc. and titrate as before. The difference represents the amount necessary to affect the indicator and should be subtracted. This procedure is accurate enough since the chlorine is used only as a check on the analytical work. The bromine value must be deducted.

BROMINE—The colorimetric procedure, as given for ordinary waters, is not usable with brines. Experiments showed that after repeated extraction with 90 per cent alcohol the residue still contained bromine. The distillation methods are time-consuming and not very easily manipulated. For these reasons a colorimetric method was developed.

Procedure—100 cc. of the brine are made alkaline with Na_2CO_3 and are evaporated to dryness. It is then taken up in water and filtered into a 250-cc. flask. It is made distinctly acid with H_2SO_4 and is diluted to the mark: 25 cc. are pipetted into a 50-cc. Nessler tube and chlorine is added until the maximum color has developed; 10 cc. of carbon tetrachloride are then added, and the mixture is shaken and compared with a set of standards made up from NaBr solution in the same way. By this rough check the approximate amount of bromine will be discovered, and a set of standard solutions are then prepared which are very close above and below the unknown solution. Again 25 cc. are taken, chlorine water is added to a maximum color and the same amount is added to the standards; the sample is then shaken with 10 cc. of CCl_4 and poured into a wet filter; when the water has drained off the filter should be punctured and the liquid caught in a 25-cc. Nessler tube (this is best done in a darkened room but darkness is not essential). If a sample does not exactly match the standard the colors can be compared by diluting with CCl_4 ; or since the operation is so simple, a new set of standards can be made up, and then a new determination made. If a test shows that all bromine was not extracted by 10 cc. of CCl_4 a second extraction should be made. This is generally not necessary.

Traces of iodine which are present in most brines will not interfere. The iodine need not be reported.

It is difficult to appreciate the unreliability of published statements regarding the occurrence of bromine. For instance, although the State of Michigan reports, and the most reliable information states, that Midland, Mich., brine contains 0.1 per cent of bromine, yet the

¹ Professor C. W. Fouke, of the Division of Analytical Chemistry of the Ohio State University laboratory, is now investigating this matter.

¹ *Charles, Ann. Chem. anal.*, 1902, 91.

most exhaustive German work on bromine¹ states on page 3 that the brine from Midland, Ohio, *sic.*, contains 4.18 per cent magnesium bromide which is equivalent to 3.63 per cent bromine, or 36 times stronger than those who operate on it claim it to be.

REPORTING RESULTS

The results should be reported in such a manner as to give the manufacturer the thing which he wants. The reporting of the constituents as ions, while strictly scientific, is of no value to the manufacturer. All of the sodium and potassium should be calculated to chloride. Since the CaSO_4 separates on the copper tubes in the evaporators the H_2SO_4 should be reported as calcium sulfate. The bromine should be calculated as magnesium bromide, since it has long been so considered in the trade; but bromine as free bromine should also be reported. The residual calcium and all the magnesium are calculated to chlorides since they go on the market as such. Strontium and barium should be given as chlorides. The silicon should be reported as the oxide since the form in which it is combined is not known. Iron and aluminum are reported together as oxides since their separation is too time-consuming. The residue which separates on standing should also be given. Results are preferably reported in percentages though some manufacturers are accustomed to *grams per liter*. The specific gravity and temperature should always be reported; for this reason also, a standard temperature should be used so that results would be really comparable.

When the positive and negative ions are calculated to compounds they should nearly satisfy each other. It should be borne in mind, however, that the iron, aluminum and silicon are given as oxides, and not as salts, in which form they usually occur in the brine. There may also be small amounts of CO_2 and iodine which are not included. If, however, the check is not reasonably close, it indicates an error, or else some undetermined constituent is present.

As an illustration of the extremes in composition which the analyst must expect to meet, two examples from Ohio brines will serve.

BRINE SOURCE	Eastern Ohio Coal Mine	Southern Ohio Driven Well
Specific gravity	1.034	1.180
Baume equivalent	4.8	22.1
Sodium chloride	3.26 per cent	12.08 per cent
Magnesium bromide	0.007	0.124
Bromine	0.006	0.107
Calcium chloride	1.63	10.81
Magnesium chloride	0.05	2.61
Calcium sulfate	0.001	0.03
Iron and aluminum oxides	0.31	0.04
Silica	0.12	0.002
Residue on evaporation	5.23	29.00

While this work considers primarily the commercial natural brines, the same procedure will doubtless apply to the analysis of artificial brines, such as used in soda ash manufacture and in electrolytic cells, although the amounts of calcium and magnesium will be much less in these solutions.

LABORATORY OF INDUSTRIAL CHEMISTRY
OHIO STATE UNIVERSITY, COLUMBUS

¹ Monograph on Magnesium Electrochemistry. Über die elektrolytische Gewinnung von Brom. By Max Schuster.

SEASONAL DISTRIBUTION OF SOIL AND FECAL STRAINS OF THE COLON-AEROGENES GROUP IN SURFACE WATERS

By MYRTLE GREENFIELD AND W. N. SEIGRIST

Received April 30, 1917

When this work was started, it was with the object of determining the variation of the organisms of the colon-aerogenes group in the surface water supplies of Kansas, during wet and dry weather, and their response to treatment.

Three supplies on the Verdigris River were chosen—Cherryvale, Independence and Coffeyville, and two on the Neosho River—Humboldt and Chanute. All the towns have rapid sand filters and coagulate with alum. Independence uses lime in addition, a part of the time. Cherryvale pumps the water from the Verdigris River into a storage basin, holding 1,288,000 gallons, which is about five days' supply. From this it flows by gravity to the city four miles distant. Table I shows the pollution at the raw water intakes of the cities in question.

TABLE I—STATISTICS OF SEWAGE POLLUTION AT RAW WATER INTAKES
—RAW WATER POLLUTION BY SEWAGE FROM—

CITY	Town	Distant Miles	Pollution	Con- sections	Purification
Cherryvale	Neodesha	20	3.011	876	None
Independence	Neodesha	24	3.011	876	None
	(Independence)	24	12.144	2600	Septic tank &
Coffeyville	1 & Cherryvale	30	4.235	800	Contact bed
Humboldt	Tola	8	2.866	2380	Septic tank
Chanute	(Tola & Humboldt)	16	2.866	2350	Septic tank
		8	2.131	150	Septic tank

¹ Contact bed for one-third of the sewage.

² Contact bed in poor condition.

METHOD OF ISOLATION

A portable laboratory was set up at Independence and the collection of all samples was personally supervised. Samples were iced and delivered to the laboratory a few hours after collection. Upon receipt at the laboratory, they were plated in standard agar and incubated 24 hrs. at 37°. Various dilutions were planted at the same time in lactose peptone bile. Streaks from the positive fermentation tubes were made on Endo plates. Three coli-like colonies were picked from each Endo plate and grown on an agar slant. These slants were sent to the main laboratory and purified again by streaking on Endo plates and picking a characteristic colony. From these, transfers were made to lactose, dextrose, saccharose, and dulcitol broth tubes and to the di-potassium acid-phosphate media of Clark & Lubs.¹ The broth tubes were incubated 48 hrs. at 37° and the di-potassium acid-phosphate tubes 72 hrs. at 47°. One half the latter was treated with methyl red to indicate the H⁺ ion concentration and the other half with 10 per cent KOH to obtain the Voges-Proskauer reaction. All cultures that did not ferment lactose and dextrose were discarded.

It was demonstrated by Rogers, Clark and Ingram² that organisms of the colon-aerogenes group occurring on grains may be differentiated from those of fecal origin by the gas ratio. Clark & Ingram think that there is a complete correlation between the gas ratio and the H⁺ ion concentration. The final affinity of their media being characterized by a high H⁺ ion

TABLE II—DISTRIBUTION OF THE ORGANISMS ISOLATED (RESULTS IN PERCENTAGES OF TOTAL BACILLI)

CITY	WATER	No. of Cultures	PERIOD	<i>B. Communi</i>		<i>B. Communi</i>		<i>B. Acid-Lactici</i>		<i>B. Aerogenes</i>		TOTAL	
				Fecal	Soil	Fecal	Soil	Fecal	Soil	Fecal	Soil	PERCENTAGES	PERCENTAGES
INDEPENDENCE.....	Raw	24	Rain	8.34	54.7	4.17	12.5	...	20.8	12.4	87.6
		8	Drouth	75	12.5	12.5	87.5	12.5
		30	Rain	11.1	25.9	...	11.1	5.42	11.14	14.19	19.5	33.17	66.8
	Tap	25	Drouth	32	20	4	...	16	4	8	16	60	40
		54	Rain	4.26	49.23	4.26	2.13	8.52	10.53	8.52	12.55	25.45	74.6
		47	Drouth	44.8	4.26	8.51	...	14.8	25.5	70.1	29.9
CHANUTE.....	Raw	27	Rain	31.8	8.8	17.2	12.05	...	50.05	50	50
		23	Drouth	39.1	8.7	8.7	...	4.35	...	4.35	34.8	56.5	43.5
	Treated	15	Rain	60	26.5	13.4	59.9	40.1
		24	Drouth	29.1	16.65	16.65	37.5	45.7	54.3
		30	Rain	14.8	36.5	12.75	4.25	14.8	4.25	...	12.75	39.2	60.8
		58	Drouth	34.5	1.73	3.46	...	18.9	...	6.9	34.5	63.8	36.2
CHERRYVALE.....	Raw	30	Rain	29	16.3	6.68	...	9.6	9.6	16.3	12.8	63.4	36.6
		21	Drouth	47.7	14.3	9.52	...	4.76	23.8	61.8	38.2
	Treated	32	Rain	13.3	30	3.36	...	5.66	13.33	3.36	30	26.6	73.4
		23	Drouth	13.1	26.1	4.35	...	13.1	...	4.35	39.1	37.8	65.2
	Tap	33	Rain	21.2	45.4	...	3.3	...	3.3	...	27.3	21.2	78.8
		28	Drouth	46.4	3.57	10.7	...	7.14	...	10.7	21.4	78.6	21.4
HUMBOLDT.....	Raw	30	Rain	3.8	19.5	...	3.8	23	11.55	11.55	26.8	23.8	76.2
		30	Drouth	35	5	15	...	10	35	60	40
	Treated	23	Rain	10.7	53.2	6.9	6.9	...	20.7	17.2	82.8
		20	Drouth	17.4	26.1	8.7	...	8.7	...	8.7	30.4	43.5	56.5
	Tap	53	Rain	16.63	20.82	12.5	4.47	14.5	18.53	...	12.53	38.1	61.9
		23	Drouth	61.7	38.3	66.7	33.3
COFFEYVILLE.....	Raw	15	Rain	...	33.3	13.3	20	...	33.3	13.3	86.7
		21	Drouth	14.6	14.6	19.1	...	19.1	33.3	52.4	47.6
	Treated	15	Rain	13.3	13.3	...	20	26.6	26.6	40.1	59.9
		21	Drouth	50	...	8.32	...	4.16	...	4.16	33.3	66.7	33.3
	Tap	9	Rain	11.1	55.5	5.55	27.8	16.68	83.3
		30	Drouth	33.3	13.3	16.7	...	16.7	...	33.3	13.3	73.3	26.7
PARSONS.....	Raw	15	Drouth	73.4	26.6	73.2	26.8
		15	Drouth	53.4	...	13.3	...	13.3	...	6.66	13.3	86.7	13.3
	Treated	28	Drouth	28.6	14.3	7.14	...	10.2	39.3	46.4	53.6
	Raw	117	Rain	16.25	25.68	5.98	0.85	9.4	12.82	6.83	25.64	67.1	62.4
		108	Drouth	42.6	8.32	10.2	...	8.32	...	0.92	29.6	62	38
		116	Rain	18.1	32.68	2.58	5.17	5.17	7.75	4.32	22.8	31.8	68.2
SUMMARY Supplies Averaged	Treated	134	Drouth	31.9	15.67	5.98	...	11.95	0.735	5.22	29.2	54.5	45.5
		193	Rain	13.49	38.82	7.26	3.14	9.32	8.82	2.59	18.12	33.62	67.4
		194	Drouth	38.7	6.18	8.25	...	14.82	...	4.15	2.78	65.8	34.2

TABLE III—CORRELATION BETWEEN THE NUMBER OF ORGANISMS OF THE COLON-AEROGENES GROUP PER CC. AND NUMBER OF ORGANISMS GROWN ON AGAR AT 37° C. IN 24 HOURS

CITY	WATER	No. of Samples	PERIOD	% POSITIVE FOR ORGANISMS OF THE COLON-AEROGENES GROUP		ORGANISMS OF THE COLON-AEROGENES GROUP PER CC.		PER CENT OF THE ORGANISMS AS		BACTERIA PER CC. ON AGAR AT 37° C. IN 24 HOURS		
				Max.	Min.	Max.	Av.	Fecal	Soil	Max.	Min.	Av.
CHERRYVALE....	Raw	10	Rain	100	66.0	10.0	30.1	63.4	36.6	80,000	6,000	34,700
		8	Drouth	100	66.0	1.0	26.3	61.8	38.2	3,400	1,200	2,200
	Treated	11	Rain	100	10.0	0.4	6.8	26.6	73.4	2,900	230	930
		8	Drouth	100	6.6	0.1	2.4	34.8	65.2	340	160	280
	Tap	12	Rain	100	0.6	0.1	0.4	21.2	78.8	160	40	85
		17	Drouth	58.8	0.4	0.1	0.2	78.6	21.4	940	9	67
INDEPENDENCE..	Raw	8	Rain	100	66.0	10	35.0	12.4	87.6	240,000	9,000	91,000
		3	Drouth	100	100.0	1	30.0	87.5	12.5	6,000	3,700	4,800
	Treated	10	Rain	100	6.6	0.6	2.4	33.17	66.83	1,800	260	700
		8	Drouth	100	33.0	0.2	3.1	60.0	40.0	3,900	260	1,280
	Tap	21	Rain	90.5	0.8	0.1	0.4	25.45	84.6	210	6	55
		20	Drouth	75	1.0	0.1	0.2	70.0	29.9	250	11	95.4
COFFEYVILLE....	Raw	5	Rain	100	66.0	6.6	29.7	13.3	86.7	170,000	60,000	88,000
		8	Drouth	100	100.0	1	28.4	52.4	47.6	4,100	1,900	2,170
	Treated	5	Rain	100	33.0	0.4	8.1	40.1	59.9	830	370	550
		8	Drouth	100	33.0	0.2	5.2	66.7	33.3	1,100	140	480
	Tap	8	Rain	87.5	4.0	0.1	0.3	16.68	83.3	140	25	75
		16	Drouth	75	0.8	0.1	0.4	73.3	26.7	310	9	67
HUMBOLDT.....	Raw	10	Rain	100	100.0	6.6	37.5	23.8	76.2	52,000	8,000	24,600
		9	Drouth	100	66.0	1	25.4	60.0	40.0	8,600	700	2,400
	Treated	10	Rain	100	10.0	0.2	5.4	17.2	82.8	2,700	330	1,040
		9	Drouth	100	10.0	0.1	1.5	43.8	56.5	300	85	220
	Tap	20	Rain	95	1.0	0.1	0.64	38.1	61.9	140	35	70
		16	Drouth	6.4	0.4	0.1	0.19	66.7	33.3	65	5	35.3
CHANUTE.....	Raw	9	Rain	100	66.0	6.6	26.4	50.0	50.0	30,000	7,000	17,000
		8	Drouth	100	100.0	1	24.8	56.5	43.5	3,700	1,200	2,300
	Treated	9	Rain	77.8	0.6	0.6	0.6	59.9	40.1	410	110	240
		8	Drouth	100	6.6	0.2	0.7	45.7	54.3	700	180	540
	Tap	32	Rain	56.2	0.6	0.1	0.25	39.2	60.8	95	3	22
		32	Drouth	46.8	0.6	0.1	0.18	63.8	36.2	230	7	36.2
SUMMARY Supplies Averaged	Raw	42	Rain	100	100	6.6	31.74	37.61	62.39	240,000	6,000	50,800
		34	Drouth	100	100	0.1	27.48	62.0	38	15,200	700	2,460
	Treated	45	Rain	95.1	33	0.2	4.86	31.8	68.2	2,900	110	260
		37	Drouth	97.2	33	0.1	3.27	54.5	45.5	4,200	110	470
	Tap	93	Rain	80.7	1	0.1	0.39	34.6	67.38	210	3	61.4
		92	Drouth	59.5	1	0.1	0.21	65.8	34.2	250	5	43.4

concentration, the cultures from grains by a low H^+ ion concentration. The difference in H^+ concentration is easily recognized with methyl red as an indicator—being bright red with a H^+ ion concentration of 1×10^{-5} and changing to clear yellow with a H^+ ion concentration of 1×10^{-6} . The work of

Max Levine,¹ Florence Hulton,² and one of us,³ indicates that there is a complete correlation between the Voges-Proskauer reaction and the alkaline methyl-red reaction. The work on the 862 cultures consid-

¹ *J. Infec. Dis.*, 18 (1916), 358.

² *Ibid.*, 19 (1916), 606.

³ *Ibid.*, 19 (1916), 647.

ered in this paper confirms the correlation. It is the opinion of the writers that for a rapid determination, the Voges-Proskauer is more delicate than the methyl-red determination. From this point, cultures that have a high H^+ ion concentration, in the media of Clark and Lubs,¹ and are Voges-Proskauer negative will be spoken of as fecal strains and those that have a low H^+ ion concentration and are Voges-Proskauer positive, as soil strains.

The first set of samples was taken daily from June 16 to June 27, 1916. From June 5 to 27, the rainfall was 9.47 inches. In the tables this period is called "Rain." The second set of samples was taken daily from August 14 to 22, 1916. During that time the rainfall was 0.64 inch. In the table this period is called "Drouth."

CHARACTERISTICS AND DISTRIBUTION OF CULTURES

The distribution of the cultures among MacConkey's² four principal groups and their division into soil and fecal strains during wet and dry weather is shown in Table II. The summary indicates that, during rainy weather, a slightly higher percentage of the cultures from raw water were fecal strains than of the cultures from treated or tap water; this checks with previous work done by one of us.³ During dry weather there was a slightly higher percentage of fecal strains in the tap water than in the raw water. These differences are so slight that no cognizance should be taken of either. There seems to be no difference between soil and fecal strains of organisms of the colon-aerogenes group from surface water supplies in their resistance to treatment, nor is there a difference between cultures of the four principal groups of MacConkey isolated from surface water supplies, and their resistance to treatment, coagulating with alum and filtering through a rapid sand filter being the treatment.

CORRELATION

Table III correlates the number of organisms of the colon-aerogenes group per cc. per cent of soil and of fecal strains, and the number of organisms grown on agar at 37° in 24 hrs. As was to be expected, dry weather conditions decreased the average count on agar and the average number of organisms of the colon-aerogenes group per cc. in the raw water. This is further shown in Table IV.

During rain or high-water periods, the greater per cent of the organisms of the colon-aerogenes group from raw water belongs to the soil strain. During dry weather, the greater per cent of the organisms of the colon-aerogenes group from raw water belongs to the fecal strain: this was noticeably true if the raw water was subject to sewage pollution.

The sanitary survey showed that the raw water at Humboldt had by far the more sewage pollution. The higher increase in the per cent of fecal strains of organisms of the colon-aerogenes group during dry weather correlates with this.

The raw water at Cherryvale shows 1.0 per cent

decrease in fecal strains during dry weather. The raw water from which this data was taken was collected at the Cherryvale plant, that is, after the 5 days' storage. This would undoubtedly account for the slight decrease in the number of fecal strains during dry weather.

CHERRYVALE			
WATER	STRAINS	PERCENT	
RAW	Fecal	1.0	100
	Soil	0.0	0
TREATED	Fecal	0.0	0
	Soil	0.0	0
TAP	Fecal	0.0	0
	Soil	0.0	0
HUMBOLDT			
RAW	Fecal	0.0	0
	Soil	0.0	0
TREATED	Fecal	0.0	0
	Soil	0.0	0
TAP	Fecal	0.0	0
	Soil	0.0	0
CONFEYVILLE			
RAW	Fecal	0.0	0
	Soil	0.0	0
TREATED	Fecal	0.0	0
	Soil	0.0	0
TAP	Fecal	0.0	0
	Soil	0.0	0
HUMBOLDT			
RAW	Fecal	0.0	0
	Soil	0.0	0
TREATED	Fecal	0.0	0
	Soil	0.0	0
TAP	Fecal	0.0	0
	Soil	0.0	0
CHERRYVALE			
RAW	Fecal	0.0	0
	Soil	0.0	0
TREATED	Fecal	0.0	0
	Soil	0.0	0
TAP	Fecal	0.0	0
	Soil	0.0	0

The raw water at Humboldt shows 1.0 per cent increase in fecal strains during dry weather. The sanitary survey offers no explanation for this decided increase. This per cent is not of much value, due to the small number of samples collected during dry weather at Humboldt.

The Cherryvale raw water, because of local strains during dry weather is that expected from the sanitary survey.

¹ *Ibid.*

² Prescott and Winslow, "Elements of Water Bact." 1913, 140.

³ *Ibid.*

L. A. Rogers¹ collected samples above and below a source of pollution on a stream. Above the pollution, the greater percentage of the organisms of the colon-aerogenes group were soil strains, while below the pollution, the greater percentage were fecal strains.

The variation in per cent of soil and fecal strains of organisms of the colon-aerogenes group from surface water supplies is shown graphically in the accompanying diagram.

TABLE IV—THE EFFECT OF DROUGHT ON THE AVERAGE NUMBER OF ORGANISMS OF THE COLON-AEROGENES GROUP PER CC. IN SURFACE WATER VS. THE AVERAGE NUMBER OF ORGANISMS GROWN ON AGAR AT 37° IN 24 HOURS AND THE PER CENT OF FECAL STRAINS

CITY	Per cent Reduction in Total Count of Organisms	Per cent Reduction in No. of Organism of Colon Aerogenes Group per Cc.	Per cent Increase in No. of Fecal Strains
Cherryvale.....	88	6.7	—1.6
Independence.....	89	7.7	75.1
Coffeyville.....	95	2.2	39.1
Humboldt.....	82	19.0	36.2
Chanute.....	76	0.31	6.5
AVERAGE.....	90.7	7.2	24.39

CONCLUSIONS

1—There seems to be no difference between soil and fecal strains of organisms of the colon-aerogenes group from surface water supplies in their resistance to treatment, nor is there a difference between cultures of the four principal groups of MacConkey, isolated from surface water supplies in their resistance to treatment.

2—There is a correlation between the increase in the fecal strains of organisms of the colon-aerogenes group during dry weather and the sanitary survey.

The writers wish to express their appreciation for the assistance and criticism of C. C. Young, Director of the Water and Sewage Laboratory, and C. A. Haskins, State Sanitary Engineer. The Kansas State Board of Health helped materially in the survey.

WATER AND SEWAGE LABORATORY
STATE BOARD OF HEALTH, LAWRENCE, KANSAS

THE EXAMINATION OF CANNED SALMON FOR BACTERIA AND TIN²

BY L. D. BUSHNELL AND C. A. VETZ

Received April 18, 1917

INTRODUCTION

Reports from the Division of Vital Statistics of the Kansas State Board of Health show a number of deaths in this state supposed to have been due to the eating of canned salmon. Data other than that are lacking. Mr. L. A. Congdon, Assistant Chief Food and Drug Inspector of the Kansas State Board of Health, suggested to us, through Dr. J. T. Willard, chief of the food laboratory of the Kansas State Agricultural College, the bacteriological examination of samples of canned salmon, with the view particularly of noting the presence of paratyphoid-like organisms. The state inspectors had sent in fifty-two samples of the various brands to the food laboratory for examination for tin. These were also used for bacteriological examination.

¹ "The Viability of Different Types of the Colon-Group in Water," L. A. Rogers. *J. of Bact.* (Abstract), 1, 83.

² Published by permission of A. M. Jardine, Dean of the Exp. Station, and J. T. Willard, Chief of the Food Laboratory, Kansas State Agricultural College, and S. J. Crumrine, Sec. Kansas State Board of Health.

The samples ranged from the most expensive to the cheapest grades on the market and included forty-four different brands from twenty-six concerns.

The samples were obtained on the open market and we have no knowledge of the method of preparation.

All cans were in good condition and all held a vacuum, no swelled ends being found. All samples were offered for sale and were in a merchantable condition.

The fish was firm and of good flavor and odor in all cases. In some of the cheaper brands the meat was somewhat dry, light-colored and contained rather small amounts of oil, but these were not sold as a high-grade product.

The following commercial grades were examined:

GRADE	Sockeye	Red and Red Alaska	Chinook	Coho	Pink	Chum
Samples.....	8	24	2	2	10	6

BACTERIOLOGICAL EXAMINATION

The tops of the cans were carefully cleaned and covered with a 5 per cent solution of carbolic acid for about 10 minutes. This was then poured off and denatured alcohol added for about 5 minutes. The excess of alcohol was removed and the remainder burned. The top was then thoroughly flamed with a Bunsen burner flame. The can was tilted several times, flamed again and opened with a previously boiled and flamed can opener, with as little agitation as possible. The floors, table top and hands of the operator were carefully washed with carbolic acid solution before the operation began.

Standard meat juice agar plates, dextrose fermentation tubes, bile lactose fermentation tubes, deep agar shakes, milk with and without calcium carbonate added, Endo agar plates and the condensation water on agar slants were inoculated. The material for these inoculations was taken from as near the bottom of the can as possible.

To the Petri dishes were added 2 cc., 1 cc. and 0.1 cc. of salmon liquor, about 0.5 cc. was added to the milk and fermentation tubes, a large loopful was added to the deep agar and to the condensation water of the agar slants. A part of the milk was heated to 85° C. for 10 minutes and cooled quickly in cold water. The agar shakes were also cooled quickly by plunging them into cold water as soon as inoculated. A large loopful of material was smeared upon a clean slide, fixed in absolute alcohol for 15 minutes and stained in dilute methylene blue for 30 min. All cultures were incubated at 37° C. for 48 hours and careful examination made. They were placed at room temperature for 5 days and again examined.

As a check upon the methods, the increase in temperature of the contents of the can due to the flaming was noted but it was not influenced. The media was checked against *B. typhosus*; *B. enteritidis*; *B. coli communis*; *B. paratyphosus*, A and B; *B. tetani*; *B. botulinus*; *B. anthracis symptomatici*; and three cultures of *B. Welchii*, all of which grew readily.

As a check on the ability of organisms to grow in the salmon, thirteen samples taken at random were placed in test-tubes and inoculated with the first five

organisms mentioned above. These were incubated at 37° C. for 48 hrs. and examined microscopically for increase in number of organisms. In every case all grew very readily.

The results obtained from the bacteriological investigations were entirely negative. In a very few cases a mold developed on the plates and in one case a spore-forming organism developed. In no case did we find growth in fermentation tubes or deep agar or milk cultures. Stained slides were made from fermentation tubes in many cases, but no organisms were seen. No organisms were ever noted upon slides made directly from the cans.

About 50 g. of this material from 10 different brands were fed to white rats. They ate most of this in two days; after that they were kept for three weeks on ordinary feed, but failed to develop symptoms of any sort.

EXAMINATION FOR TIN

Twenty of the above samples were analyzed for their tin content. These included the best and cheapest brands on the market and were picked at random without any reference to their quality.

Tin determinations were made according to *Journal of Official Association of Agricultural Chemists*, Vol. II, No. 2, page 173.

All tin determinations ran below 50 mg. per kilogram, showing they were well below the tolerance of 300 mg. per kilogram.

CONCLUSIONS

Canned salmon as found on the market in this state is sterile. It does not contain organisms of *B. paratyphoid* type, and does not contain aerobic or anaerobic spore formers. This is to be expected if the packers process their goods according to advertising material which they publish.

In one case they claim to heat the cans to 220° F. for 50 mins., followed by a heating to 240° F. for 60 mins. on a second day. This is necessary to protect the packers against loss of goods after it has been put on the market.

From the fact that this material will readily support the growth of pathogenic and other microorganisms, great care should be exercised in handling it after removal from the can.

KANSAS STATE AGRICULTURAL COLLEGE
MANHATTAN, KANSAS

THE INDUSTRIAL CHEMISTRY OF CHICLE AND CHEWING GUM¹

BY FREDERICK DANFORTH

The official estimate of chicle imported and converted in the United States in 1916 approximated 7,147,000 lbs., equivalent to at least 40,000,000 lbs. of chewing gum. An industry which has assumed these proportions may well be said to exert an influence on our national life. The retail selling price of the finished article is at the rate of \$1.50 per lb., from which some idea of the financial strength of the industry may be obtained.

¹ Presented at the 54th Meeting of the American Chemical Society, Kansas City, April 10 to 14, 1917.

In view of this it has become necessary to establish standard methods for the purchase of the Crude Block Chicle. As it arrives at the port of New York or New Orleans it contains a considerable amount of moisture—usually about 40 per cent. The factors which influence the purchaser may be summarized as follows:

- (1)—The moisture the gum is estimated to contain.
- (2)—The shrinkage when cleaned (dirt and bark).
- (3)—The chewing quality of the clean purified chicle.
- (4)—The color of the crude chicle.

MOISTURE

The amount of moisture contained in crude chicle was until very recently ascertained in the course of factory operations. For example, a 100-lb. lot was chopped up into 1/2-in. crumbs and dried in a hot air chamber. The loss of weight was recorded as moisture. A somewhat better idea of the value of the chicle can be obtained by proximate analysis. Thus one sample of Yucatan chicle when examined in the laboratory showed:

	Per cent		Per cent
Acetone-soluble matter		Sand and foreign matter.....	2.3
(resins).....	40.0	Water.....	35.0
Gutta (and carbohydrates).....	17.4	Mineral matter (ash).....	4.7
Proteins.....	0.6		

Obviously, if this chicle costs \$0.55 per lb., crude, its value is \$0.877 per lb. after drying and cleaning. In other words, 100 lbs. of crude chicle in this case yielded 62.7 lbs. of dried and cleaned chicle.

SAMPLING—In sampling crude chicle after it has arrived at the factory a 1-lb. sample is cut from a block. This is cut up into 1/2-in. crumbs just as rapidly as possible. The crumbs are transferred to a "Lightning Jar" provided with a glass lid and rubber gasket. The jar should be not more than two-thirds full, leaving room for a thorough mixing by shaking the contents, and should be kept in a cool place to prevent caking. The large amount of moisture usually present in crude chicle makes it imperative to handle the sample rapidly. Wet chicle cannot be stored in sealed jars for more than one week as molds grow rapidly, especially if the jars are kept in the dark.

METHOD 1 A weighed portion of crude chicle (about 5 g.) is dried in a well-ventilated air bath for 5 hrs. at a temperature not above 50° C. As a container for the sample, a glass dish 2 or 3 in. in diameter with a ground glass lid is used. If the temperature in the oven rises, fusion will occur and evaporation of the water will be retarded. If the oven is poorly ventilated the drying will take longer. It is complete when two consecutive weighings vary not more than 0.5 per cent.

METHOD 2 The moisture in crude chicle may be determined simultaneously with the determination of resins. During extraction with carbon tetrachloride and water from the sample by extraction. The solvent in the flask is dried at 100° C. and the residue in the flask is dried in a similar manner. The loss of mass, weight subtracted from the weight of the

original sample will represent water. This method has given very satisfactory results in practice.

NOTE—If wet chicle is heated to 105°C . in an oven, a certain amount of moisture is driven off, the chicle fuses and becomes "tacky" and if this product is chewed it will be found to be quite rubbery. At such temperatures the gum undergoes a chemical change as is seen by its solubility in acetone and in alcohol. For these reasons the usual methods of determining water by heating in an air bath at 105°C . are not applied in the analysis of chicle. As soon as an attempt is made to chop up a block and granulate the chicle, the gum commences to lose water so that due consideration must also be given this fact.

VISCOSITY

The valuation of crude chicle by means of a viscosity test has, so far as I know, not been attempted by other investigators. This is probably due to the fact that it is very difficult to prepare a fluid mixture which would not settle out. The results here presented have been obtained by means of over 200 determinations and it is believed that the method is of practical value. The solvents used experimentally for suspending the chicle included xylol, benzol, toluol, turpentine and kerosene. Kerosene (boiling point above 140°C .) was finally chosen, as the loss by evaporation is negligible. Before proceeding with the test, commercial chicle must be dried for 12 hrs. in a vacuum at a temperature not exceeding 70°C .

METHOD—20 g. of the dry chicle are weighed off accurately to tenths of a g. and placed in a wire basket fitted in size for a "Joint Rubber Committee" extraction apparatus.¹ In the flask are placed 75 cc. of kerosene. The wire basket is made of 100-mesh wire gauze so that it retains the gritty and fibrous matter with which commercial chicle is contaminated. The weight of the residue in the basket will give some idea of the percentage of foreign substances in the crude chicle.

The liquid thus obtained by suspending strained chicle in kerosene is poured into a 100 cc. graduated cylinder. Fresh kerosene is now poured into the cylinder so that the total volume will have a concentration of 20 g. of strained chicle in a total of 100 cc. of liquid. After cooling the liquid to 20°C . it is introduced into the small tank of a Stormer viscosimeter.² The lower portion of the capsule of the viscosimeter is removed and filled with shot so that the total weight of this lower portion of the capsule together with the shot is exactly 20 g. As a matter of convenience the records of viscosity may be kept in terms of *Revolutions per minute*. The weight is allowed to fall for a definite number of seconds, taking care that the total length of cord is never unwound. The upper surface of the rotating cylinder in the viscosimeter should be adjusted in such a position as to be on a level with the upper edge of the projecting bracket in the tank which holds the test liquid.

Mr. Charles Kernahan, of this laboratory, who has assisted me in many of these determinations, reports that benzol appears to be a desirable medium for suspending the chicle in the viscosity test. It has the advantage that chicle may be boiled in it without exceeding a temperature of 81°C ., thus precluding decomposition of the gum. The precaution which should be observed in the use of benzol is that the test should be carried out in a room having a temperature not much above 20°C ., as there will otherwise be a considerable loss of solvent by evaporation.

ACETONE-SOLUBLE MATTER

The extraction of rubber and related gums with boiling acetone is carried out principally for the purpose of determining the percentage of "resins" in the material. In fact many analysts use these terms synonymously. The peculiar chewing properties of chicle are due to the presence of these resins so that a determination of their amounts and characters would seem to be of paramount importance to the industry. An idea of the resin content of the principal minor gums may be obtained from the following approximate percentages: Pontianak, 75; chicle, 60; gutta percha, 50; balata, 40; guayule, 20. One of the principal properties of the resin which affects the chewing quality of the gum is its melting point so that this should be determined in most cases.

METHOD—If the acetone extraction is carried out without regard to the moisture content of the chicle, the material is granulated so that it will pass through a wire screen of $1/8$ -in. mesh. Five grams of the material are accurately weighed out and placed in a folded filter fitted for a Soxhlet siphon cup. The apparatus used is the Soxhlet extractor of the Joint Rubber Committee.¹ Acetone having a boiling point not higher than 65°C . is used and the extraction is continued for 5 hours. The acetone in the flask may be evaporated by placing the flask on a hot plate or it may be distilled off and the flask then dried to constant weight in the oven at a temperature not above 105°C . It is finally cooled in a desiccator and weighed. The residue is dried at 85°C . in the oven. The sum of the extract and the residue is now subtracted from the weight of the original sample. The difference is the moisture in the sample. If the acetone solution in the flask is allowed to cool before it is distilled off, it will be noticed that a large part of the resins has separated out in the form of a wax-like incrustation. After all the acetone in the flask is expelled and the temperature reaches 105°C . the residual resins appear amber-colored and quite clear. These resins are brittle at room temperature. The residue of gutta on the filter should be dried at temperatures not above 85°C ., as it otherwise readily carbonizes. This is apparently due to the low "ignition temperature" of this gutta.

In 30 samples of chicle from Mexico, the resin content varied from 59.0 to 63.3 per cent with a grand average of 60.8 per cent based on the dry chicle. Twelve specimens of dried chicle which had an aver-

¹ THIS JOURNAL, 9 (1917), 340.

² Seaton, Probeck and Sawyer, THIS JOURNAL, 9 (1917), 38, have presented much interesting data on the viscosity of varnishes and the limitations of the various viscosimeters.

age resin content of 61.8 per cent were tested for viscosity according to the method previously described. The results showed an average of 276 revolutions per minute. Twelve other specimens which were examined showed an average resin content of 60.0 per cent and an average of 284 revolutions per minute. The rule then would seem to be that the R. P. M. is inversely proportional to the resin content, or rather that the viscosity is directly proportional to the resin content. This was in fact found to be the case for the particular conditions under which these determinations were carried out.

PROTEINS—The peculiar character of vegetable proteins, their complex chemical constitution and the fact that they do not crystallize all have combined to retard the investigation of this constituent. Spence has given considerable attention to these bodies so far as they occur in the rubbers prepared from *Hevea*, *Funtumia* and *Ficus*.

In a recent paper Spence and Kratz¹ have proposed a method for the determination of proteins in washed and dried rubber and it is planned by the present author to adapt this method, if possible, to the estimation of proteins in chicle.²

CARBOHYDRATES—Previous investigators have suggested that the sugars contained in chicle may be related to hexa-hydroxy-hexa-methylene. The monomethyl derivative of this sugar has a melting point of 192° C. and is found in the latex of *Hevea brasiliensis*. Plantation crepe *Hevea* rubber contains from 2.0 to 3.0 per cent of this substance. An investigation on the sugar content of various chicles is now in progress at this laboratory. A paper on this subject was published by Pickles and Whitfield³ as early as 1911.

MINERAL MATTER

This determination is carried out with a sample of one gram, and in any case not more than two grams of dry chicle. An asbestos shield is used and a hole inserted so that the crucible bottom is exposed to the flame. At first a low flame is used so that the organic matter can volatilize without catching fire. After all the carbon has been burnt off, the crucible is dried and weighed in the usual manner. Of 25 specimens examined, the lowest value obtained was 3.9 per cent and the highest was 5.95 per cent of ash. The grand average was 4.53 per cent of ash.

It will be noted that this figure is much higher than that usually given for the ash content of washed and dried rubber. The highest values recorded for rubber are 1.0 per cent for *Funtumia*.

FERMENTATION OF CRUDE CHICLE

Mention should be made of the influence of fungi on crude chicle. These low forms of plant life do not attack the gum if it is kept in dry air, but if a small amount of moisture is present, the molds begin to flourish. Their nourishment is derived from the proteins, resins, and sugar which the gum contains. This results in a discoloration of the chicle, turning it

pink or light buff in color, but it is not materially altered thereby. On the other hand, certain species of *Actinomyces* which occur in garden earth and canals are capable of assimilating the chicle-hydrocarbon with the result that its properties are so modified as to alter its chewing quality very decidedly. The principal varieties thus far recognized are *A. elastica* and *A. fustus*. The fermentation of chicle is also induced by the presence of uncoagulated milk in the pores of the block. In fact a piece of crude wet chicle, if chewed, will be found to taste quite acid.

INDUSTRIAL RESEARCH

The methods of the chewing gum industry have up to the present time been based largely on experience, but there is a distinct tendency toward a scientific study of the technical problems which arise. Some of these problems have already been successfully attacked and solved while others are still in a state of investigation. A review of these will be of value to those interested in these gums:

- 1—How can brittleness in the finished chewing gum be prevented?
- 2—How can the absorption of moisture by the finished gum be prevented?
- 3—What properties are most desired in a substitute for chicle?
- 4—Which is the best method for introducing flavors into a batch of gum?
- 5—What influence has heat on the chicle dough in the kettle?
- 6—What influence has the duration of the "cooking" on the dough in the kettle?
- 7—What influence have substitutes on the "keeping" qualities of the finished gum?
- 8—What influence have temperature and moisture on the finished gum during storage?
- 9—What are the advantages of drying or moistening the air in chewing gum factories?
- 10—What relation has the resin content to the chewing qualities of the chicle?
- 11—How can crude chicles be averaged in order to secure a finished gum of uniform characteristics?
- 12—What influence has the coagulation method on the quality of the crude chicle produced by the *Sapoteros*?
- 13—How can "stiff" chicles be softened and how can "soft" chicles be stiffened?
- 14—What influence have the several constituents of a chewing gum compound on the chewing quality of the finished gum?
- 15—How can the dirt and the bark be removed from crude chicle without destroying the desirable qualities of the gum?
- 16—How can low grade chicle be improved?
- 17—What relation has the viscosity of chicle to the chewing properties of the gum?
- 18—How can rubbers and related gums be converted into plastic gums suited for chewing?
- 19—Can chicle be strained while in a molten condition, without altering the chewing properties of the finished gum?
- 20—Is the protein content of chicle a determinant of its quality?

APPENDIX

The Custom House statistics of the United States show that the gross imports of chicle and Sapo from 1911 to 1916 were as follows:

Year	U. S. Customs	U. S. Customs
1911	1,000,000	1,000,000
1912	1,000,000	1,000,000
1913	1,000,000	1,000,000
1914	1,000,000	1,000,000
1915	1,000,000	1,000,000
1916	1,000,000	1,000,000

¹ Pickles and Kratz, *Anal. Chem.*, **1914**, 362.

² Pickles and Whitfield, *Anal. Chem.*, **1911**, 171.

³ Pickles and Whitfield, *Proc. Chem. Soc.*, **27**, 1911, 33.

In order to obtain a more correct idea of the importations it is suggested that the figures for these two gums be added and classed together. The present Tariff Act went into effect October 3, 1913, so that it was natural that large quantities of chicle should be imported before that time. The new act provided for a duty of 15 c. per pound on crude chicle and 20 c. per pound on refined chicle while balata was admitted free. This no doubt resulted in the importation of some chicle under the name "Balata" and caused the drop in the chicle imports from 1914 to the year 1915.

At this point it is also interesting to note that exports of finished chewing gum to foreign countries have risen from \$479,000 in 1914 to \$574,400 in 1916. This has been shipped principally to England and Australia. At a valuation of \$0.80 per lb. this would represent approximately 718,000 lbs. of chewing gum or 170,000 lbs. of dry chicle. The amount of chicle imported, manufactured and consumed in the United States in 1916 was approximately 7,031,000 lbs., equal to over 28,124,000 lbs. of chewing gum. This represents a national consumption of over 844 million packages per annum.

THE RUBBER TRADE LABORATORY
325 ACADEMY STREET
NEWARK, NEW JERSEY

REVERSION OF ACID PHOSPHATE

By CARLTON C. JAMES

Received March 3, 1917

There seems to be an inclination of late among fertilizer and State control chemists to do more investigating of phosphates, their properties, and their effect upon soils and growing crops. Where State laws call for water-soluble phosphoric acid, careful investigation and attention is necessary, particularly in order that the different brands may not fall below guarantee. A recent article in *THIS JOURNAL* by Mr. E. W. Magruder¹ recalled some work which was done by the writer in 1910, upon the reversion of acid phosphate by lime, a matter which has claimed the attention of chemists in the Southeastern states for the last two or three years.

After having his attention called to a fertilizer from San Francisco, which had evidently undergone reversion during transit to the Hawaiian Islands, the writer undertook several experiments with different materials to find the effect these had upon the acid phosphate of lime.

To 475 g. of acid phosphate in three separate bottles were added 25 g. lime (CaO), 25 g. unground coral sand and 25 g. unground brown guano, respectively; that is, in each experiment there was added 5 per cent of the reverting agent to the superphosphate, which we may consider a maximum amount to use in practice. It should be explained that the unground coral sand is carbonate of lime of 95 to 98 per cent purity, and coarsely granular. The brown guano is a low-grade sandy phosphate from Laysan Island, formed by the action of bird droppings upon coral sand with which it is intimately mixed. These mixtures were allowed to stand 20 days, analyses being made of the water-soluble phosphoric acid from time to time as other work permitted. The following table shows the water-soluble phosphoric acid found in the mixtures at intervals after mixing.

¹ *THIS JOURNAL*, 9 (1917), 155.

TABLE I. PER CENT WATER SOLUBLE PHOSPHORIC ACID IN MIXTURES OF ACID PHOSPHATE WITH

5 Per cent.....	Lime (CaO)	Coral Sand	Brown Guano
On mixing.....	21.37	21.37	21.37
After 2 days.....	20.83	21.08	21.24
After 5 days.....	20.18	20.75	21.16
After 10 days.....	19.69	20.50	21.00
After 20 days.....	19.12	20.81	21.00

This table shows that superphosphate in which there is 5 per cent coral sand reverts 0.62 per cent in 5 days or 0.86 per cent in 20 days. With brown guano the reversion is not as great, while with lime it is 3.75 times as much. If then in a fertilizer guaranteed to contain 10 per cent of phosphoric acid water-soluble, we should have 50 per cent acid phosphate of lime and 5 per cent calcium carbonate (coral sand), we should expect to find after 5 days that instead of 10 per cent water-soluble phosphoric acid it would contain only 10—(0.62 × 0.50) = 9.69 per cent, the difference being caused by coral sand alone. In order that this fertilizer might show a 10 per cent water-soluble phosphoric acid content after 5 days, 51.5 per cent acid phosphate would have to be used originally. This example gives the effect of but one reverting agent, but it is sufficient to show that quite a material allowance has to be made in certain fertilizers to cover reversion during transit.

THE PACIFIC GUANO AND FERTILIZER COMPANY
HONOLULU, HAWAII

A RAPID METHOD FOR THE DETERMINATION OF WATER-SOLUBLE ARSENIC IN LEAD ARSENATE

By H. A. SCHOLZ AND P. J. WALDSTEIN

Received March 5, 1917

The method for the determination of water-soluble arsenic in commercial lead arsenate described by Gray and Christie¹ is very similar to the method used by the writers for factory control during the past three years.

The procedure follows: Weigh 0.5 g. of the dried and pulverized sample, or 1 g. of paste, into a 250-cc. volumetric flask. Add 200 cc. of recently boiled, distilled water and boil vigorously for 3 to 5 min. Allow to stand 10 or 15 min., cool, make to volume and filter through a dry paper. Ordinary, quick-filtering qualitative paper is used and there is rarely any difficulty in obtaining a clear filtrate. Measure 200 cc. into a 500-cc. Erlenmeyer flask, add a few crystals of potassium iodide and 7 cc. concentrated sulfuric acid, and boil down to about 50 cc. Dilute with cold water, make alkaline to methyl orange with sodium hydroxide, acidify with dilute sulfuric acid, and add an excess of sodium bicarbonate. Titrate with $N/20$ iodine solution.

This method was checked many times on lead arsenates of different compositions against the A. O. A. C. method² (24 hrs. digestion at 32° C.), and a few times against the 10-day method.³ The results always either agreed or came higher by the boiling method. Table I gives a few typical results. The arsenates of lead used included the products of several other manufacturers and represent practically every known commercial method of manufacture.

¹ *THIS JOURNAL*, 8 (1916), 1109.

² *J. of A. O. A. C.*, 1913, Nos. 1 and 2.

³ Bureau of Chemistry, *Bull.* 107, Revised, p. 240.

TABLE I—WATER-SOLUBLE ARSENIC CALCULATED AS PER CENT As_2O_3 ON THE DRY BASIS

No.	A. O. A. C. Method 24 hrs. at 32° C.	Devos & Raynolds Boiling Method	No.	A. O. A. C. Method 24 hrs. at 32° C.	Devos & Raynolds Boiling Method
1.....	4.52	4.62	6.....	0.56	0.68
2.....	0.47	0.47	7.....	0.23	0.30
3.....	trace	0.06	8.....	0.18	0.21
4.....	trace	0.46	9.....	0.18	0.33
5.....	0.22	0.23	10.....	0.44	0.46

There is no provision made for the removal of lead, as we have never found water-soluble lead in more than traces in any sample of lead arsenate. Furthermore, as has been pointed out by Gray and Christie, there is great danger of volatilization of the arsenic by evaporating the solution to sulfuric acid fumes, as the results given in Table II will show. The extractions were made by boiling as in the method given above.

TABLE II—WATER-SOLUBLE ARSENIC CALCULATED AS As_2O_3 ON THE DRY BASIS

	No. 1	No. 2
Evaporated to SO_3 fumes.....	2.40	1.61
Reduced and Titrated without Evaporation.....	3.56	2.50

The water-soluble arsenic in commercial lead arsenate very often is largely in the arsenious form. Commercial sodium arsenate and arsenic acid often contain small amounts of unoxidized arsenic trioxide, and this precipitates with the lead arsenate in a form which is very difficult to wash out with cold water, but which dissolves readily in hot water. This may be the reason why the boiling methods of Gray and Christie, and of the writers, and the hot water method of Robinson and Tartar¹ give higher results than the cold and 32° C. methods of the A. O. A. C.

By the method given a determination of water-soluble arsenic may be made in less than an hour, which is a very important consideration for factory control work.

The same method of extraction may be used for the determination of other water-soluble impurities.

DEVOS AND RAYNOLDS COMPANY
1416 WEST LAKE STREET, CHICAGO

¹ THIS JOURNAL, 7, 1915, 499.

LABORATORY AND PLANT

SAFEGUARDING THE EYES OF INDUSTRIAL WORKERS¹

The Seaman Gold Medal, gift of Dr. Louis Livingston Seaman, Trustee, is annually awarded by The American Museum of Safety for progress and achievement in the promotion of hygiene and the mitigation of occupational disease. This year the distinction of the Seaman Medal has been conferred upon the Julius King Optical Company, of New York, for scientific research and practical achievement in overcoming the harmful effects of ultra-violet and infra-red rays of light in connection with arc-welding and other industrial processes at very high temperatures.

For a number of years the necessity of protecting the eyes of workers against chips of steel, splashes of metal and flying particles of emery, concrete and other materials, has been recognized, and the wearing of an approved type of safety goggles made compulsory. A far more insidious and hazardous danger to eyesight is caused by certain invisible rays of light, such as the ultra-violet and infra-red rays, which are present in injurious quantities in the manufacture and working of iron and steel. These rays may cause electric ophthalmia.

Any light source over 2000° Fahrenheit is a distinct menace and when a temperature of 6400° is reached, such as is encountered in electric carbon arc-welding, the volume of ultra-violet radiation is so great as to impair vision permanently. On account of its destruction of animal tissue, these rays must positively be guarded against. Being invisible, their presence is detected by the operator only after harm has been done.

Until an investigation was made about three years ago, practically 99 per cent of all colored glass in goggles for industrial use was incorrect, and without a doubt a large number of blind men, or those unfortunately

who are afflicted with cataract, would have their full sight to-day if they had been provided with scientifically correct colored glass.

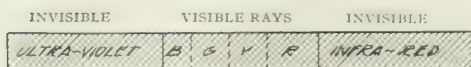
One of the first forms of eye protection from glare was the wearing of blue glasses in the manufacture of steel, particularly in the open-hearth process. Glare is made up of non-injurious rays of the spectrum, namely green, yellow, orange, and red rays. As a matter of fact, blue is one of the worst colors which could possibly be selected for this process, as it allows ultra-violet, violet, blue and also infra-red rays to enter the eyes freely, cutting out only that part of the light which is essential to vision, but affording no protection from dangerous light.

The higher the temperature, the more rich it is in ultra-violet rays. At the temperature encountered in oxy-acetylene welding and cutting, which is about 4350° Fahrenheit, grave danger exists and the glasses formerly supplied by the oxy-acetylene companies, who manufactured and furnished the outfits, were without any scientific value whatever. They were using blue glass, as described, or else smoked lenses, which allowed a large proportion of injurious rays to enter the eye. Where a wrong color is used a much darker shade is necessary than if a correct color is prescribed.

All colors have been analyzed and tabulated, by spectral photography, so the relative value of each is known.

A temperature of 2000° requires a lens but slightly tinted, while a temperature of 6400° requires a lens so dark that one can barely see the sun through it. The Julius King Optical Company has plotted all colors on a photometric scale, the standard adopted being a white card illuminated by the sun, which may be looked at indefinitely without symptoms. A temperature of 2000° at 1000 ft. seen through a slightly tinted glass has the same effect on the eye as if the

¹ Abstracted and adapted from the May, 1917, issue of "Safety," pp. 118 and supplement, published by the American Museum of Safety, 14 to 18 West 21st Street, New York City.



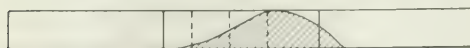
Harmful Harmless in Moderate Amounts Harmful

[B, G, Y, R areas printed Blue, Green, Yellow and Red in Original.]



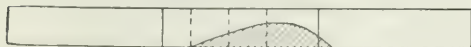
AKOPOS Glass

Recommended for Temperatures around 2000° F. such as Gas Heating Furnaces, etc.



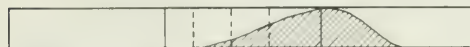
Light SANI-WELD Glass

Recommended for Temperatures around 3500° F. Oxy-Acetylene Cutting, Pouring Steel, etc.



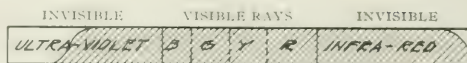
Dark SANI-WELD Glass

Recommended for Temperatures around 4300° F. Heavy Oxy-Acetylene Welding, Electric Furnaces, etc.



ARK WELD Glass

For Temperatures around 6400° F. in Combination with AKOPOS or SANI-WELD (to eliminate infra-red rays). Correct for Iron or Carbon Arc Welding and for Electric Furnaces: in these Processes Face-burn will Result unless a Helmet is Used.



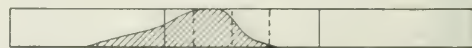
Clear "White" Glass

Should Not be Used where Temperature is over 1500° F.



Red Glass—Harmful

Should Never be Used as it Transmits Infra-Red and is Very Fatiguing to the Eye.



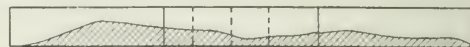
Green Glass—Incorrect

Should Not be Used as it Distorts Colors and is of Low Optical Value.



Cobalt-Blue Glass—Exceedingly Dangerous

Transmits Invisible Rays as freely as Clear Glass. Should be Abolished except for Open Hearth Temperature Judging where it is not Practical to Teach Melters a New Color.



Smoked Glass—Dangerous

Reduces Visible but Transmits Invisible Rays; Although sometimes Furnished with Oxy-Acetylene Outfits, it is about the Worst that could be Used for the Process.

wearer had nothing over the eyes, and was looking at a white cloud. The same photometric standard applies in looking at a temperature of 6400° through the darkest glass, the effect on the eye being the same.

These new values of lenses were determined by flowing colors over photographic plates. Spectral photographs were taken through this medium, the efficient ones being tabulated and reproduced in pot glass.

All of this research was conducted in what was practically an unknown field and it will be difficult to find any other line of work where more good has been accomplished in the prevention of ocular diseases, disturbances and actual loss of sight than has been accomplished by this patient research conducted with considerable expense of time, money and material.

The process of arc-welding requires protection not only for the eyes, but for the entire face and neck. Welders have experienced such intense eyestrain and face burns after a few minutes' work, that all sorts of crude shields have been devised. The majority of these, however, were heavy and cumbersome, being made of metal and leather; and all were inefficient and uncomfortable. Frequently, the workmen themselves selected glass to reduce the light intensity, but they were, of course, wholly ignorant of the fact that the character of the light caused more damage than its brilliancy.

Since metal is a conductor of heat and electricity, the Julius King Optical Company have constructed a helmet of fiber, finished within and without in dead black so as to minimize the danger from reflected light. The top of the head is protected by a fireproof cap, to

which the helmet is pivoted so that it may be turned back out of the range of vision when it becomes necessary for the wearer to inspect his work or to move about. The lenses mounted in this helmet are a combination of "Ark-weld" and "Akopos" glass, the former to reduce the intensity and the latter to eliminate the injurious rays of the arc light.

As the lenses are of the proper scientific color, no danger exists from electric ophthalmia or other diseased condition of the retina or conjunctiva.

The accompanying drawing was adapted from the special colored supplement accompanying the May issue of *Safety*, and furnished through the cooperation of the Julius King Optical Company. It indicates quite clearly the transmission of the invisible dangerous rays of light through the ordinary colored glass, and their absorption by the "Akopos," "Sani-weld" and "Ark-weld" glasses. The kinds and proportions of the various parts of the spectrum transmitted are indicated by the shaded areas.

RECOVERY OF MOLYBDENUM RESIDUES

By VICTOR LIEBER AND M. P. SCHULTZ

Received June 6, 1917

A number of methods for the recovery of molybdc acid residues have been suggested in the past few years. The scheme of Armstrong¹ consists in the precipitation of molybdc acid from the residues, while the procedures of Brown² and of Prescott³ have in addition the removal of the phosphates by means

¹ THIS JOURNAL, 7 (1915), 764

² *Ibid.*, 7 (1915), 213.

³ *The Analyst*, 40 (1915), 390.

of magnesium salts. Both of these principles we have found in our hands to be efficient. We wish, however, to present an additional method which is based on a somewhat different principle, and in certain kinds of molybdate residues may be desirable. The method consists in the precipitation of molybdenum sulfide from a solution slightly acid with nitric acid by means of hydrogen sulfide or the formation of a sulfomolybdate solution by adding hydrogen sulfide to the alkaline solution of the "yellow precipitate" and subsequently adding hydrochloric acid to precipitate the molybdenum sulfide. Molybdenum sulfide when ignited gives MoO_3 , which is in condition to be used again.

In applying the method to waste molybdate liquors which are usually quite strongly acid with nitric acid, the solutions should be strongly diluted or the excess of free acid should be in large part neutralized with sodium hydroxide, so that the limits of acidity should be between 0.1 and 0.4 per cent. Hydrogen sulfide gas is then passed through the solution. The sulfide settles more rapidly, however, if the solution is previously heated. The supernatant liquid can then be siphoned off and the sulfide washed with water, after which it can be filtered, dried and roasted.

When much iron is present in the liquors the sulfide should be washed with water containing hydrochloric acid to remove the iron completely.

The "yellow precipitate" is handled by dissolving in sufficient sodium hydroxide to make a solution just slightly alkaline to phenolphthalein. Should the precipitate be contaminated by iron, the ferric hydroxide produced by the addition of the alkali should be filtered off. The filtrate is then diluted and hydrogen sulfide conducted through the solution to saturation. Dilute hydrochloric acid is now added until an excess is present, when molybdenum sulfide separates. The sulfide of molybdenum can be filtered, washed with hot water containing dilute hydrochloric acid, dried and roasted in the air to molybdenum trioxide.

CHEMICAL LABORATORY
UNIVERSITY OF WISCONSIN, MADISON

NOTE: ORGANIC CHEMICAL REAGENTS FOR SCIENTIFIC AND TECHNICAL LABORATORIES

By ROGER ADAMS

Received June 1, 1917

During the last three summers it has been the custom at the University of Illinois to manufacture on a semi-commercial scale (1- to 2-lb. lots) certain organic chemicals, which had hitherto not been produced in this country and which were necessary for the researches in organic chemistry. Each year the number manufactured has been increased till at present satisfactory products have been developed for over forty of the common organic chemicals used primarily in theoretical organic research, but to some extent in technical laboratories. Thus it has been possible to supply the Illinois laboratories with many of the materials formerly imported from Germany.

The majority of these substances are not purchasable in the open market at the present time, so it was thought it might be a great aid to other laboratories if they had the benefit of the experiences at Illinois and the opportunity of purchasing such chemicals as might be desired at a price slightly above cost. In nearly every case the substances produced have been compared with Kahlbaum's products and in every instance the products have been found as pure, or purer.

Below is given a list of chemicals which have been manufactured, many of which are on hand at the present time. In continuing the manufacture of chemicals this summer, only those chemicals mentioned below, which are out of stock, will be made, unless there may be an outside demand for others. Processes for at least ten substances not included in the list will be studied also in the next few months.

Acetamide	Ethyl benzoate
Acetoacetic ester (ethyl)	Ethylene bromide
Acetonitrile	Ethyl oxalate
Acetophenone	Glycecol
Anisole	Hippuric acid
Anil bromide (iso)	Magnesium (especially prepared for use in the Grignard reagent)
Benamide	Malonic ester (ethyl)
Benzene sulfonyl chloride	Malonic ester (methyl)
Benzonitrile	Mesitylene
Benzoyl acetone	Methyl oxalate
Benzoyl chloride	Methylene iodide
Benzoyl cyanide	Nitrobenzene acid
Benzyl alcohol	Nitromethane
Benzyl bromide	Oxalyl chloride
Benzyl cyanide	Phenyl acetic acid
Bromoacetyl bromide	Phenyl acetic ester (ethyl)
Bromobenzene	Phenyl alanine
Bromonaphthalene (alpha)	Trimethylene bromide
Dibromo (p) benzene	Trimethylene chlorhydrin
Dichloroacetic acid	Trimethylene cyanide
Dimethyl glyoxime	Trimethylene glycol
Diphenylmethane	

If there is a reasonable demand for any particular chemical, which has not been prepared here and which cannot be purchased from any commercial concern, the laboratories at Illinois will be glad to undertake such manufacturing at their expense and sell the product at a price slightly above the cost calculated from the past results.

The Division of Organic Chemistry at the University of Illinois has organized itself for this work, the preparation being carried out for the most part by the junior members of the staff and other graduate students in organic chemistry. These men receive from 25 to 35 cents per hour for their services. In this way it has been possible to retain many men who might earn much larger salaries outside, but who are willing to stay for this particular kind of experience. A number of other laboratories have offered to assist in this work, if necessary, so as to aid scientific and technical investigation as much as possible. Prof. P. A. Bond, of Cedar Falls, Iowa, has kindly offered to prepare sodium acrylate for the benefit of any who might need this substance. In addition to the above work, in connection with Prof. M. T. Rogers, information concerning the organic chemical reagents purchasable in this country is being collected. quotations of prices on any of the substances given or any information which it has been possible to obtain in regard to organic chemicals will gladly be given on request.

UNIVERSITY OF ILLINOIS
URBANA, ILLINOIS

AN EVAPORATING BATH OF SEA SAND HEATED BY STEAM

By P. P. PETERSON

Received February 24, 1917

The apparatus herewith described has been found so convenient and useful in the laboratories of the Department of Soils at the University of Idaho that it is thought worth while to tell other chemists about it. It is made of coils of pipe in a bath of sea sand. The heat is supplied by superheated steam, the flow of which is controlled by a Sarco steam trap.

The tray (A, Fig. I) is made of No. 24 galvanized iron. Of course, it may be any size. Ours is 2 ft. square and 4 in. deep. B is a coil of $1\frac{1}{2}$ -in. iron pipe well fitted so that it can carry a pressure of 100 to 150 lbs. per sq. in. At the end of this pipe is a Sarco steam trap, C, which allows the escape of steam until a certain temperature is reached when it closes automatically. The coil B is covered with sifted sea sand of about the size that will pass a 20-mesh sieve and washed free from small adhering particles.

It is found that by the use of this bath a much more rapid evaporation can be obtained than with a hot water or steam bath. Aside from this the escape of large amounts of steam into the room and the noise often accompanying the same is avoided. To obtain the best results the sand should cover the coils to the depth of $1\frac{1}{2}$ to 2 in. so that the evaporating dish or casserole may be pressed down into it. When the hot sand is allowed to come up on the side of the evaporating dish the evaporation is greatly accelerated. A temperature of 140° C. can be obtained in the sand be-

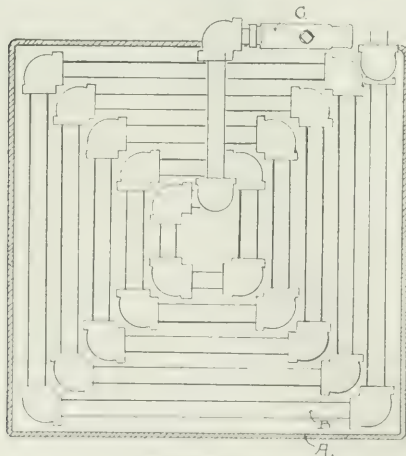


FIG. I—TOP VIEW

tween the pipes. Over the hot plate, whether heated by a gas flame or electricity, this bath has the advantage that there is almost no danger at all of spattering. With the hot plate it is almost impossible to avoid this trouble.

The objection that contamination from the sand is likely to take place may be raised and, of course, is to be taken into account. In this laboratory,

however, it has been found that to avoid this contamination requires no more care than is necessary with the old style boiling water bath or the steam

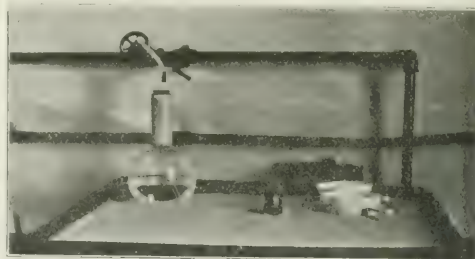


FIG. II—THE BATH COMPLETE

bath. Thorough washing of the sand to remove all small particles makes the avoidance of contamination rather easy.

Fig. II is a cut of the completed bath.

SOIL FERTILITY LABORATORY
UNIVERSITY OF IDAHO, MOSCOW

AN IMPROVED FORM OF A FUMELESS DIGESTION APPARATUS

By J. S. MCHARGUE

Received February 23, 1917

In a recent investigation involving a relatively large number of nitrogen determinations, it became necessary, on account of the lack of flue facilities, to make use of a Sy Fumeless Nitrogen Digestion Apparatus. During the time the nitrogen digestions were being made, a number of objectionable features to this particular apparatus were experienced. The writer has, therefore, enlarged and modified the Sy apparatus in such an advantageous manner as to consider the changes so made worthy of brief notice in the chemical literature.

The chief points in which the apparatus shown in the accompanying photograph differs from the Sy apparatus and the advantages gained thereby are as follows:

1—Increased capacity. Since most ready-made nitrogen distillation apparatus provides for 6 distillations to be carried on at the same time, there is a saving of time by having an equal number of digestions provided for.

2—The lead pipe and the absorption bottle is a more permanent and satisfactory arrangement for controlling and disposing of the acid fumes during digestion. Practically all the fumes are absorbed in the bottle which can be easily emptied and the acid recovered by evaporation, thereby effecting a saving of acid and the corrosive action on the drain pipes as well. The pump used in drawing the fumes into the absorption bottle is the ordinary type in general use in laboratories.

3—The shelf E holds 6 beakers which are placed beneath the lower end of the condensing bulbs, and catch the acid that drains from the condensing tubes after the digestion flasks are removed. After the digestion is stopped and the flasks become cool, a

small amount of concentrated acid adheres to the inside of the condensing bulbs, which, after the removal of the digestion flask, absorbs moisture from

draws the fumes through the water in the wash bottle C, where they are absorbed.

The adjustable shelf E holds 6 small beakers, which are placed so as to catch the few drops of acid that always drain from the lower end of the condensing tubes after the digestion flasks are removed.

F indicates the rings which support the digestion flasks. The rings are attached to a $\frac{1}{2}$ -in. iron rod by means of clamps. The iron rod is attached to the vertical rod of the stand by an adjustable screw clamp.

G is a $\frac{7}{8}$ -in. gas pipe carrying the 6 burners placed 5 in. apart and is attached to the iron stand at the base by means of a screw clamp.

Although the above apparatus has been in use but a short time, it has worked so well as to leave but little to be desired in the way of a fumeless digestion apparatus.

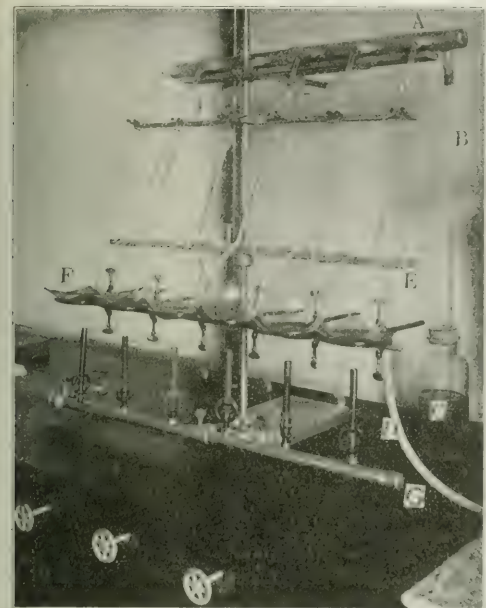
DEPARTMENT OF CHEMICAL RESEARCH
AGRICULTURAL EXPERIMENT STATION
LEXINGTON, KENTUCKY

A NOTE ON AN AUTOMATIC SUCTION ATTACHMENT FOR AN ORDINARY PIPETTE

By J. F. SCHROEDER

Received March 7, 1917

In analytical laboratories it is often necessary to measure a number of aliquot portions of a solution or equal portions of different solutions with a pipette. This process becomes tiresome, especially when the portions to be measured are large. The laboriousness of the operation can be done away with to a large extent by attaching to the pipette an ordinary three-



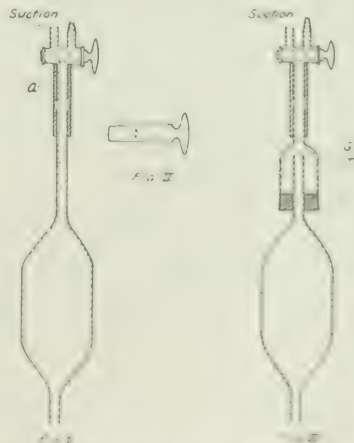
the atmosphere and continues to drip until the acid becomes saturated with moisture.

It is advisable to wash out the condensing bulbs previous to starting a new set of digestions as the acid in the bulbs may in some cases absorb enough ammonia to affect the nitrogen estimation.

DESCRIPTION OF THE APPARATUS

A is a lead pipe $1\frac{1}{2}$ in. in diameter and about 28 in. long. It rests upon and is attached to a board, which is also attached to an adjustable clamp that can be moved back and forth on the iron rod that supports the lead pipe. The iron rod is also adjustable on the vertical rod of the iron stand and is easily lowered or raised to accommodate either long or short neck flasks. The lead pipe is sealed at each end and has 7 lead tubes 1 in. long and $\frac{1}{8}$ in. in outside diameter sealed into the pipe for connections. The 6 tubes on the side of the pipe are placed 5 in. apart and are connected with the upper end of the condensing bulbs by means of a short piece of rubber tubing. The seventh tube, which is placed near the end and at right angles to the 6 tubes on the side, connects, by means of rubber tubing, to the glass tube B, which extends through the rubber stopper to near the bottom of the wash bottle C.

The rubber tube D is attached to one end of a glass tube bent at right angles, and extending through the rubber stopper in wash bottle C. The other end of the rubber tube is attached to a suction pump which



way stopcock, as shown in the diagram, and using a vacuum to draw up the solution desired and holding it up. The tube of the suction connection with the other two leads (in Fig. 1) is connected to the pipette by means of a short piece of heavy-walled rubber tubing. The glass tube (see right) is connected to the other leads (Fig. 1) is connected by means of ordinary rubber tubing of sufficient length to give freedom of movement, as the vacuum, while the third lead

is left open to the atmosphere. The suction can readily be adjusted by placing a screw clamp on the rubber tubing.

To aid the operator in drawing the solution exactly to the graduation mark on the pipette a niche is filed on the surface of the stopcock on the edges of the hole (Fig. II) so the suction may be closed off gradually when the meniscus nears the graduation mark. By this means the adjustment may be made more readily than by the ordinary manipulation by hand.

By the arrangement shown in Fig. III the volume of solution is adjusted automatically. The stem of the pipette is broken off at the graduation mark G and a Gooch crucible filter tube, T, is attached by means of a rubber stopper as shown in the diagram. The manipulation is evident from the illustration.

The advantages of this arrangement are:

- 1—A large number of solutions can be measured in a minimum length of time.
- 2—The measurements can be made without tiring the analyst.
- 3—The meniscus can be observed from a point at right angles to the position of the pipette
- 4—The solution is held automatically without loss until ready to be delivered.
- 5—The danger of drawing poisonous liquids, acids or alkalis into the mouth is eliminated.
- 6—The arrangement can be easily made and attached to any ordinary pipette.

U. S. DEPARTMENT OF AGRICULTURE
BUREAU OF SOILS, WASHINGTON, D. C.

ADDRESSES

POTASH AND A WORLD EMERGENCY¹

By W. C. EMMETT

Without a doubt we are now passing through an epoch-making period in the world's history—epoch-making in national politics, in social changes, in economic conditions and in industrial revolutions. Things are done under the pressure of stern necessity that would have been deemed impossible by the average man five or ten years ago. Obstacles in the way of progress, either constructive or destructive, are swept aside by master hands, tremendous organizations or by embattled nations, and we cease to wonder at things that would have held the world's attention just the other day.

But even with all this one can observe some things that are not subject to increased production, even though they are in strong demand, for the simple reason that nature has not placed stores of the raw materials at our disposal in many places. Take platinum as an example. Russia is practically the only producer of this metal, and since the outbreak of the World War the price has soared. The *Engineering and Mining Journal* of April 7, 1917, quotes platinum at \$102.50 per oz. In spite of this demand the quantities of platinum available have not increased, even though strenuous efforts are made in all parts of the world to locate new sources.

Similarly, potassium salts have become very scarce and prices obtained reflect the market condition. It was deemed bad enough some six or seven years ago when the Kali Syndikat, under control of the German government, arbitrarily advanced prices somewhat, but it is safe to say no one thought it within the realm of possibility for such new high prices to be multiplied by ten, twelve or fifteen, as has actually occurred during the past months.

Why are these things so? Cannot substitutes for potassium compounds be found? Cannot new sources of potash be discovered? Is it not possible to enlarge the output from our known sources?

Answering these questions is not difficult if we consider the uses for potassium salts, the place from which they have come and present international conditions.

Primarily potash salts are valuable for fertilizers. About seventy-five years ago Justus von Liebig and his co-workers pointed out the necessity of restoring to the soil the materials removed from it in the form of crops. One economist states it crudely thus: "For every fourteen tons of fodder carried off from the soil there are carried away two casks of

potash, one of soda, a carboy of vitriol, a large demijohn of phosphoric acid, and other essential ingredients." In our recently settled lands we are inclined to ignore this fact, and simply take off crop after crop without using fertilizers. Our farmers in older communities, both here and abroad, have learned the folly of robbing their soil, and provide fertilizers to replace the inorganic substances removed.

"In the many-sided technical and industrial life of to-day there are but few enterprises that can dispense with the products of the potash industry. In a number of ways it is employed, as for example in medicine, photography, painting, dyeing, laundry work, bleaching, spinning works, soap manufacture, refrigeration, preservatives, electrotechnics, fireworks, explosives, matches, paper, glass, aniline colors, metallurgy, etc. Its use in agriculture is especially important. In 1909, the 6,900,000 metric tons of potash salts produced contained 675,330 metric tons of potash. This was used as follows:

	Metric Tons	Per cent
Agriculture.....	590,027	87.37
Industries.....	85,304	12.63

In the same year Germany used 53,281 metric tons in its industries and only two other countries used more than 5,000 tons in a similar way, viz., the United States and France. In its agriculture Germany itself used more than one-half of the total potash employed for this purpose."

The fact that plants take up potash from the soil has been known for centuries. Wood ashes were called "potashes" and used for the preparation of soap and as a raw material for manufacture of various potassium compounds. One of the most highly prized potassium compounds prepared from wood ashes was saltpeter or niter, used in gunpowder, as a preservative, etc. Prior to the Napoleonic Wars potash was used for many purposes where soda is now employed, because the former was found in wood ashes, and the latter could be gotten only with difficulty. Then came Le Blanc's process for making sodium carbonate from salt, with hydrochloric acid as a by-product, and the demand for potash fell off. Glass and soap are now made from soda, rather than from potash, unless for special reasons. But sodium compounds cannot replace potash as a plant food substance.

A shortage of potash was felt in the two decades 1840 to 1860, following the acceptance of Liebig's doctrines on restoring soil fertility. Saline lakes, springs and wells were tried as sources of potash, but with poor results.

At Stassfurt, in northwestern Germany, a salt industry has been carried on for centuries. In order to increase the yields from this source, in 1837 the Prussian government undertook

¹ Presented at the regular monthly meeting of the Utah Society of Engineers and Scientists, Salt Lake City, April 18, 1917.

deep boring operations for rock salt, which was discovered in 1843. Between 1851 and 1856 the first shafts were sunk. Great was the disappointment because "bitter salts," and not rock salt, were found. It was not long, however, until the true value of these "waste salts" as a source of potash was recognized, and in 1861 the first potassium chloride factory at Stassfurt was erected. From that time to the present Stassfurt deposits have supplied practically all of the potash used throughout the world.

STASSFURT DEPOSITS

A glance at the diagram shown herewith reveals the way in which the various layers of salts are found. It will be noted that potassium salts are not found at the surface. This should be borne in mind when we talk about discoveries of potash in our western country. As potassium salts dissolve readily in water they are transported to lakes or the ocean, except in so far as they may be ingested and used by plants. Water from Great Salt Lake illustrates this.

It is supposed that in early geological ages North Germany and adjacent countries were an inland lake or sea, similar to our own Lake Bonneville; and from this residual lake at Stassfurt, left after evaporation through the milleniums, there separated out annually 3 to 5 inches of salt and thin layers of gypsum and anhydrite. These can be counted like rings of yearly growth in trees, and indicate a period of 10,000 years required for the formation of this salt deposit. Finally the mother liquors themselves crystallized out, giving rise to rock salt mixed with polyhalite, kieserite and carnallite as indicated. The same salts can be obtained by the evaporation of seawater and saline lakes, only in different proportions. These deposits were then buried by dust, which now is found as the "salt clay" immediately above the potash salts. In subsequent ages anhydrite and shales were laid down, and then extensive folding and pressure occurred. That climatic conditions at the time these salt beds were formed were far different from what they are to-day is indicated by van't Hoff's calculations that often temperatures of 73° C. (163° F.) occurred.

TABLE I—NATIVE POTASSIUM SALTS

NAME	Formula	Potash (K ₂ O) Equivalent
Carnallite.....	KCl, MgCl ₂ , 6H ₂ O	16.9 per cent
"Hartsalz" (Mixture of Sylvinite and Kieserite).....
Sylvinite.....	KCl, NaCl	35.4
(Kieserite).....	MgSO ₄ , H ₂ O
Schönite.....	K ₂ SO ₄ , MgSO ₄ , 4H ₂ O	27.0
Polyhalite.....	K ₂ SO ₄ , MgSO ₄ , 2CaSO ₄ , 2H ₂ O	15.6
(Boracite).....	6MgO, 8B ₂ O ₃ , MgCl ₂
(Anhydrite).....	CaSO ₄
Kainite.....	KCl, MgSO ₄ , 3H ₂ O	29.0
Orthokase.....	KAlSiO ₄	16.9
Leucite.....	KAlSi ₃ O ₈	21.6
Alunite.....	KAl ₃ (SO ₄) ₂ , 9H ₂ O	11.4
Granites, Porphyries, etc.....	3 to 8
Leucite Rocks.....	5 to 10

The individual salts found at Stassfurt have the names, formulas and potash content given in Table I; the average compositions of the crude and manufactured salts are given in Table II.

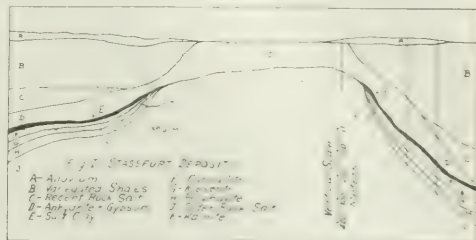
TABLE II—AVERAGE COMPOSITION (PERCENTAGES) OF STASSFURT SALTS

SALTS	NAME OF SALT	K ₂ SO ₄	KCl	MgSO ₄	MgCl ₂	CaSO ₄	NaCl	Insoluble	Water	As K ₂ O
CRUDE (as mined)	Kainite.....	22.3	10.8	7.5	4.4	41.6	4.4	1.1	11.1
	Carnallite.....	18.3	12.1	21.8	1.9	8
	Sylvinite.....	26.3	2.6	2.8	56.7	3.2	4.5	17.4
	Potash Fertilizer, 20%.....	2.0	31.6	10.6	5.3	2.1	40.2	21.0
CONCENTRATED (as manufactured)	Potash Fertilizer, 40%.....	1.7	41.6	9.4	4.8	2.2	26.2	30.6
	Potash Fertilizer, 10%.....	1.9	62.5	4.4	20.2	40.4
	Potassium sulfate, 96%.....	97.2	0.3	0.7	0.4	0.3	0.2	0.2
	Potassium sulfate, 93%.....	99.6	1.6	2.7	1.0	0.4	1.2	0.3
	Potassium Magnesium sulfate.....	2.5	0.6
	Potassium Chloride (Muriate).....	91	0.2	0.2

The Stassfurt salts are mined by the room and pillar method, about 25 per cent of the salt being allowed to remain as pillars, and the stops filled with sand or waste. The penetration of water to the deposits is fatal, for causing loss of salt and destruction of surface property results. In parts of the Stassfurt district one can see humps and hollows on the surface, with houses

and churches standing at all angles, caused by water getting to the underlying salt.

The crude salts are sold largely as fertilizers, but immense amounts are refined in the "potassium chloride factories." By recrystallization under definite conditions of concentration and temperature there are made potassium chloride, potassium sulfate, potassium magnesium sulfate, Glauber's salt, magnesium sulfate (Epsom salts), magnesia, bromine, boric acid, etc.



"The supply of potash salts in the deposits found to date is so great that even in the case of greatly increased production it will suffice for much more than a thousand years."

"Kali Syndikat has more than 70 establishments and employs more than 30,000 miners and workmen."

"The majority of the carnallite and about 1/2 of the kainite and sylvinite salts are concentrated."

During the last twenty-five years the production of salt at Stassfurt has grown by leaps and bounds, the total production in 1909 being approximately ten times what it was in 1882. In the former year more than \$25,000,000 worth of potash salts were produced, including:

Potassium Chloride (80 per cent KCl).....	349,890 tons
Potassium Sulfate (42 per cent K ₂ O).....	70,580
Potassium Magnesium Sulfate.....	38,100
Poorer grades, used chiefly in Germany.....	3,547,420

In 1912 the exports from the German Empire and the imports into the United States were:

METRIC TONS:	Exported from Germany	Imported into U. S.
Crude Potassium Salts.....	1,300,559	650,297
Potassium Chloride.....	286,528	190,775
Potassium Sulfate.....	85,452	35,366
Potassium Magnesium Sulfate.....	48,540	14,172

TOTAL..... 1,721,079 890,610(a)

(a) Equivalent to 65 cars of 100,000 lbs. capacity each, 6 days per week

The prices of "Potassium Muriate," 1913 to Mar., 1917, are given in Table III and shown graphically in Fig. II.

The potash production in the U. S. during 1916 is given in Table IV. A similar report for 1915 showed a small quantity produced equivalent to about one week's consumption, and valued at \$300,000. Fig. III enables one to compare the im-

ports of potash before the war with the production in the United States during 1916.

From the above it can be seen that Germany has been forced into a national emergency of the first rank, which production at depth was done at Stassfurt some twenty years ago. Her preeminence in this field is therefore assured until equally im-

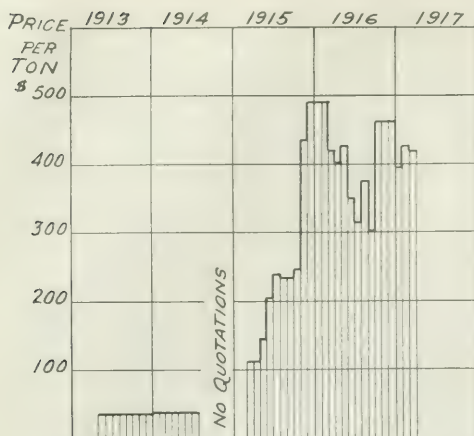


FIG II—PRICES FOR "POTASSIUM MURIATE" (80%)

portant finds are made elsewhere, or until methods are evolved for producing potash commercially from other sources.

TABLE III—PRICE PER TON OF POTASSIUM MURIATE (BASIS 80 PER CENT)

1913	Month	1915	1916	1917
\$38.55	January	Nominal	\$490	\$390-400
	February	Nominal	490	475-430
	March	(?)	415-420	415-425
Jan.-July	April	(?)	400	...
\$38.85	May	213-155	425	...
	June	200-216	350	...
Aug.-Oct.	July	230-250	300-325	...
No quotation	August	220-250	350-400	...
	September	220-250	300	...
Nov.-Dec.	October	245-250	450-475	...
Nominal	November	435	450-475	...
	December	480-500	450-475	...

TABLE IV—POTASH PRODUCTION (SHORT TONS K_2O) IN U. S. DURING 1916
(Data compiled by U. S. Geological Survey)

Approximate Total Production(a)	10,000
A—MINERAL SOURCES	5,750
Natural salts or brines(b)	3850
Alunite and Silicates, including furnace dust	1900
B—ORGANIC SOURCES	3,070
Kelp	1100
Pearl ash	220
Miscellaneous industrial wastes	1750

(a) Equivalent to about two weeks' consumption.

(b) Largest output from Nebraska alkali lakes.

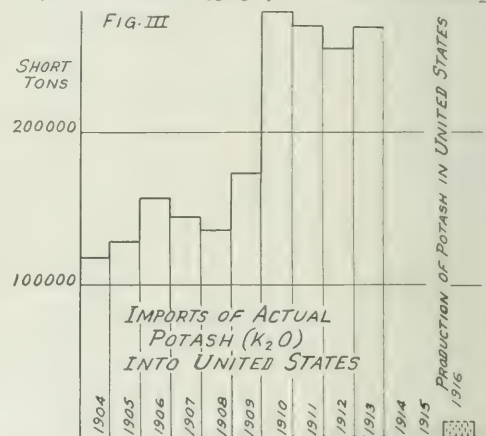
(c) 23 out of 70 establishments reported.

Potassium compounds are very widely scattered throughout nature. That potash constitutes an important part of plant ashes shows that it is in practically all soils to some extent. The composition of saline lakes and of the ocean indicates the important rôle the circulation of atmospheric water plays in removing it from the soil. As is well known, potash in plants and circulating waters gets there from the slow decomposition or weathering of certain potash-bearing minerals, chiefly silicates like feldspars and micas. At once the suggestion arises, why do we not manufacture potash from the same sources? An immense amount of investigation has been given to the problem, but thus far with no marked commercial success. The fact that to-day, almost three years after supplies of potash from Germany have been cut off, the price of potash is ten times what it used to be, is ample proof of this statement.

As sources of potash, feldspars—especially orthoclase, $KAlSi_3O_8$ —have been tried. These minerals contain from 1 or 2 up to 16 or 17 per cent potash. Immense tonnages of orthoclase too impure for use in good ceramic products would be available for potash work. The leucites of Wyoming and Idaho are even better than feldspars for potash extraction. Far more abundant than either feldspars or leucite are granites, syenites,

porphyries, lavas and other primary rocks, but their potash content is lower and difficulties in the way of treatment have not been overcome. Especially valuable for potash would be many tailings dumps—if the materials could only be "unlocked" chemically, and the one or two hundred lbs. of potash contained in each ton converted into merchantable forms economically. There are patents galore covering proposed processes, but none seem to work out commercially. Among such methods might be mentioned decomposition by treatment with (a) alkaline carbonates, (b) lime or magnesia, (c) acids, (d) calcium carbonate and ammonium salts, (e) calcium, strontium, barium or magnesium chlorides or oxychlorides, (f) calcium fluoride (fluorite), (g) water and carbon dioxide under pressure at high temperatures (an effort to effect in a short time what nature accomplished in the course of centuries), (h) high temperature, quenching, pulverizing and action of acids successively, etc.

One of the most complete papers covering the economic feasibility of producing potash from feldspathic rocks was published by Cushman and Coggeshall.¹ According to these authors a 100 ft. cube of impure feldspar containing 10 per cent of potash would have in it 17,000,000 lbs. of potash substance, valued at \$100,000 before the war. One ton of it, with only a 75 per cent extraction, would have given \$5.00 worth of potash. By the use of modified cement mill equipment these authors believed that ground feldspar and burnt lime, properly moistened with calcium chloride solution, could be granulated, burned in rotary kilns to convert the potash into potassium chloride, and then this salt leached out, recovered by concentration and crystallization, and a product obtained that would run 70-80 per cent potassium chloride. With a 300-ton mill using three 100-ft. rotary kilns, with feldspar delivered at \$1.00 a ton and lime costing \$2.33 a ton, they estimated that a product running 50 per cent K_2O (equivalent to potassium muriate, base 80 per cent) could be made for \$31.30 per ton. This would allow a



slight profit even under ante-bellum conditions. The fact that nothing has been heard about the scheme's going into actual operation may be significant.

But strange to relate, the only way for eliminating potash economically from materials such as feldspars, rocks, clays, etc., seems to be by getting it as a by-product from other commercial operations. To illustrate, potash is volatilized from the raw mixture fed into cement kilns, and the dust collected from cement stacks constitutes a source of potash of no mean proportions. The Cottrell system of electrostatic precipitation of solids and liquids from gases is very effective in this connec-

¹ THIS JOURNAL, 7 (1915), 145.

TABLE V—COMPOSITION OF SOLIDS FROM SALINE WATERS

		OCEAN Challenger Expedition	ALLEN (1869)	GREAT SALT Lake Talmage (1889)	LAKE Macfarlam (1909)	SALDURU, UTAH Gale (1916)	OWEN'S LAKE Stone (1905)	SEARLE'S LAKE Ross (1912)
Chlorine	Cl.....	55.292	55.99	56.54	52.23	24.82	37.02
Bromine	Br.....	0.188	0.093	0.094
Sulfate	SO ₄	7.692	6.57	5.97	6.65	4.93	12.96
Carbonate	CO ₃	0.207	24.55	6.70
Borate	BO ₃	0.14	3.00
Sodium	Na.....	30.593	33.15	33.39	34.64	38.09	33.57
POTASSIUM	K.....	1.106	1.60	1.08	3.66(?)	0.76-1.03	1.62	6.06
Calcium	Ca.....	1.197	0.17	0.42	0.39	0.02
Magnesium	Mg.....	3.725	2.52	2.60	2.14	0.01	Tr.
Salinity	3.30-3.74	14.994	19.558	18.39

tion, as is illustrated at the Riverside, Cal., plant. The addition of chloride or fluoride of calcium seems to assist in expelling potash from the raw mix. It has been found also that dust collected in preheating stoves or ovens at iron blast furnaces sometimes contains important quantities of potash.

Near Marysvale, Utah, are immense deposits of alunite, a basic sulfate of aluminum and potassium, with potash contents varying from almost nothing to twelve or fourteen per cent. A plant erected by the Mineral Products Company has now been making potassium sulfate from alunite for more than a year by a process very simple, but also very wasteful. Briefly it consists in burning or roasting the alunite in rotary kilns such as are used in cement plants, allowing part of the sulfur to escape as sulfur trioxide (and probably dioxide) through the stack, expelling potassium sulfate in a volatile condition by subsequent firing at a high temperature, or leaching the residue for the removal of potassium sulfate and recovery of the salt by evaporation. The alumina and silica are now treated as waste products. In the present condition of the market such a method can be carried on profitably, but under normal conditions it would be ruinous economically. The owners of the Marysvale plant recognize this fact, and have spent large sums of money, as well as much time and effort, in endeavors to convert their waste products into valuable by-products. It is said that the plant produces 25 to 30 tons of potassium sulfate daily.

It might be remarked parenthetically that many persons make the serious mistake of supposing that native alum or alunite (not alunite) is a valuable source of potash. This mineral is a basic sulfate of aluminum, usually with more or less iron, and contains no potash. Because of its astringent taste it is easily recognized, and samples without number have been submitted to examination, but no potash has been found. Even pure common or potash alum, $KAl(SO_4)_2 \cdot 12H_2O$, contains only about 10 per cent of potash (K_2O), and is a product of chemical factories, not of the earth.

Under present conditions efforts have been directed toward recovering potash from wood ashes, sage brush, beet residues and other organic wastes. A favorite scheme seems to be to burn or char carefully, usually in kilns or retorts, and then leach the residue with water, filter and evaporate. Many high hopes are blasted when the dollars and cents side of the processes comes to be worked out.

According to Harlow and Bradley the U. S. Census showed the world production of potash in 1890 from wood ashes as 20,000 tons. The census for 1900 gave the cost of a barrel (650 lbs.) of potash as \$18.25 and its selling price as \$25.00.

The composition of wood ashes is said to be:

	Mean	Maximum	Minimum
Potash (K_2O).....	5.8	10.2	2.5
Phosphoric Anhydride (P_2O_5).....	1.9	4.0	0.3

Sage brush contains 4 to 7 per cent of potash, and its ashes are said to run 20 to 30 per cent of this constituent. The authors draw the conclusion that wood ashes could be made in lumbering districts and utilized for the extraction of potash with assured profit.¹

Particularly disappointing must have been the results of attempts to recover potash from seaweed or kelp along the Pacific Coast. This proposed source has been under investigation

for some years by the U. S. Department of Agriculture, and at least four large plants were constructed by corporations used to handling affairs in a big way. It was stated that practically limitless tonnages of kelp could be cut annually, and that an inexhaustible supply of potash was thus assured. Special machinery for harvesting the kelp, loading it upon barges and treating it at the factories was devised and constructed, but statistics for 1916 show how far realization has fallen below expectation. For example, the plant of the Hercules Powder Company at San Diego has utilized only 1000 tons of wet pulp per day instead of 1500 to 2000 tons, and experience to date indicates that only 22,000 tons a year are available as against an official estimate of 696,000 tons.¹

The last source of potash to be mentioned is one of particular interest to us in the intermountain country, *viz.*, saline waters. It has long been known that water from Great Salt Lake and other land-locked seas or lakes contains potash in considerable amounts, and that sea-water itself contains appreciable quantities (see Table V). In the early part of this paper it was shown that the Stassfurt deposits themselves resulted from the evaporation of such an inland sea during milleniums long since past.

Unfortunately, potassium salts are not found anywhere in concentrated form, as is the case at Stassfurt. On the contrary, evaporation must be resorted to in order that sodium salts may be removed to a great extent before potassium compounds can be recovered in even a very impure condition, and more or less complicated methods of treatment are required to prepare concentrated potassium salts. Plants are now operating on mother liquors from salt ponds at Saltair, Utah, Searle's Lake and Owen's Lake, Cal., and on certain salt deposits at Salduro, Utah, 112 miles west of Salt Lake City.

Facts and figures shown in this paper lead to the inevitable conclusion (a) that independence of the United States from a foreign source of potash is a "consummation devoutly to be wished," (b) that thus far most extensive surface prospecting by private parties and government agents has failed to locate soluble potash deposits of any value, (c) that certain potash extraction plants of the "war baby" type have sprung up and can continue operations only as long as importations from Europe are stopped or under price conditions essentially higher than those obtaining prior to July, 1914, (d) that slight additions to potash supplies can be looked for from the utilization of cement kiln and blast furnace dusts, distillery and sugar factory wastes, wood ashes and wool scouring, and (e) that a reverse of incalculable benefit to mankind will be rendered by the discovery of a process whereby soluble potassium compounds can be made cheaply from feldspar, leucite and other aluminous containing potash.

The "World Emergency" confronting us today is therefore not one of military or national politics only. It is one of economic independence also. Because Germany alone is layered with deposits of potash salts, because extraction has found its commercial quantities only in the dry regions of western North America, because France has the distinction of producing practically all the potassium needed for those processes which scientists and engineers the world over accept, those of this war and the

¹ See THE JOURNAL, 8 (1916), 105; (1917), 1281.

² See J. H. Mendenhall, *ibid.*, 10 (1918), 1131 and 1132.

nothing to meet the great emergency? By no means! Economic campaigns more alluring and important than any planned by military leaders are called for, and the rewards to be reaped are almost beyond conception. Already special alloys have been prepared for use as substitutes for platinum. The "fixation of nitrogen," or its conversion from inert, free nitrogen of the atmosphere into valuable products like ammonia, nitrates, and cyanides, is a commercial success. But the greatest of the three desiderata remains an unsolved problem, *viz.*, how can immense stores of potash locked up in our feldspars, leucites and many rocks, be freed from their "entangling alliances," and made available to our manufacturers and—most important of all—to our farmers? The problem is not necessarily incapable of solution, but prolonged, persistent, painstaking effort, with ample provision for large scale experimenting, are needed. The Napoleonic Wars gave us cheap soda; will the World War of a later century give us cheap potash?

809 KEARNS BUILDING,
SAULT LAKE CITY, UTAH

THE RECOVERY OF POTASH FROM BEET-SUGAR HOUSE WASTE LIQUORS¹

By H. E. ZIEKOWSKI

The recovery of the residual values from beet-sugar waste liquor has been the subject of serious investigation even prior to the war. However, the abnormally high potash prices of the past few years have brought about renewed efforts in this direction.

FUNDAMENTAL CONSIDERATIONS

During the 1916 season approximately 6,000,000 tons of sugar beets were produced in the United States. In all probability a materially greater tonnage will be produced this year, and the possibilities for increased production in the immediate future are promising, though this phase of the problem is so intimately related to the tariff, the agricultural labor supply, and ruling prices of other agricultural products, that prophecy is fruitless.

The composition of the beet, and therefore its content of potash, is variable from season to season and in different localities and soil conditions. The following analyses of beets from three widely separated localities in the United States can serve as a basis.

	Colorado	California(a)	Wisconsin(a)
Moisture	78.36 per cent	63.99 per cent	74.37 per cent
Dry substance	21.64	36.01	25.63
Ash (carbonate)	0.89	0.88	
Total nitrogen	0.199	0.254	0.1817
Sugar	15.40	25.60	18.7
MINERAL MATTER PER CENT ON BEETS			
Cl	0.102	0.065	0.040
SO ₄	0.028	0.034	0.024
P ₂ O ₅	0.046	0.121	0.023
K ₂ O	0.320	0.269	0.320
Na ₂ O	0.097	0.106	0.089
CaO	0.032	0.078	0.041
MgO	0.058	0.051	0.047
Fe ₂ O ₃ .Al ₂ O ₃	0.042	0.014	0.027
SiO ₂	0.005	0.016	0.036

(a) Both the California and Wisconsin samples were several days in transit to the laboratory at which the analyses were made, and undoubtedly lost considerable moisture by evaporation, which consequently increased the percentage content of dry matter. Aside from that the California sample was abnormally high in sugar content.

From an agricultural and economic view-point—aside from the sugar—the nitrogen, phosphoric acid and potash content of the sugar beet is of more than passing importance. Accepting the average of the three analyses herein reported as the average for the entire production, the 6,000,000 ton crop of beets of 1916 contained:

NITROGEN	PHOSPHORIC ANHYDRIDE	POTASSIUM OXIDE
12,700 tons	3,780 tons	18,180 tons

Investigations indicate that in extracting the sugar values by the diffusion process approximately 60 per cent of the nitrogen

and 90 per cent of the phosphoric acid and potash content are extracted with the sugar and pass into the process, the rest remaining with the pulp. As this pulp is now completely utilized for live stock feeding purposes, the plant food values of this pulp are not lost to agriculture except in so far as farmyard manures are inefficiently utilized.

Of the plant food values extracted and now in the juices phosphoric acid is completely eliminated as calcium phosphate, and to date largely wasted. A part of the nitrogen content is eliminated as coagulated protein and otherwise, together with the phosphoric salts. The potash, however, is not eliminated from the juices by the usual processes of purification and is found in the final molasses, *i. e.*, the mother liquors, from which sugar cannot be further recovered by direct crystallization, and for this condition potash salts are partly responsible.

The production of molasses from beets is somewhat variable from season to season, but an average percentage production for the United States will be somewhere between 5.5 to 6.0 per cent on beets. With a six million ton crop of beets this totals 330,000 to 360,000 tons.

A study of a series of thirteen samples of American beet molasses as reported in *Sugar*, Vol. 18, No. 4, indicates an average content of 1.69 per cent nitrogen and 4.66 per cent potassium oxide (K₂O).

On this basis the beet sugar molasses production of the past campaign contained between 15,400 and 16,700 tons of K₂O, which checks fairly closely with the figures above estimated. Of the total beet molasses production perhaps 5.0 per cent under normal conditions, but under present conditions double this amount or more, is used in alcohol production and the still residues, containing the potash, are concentrated and usually enter the fertilizer trade and are, therefore, not lost to the general economy.

Approximately 40.0 per cent of the total molasses production is used for stock feeding purposes, in part direct as such, but by far the greater part is mixed with some absorbent feed, frequently beet pulp, either fresh or dried, and also many of the foddors. The potash values in this case are recovered in proportion as the manurial values from these feeding operations are recovered.

The remainder of the United States molasses production, perhaps 45.0 per cent of the total (during the past season from 148,000 to 152,000 tons) is desugared, that is, sugar is extracted in marketable form. It is this portion of the beet crop that contains the possibilities of potash production in commercial form at the sugar factories.

STEFFENS PRECIPITATION PROCESS

The process now used almost exclusively in this country in extracting sugar from this molasses is known, after its inventor, as the Steffens precipitation process, in which sugar is precipitated as tri-calcium saccharate.

PROCEDURE—Molasses of about 80.0 per cent solids is diluted to 10 to 12 per cent solid content, cooled to about 15.0° C. and under suitable means for cooling and stirring, finely powdered calcium oxide is dusted into the solution. If the conditions essential to the process are adhered to, 90.0 per cent or more of the sugar is precipitated as a calcium compound and is removed from the mixture by filtration. The filtrate, now with a content of solid matter of 5 to 7.0 per cent contains practically all of the potash originally in the molasses and also variable percentages of sugar not precipitated above. The sugar in solution is probably present in the form of di-calcium saccharate, C₁₂H₂₂O₁₁.2CaO. If this cold filtrate is heated to 85° C. approximately 60.0 per cent of the sugar in solution is precipitated as a calcium saccharate probably according to the following reaction:



¹ Presented at the Buffalo Meeting of the American Institute of Chemical Engineers, June 20 to 22, 1917.

The reaction is reversible and on cooling the saccharate formed dissolves; hence it is necessary to filter at the precipitation temperature.

This, known as the "Hot Saccharate" process, is now quite generally used to recover from the solution additional sugar values which are not readily and economically recovered by the first step or cold process.

The filtrate, now known as Steffens hot waste water, still contains from a few hundredths to 0.4 or 0.5 per cent of sugar, some lime, practically all of the potash and most of the other non-sugars present in the molasses. This is the waste liquor forming a potential potash supply.

PRESENT USES OF WASTE LIQUORS

In several instances where the sugar company controls agricultural lands in quantity adjoining the factory, these waste liquors, together with other residues, are used to irrigate the lands. This is perhaps the most economical method of utilizing the residual values, as all of the potash and phosphoric acid and nearly all of the nitrogen of the beet can be returned to the soils, but this is practical only in isolated instances, and only about 8.0 per cent of the total beet crop is handled in this manner.

In still other of the irrigated sections where the residual waters are discharged into existing streams and the streams are subsequently diverted for irrigation purposes some of the values may be inadvertently utilized, but in any event the losses to the economy of the state must be very considerable by this method of disposal.

In most cases the waste residues are sent into settling basins, the clear effluent of which reaches the streams and is carried away. Efforts had been made even before the war to recover these values, and owing to the stimulus of high potash prices of recent years the work in this direction has been followed with more than usual vigor. However, the problem has its difficulties.

Since the hot waste water as produced is very dilute, containing 96.0 per cent or more of water, it is necessary to concentrate it. As produced it contains 0.2 to 0.5 per cent of free lime, CaO , which will foul the evaporating surfaces if not removed. This is readily enough accomplished by carbonating (injecting CO_2 gas) and filtering.¹

The carbonated and filtered waste water varies in composition with the season, locality and factory practice, but the following is typical:

PERCENTAGES	Dry Substance	Carbonate Ash	Sugar	Organic Non-sugar	Nitrogen	Potash K_2O
97.00	3.00	1.00	0.30	1.70	0.16	0.35

This indicates at once that the content of values is low, the cost of evaporation comparatively great, and also that, under normal conditions, when the value of a unit of nitrogen is two or three times that of a unit of potash, the nitrogen values are as great or greater than those of the potash contained in these waters. Up to a content of 50 to 55 per cent dry substance this water can be readily enough concentrated in multiple effect evaporators, and quadruple as well as quintuple effect evaporators have been used very successfully. With a content of more than 55 per cent dry matter the liquor begins to salt out and foul the heating surfaces. However, beyond this point the material can be readily enough concentrated still further, and brought to a dry state by the use of one of the various types of vacuum drum driers. The trouble is to keep the material dry.

It might be stated that during the past campaign in one of these waters were concentrated by the direct process from an oil free press cake used through a direct metal transfer case which the water was heated by the direct removal of the lime by not using a pre-heated transfer case brought about the direct contact without an intermediate heating stage. The method of evaporating a product is not to be used under normal conditions.

The dried material containing 10 to 12 per cent of K_2O and 5.0 per cent nitrogen is so exceedingly deliquescent and absorbs atmospheric moisture so readily that it becomes fluid in a very short time.

Various absorbents have been used to overcome this difficulty, one of the most successful being dried slaughter-house wastes, which incidentally are deficient in potash so that the two materials complement one another. Ultimately this may prove to be a direction in which considerable quantities of the sugar-factory waste waters will be utilized, but unfortunately only a few beet-sugar factories are now located within reasonable distance of the meat packing centers so that the cost of freight enters.

In some localities small quantities of 50 to 55 per cent dry substance have been disposed of in tank car lots directly to the agricultural industry as a liquid fertilizer. In other instances it is urged to sell the liquid fertilizer direct to the farmer for use by saturating barn manure with it. It is doubtful whether material quantities can be disposed of in this form at present.

With present potash prices the nitrogen values have lost their relative importance with the result that in at least one instance these have been sacrificed in order to obtain a product comparatively high in potash content, which would permit its shipment considerable distances to the potash consuming centers.

When the Steffens water is concentrated to about 55.0 per cent dry substance it can be quite readily ignited and charred, owing to its high content of sugar and other organic matter, its own content of combustible matter then furnishing most of the necessary heat. The char, or crude ash, thus produced contains from 30 to 35 per cent potassium oxide, but only traces of nitrogen. This procedure is economically justifiable only with present potash prices. In other directions experiments are being made towards a recovery of the potash salts in comparatively pure form, at the same time saving the nitrogen values.

The above roughly covers the efforts made in the recovery of the values of the beet-sugar liquor residues.

PROGRESS IN RECOVERIES

Technically, the recovery of the potash values from these liquors is a comparatively simple and perfectly feasible problem. It is simply one of evaporating the dilute liquors as economically as is practical, charring the residue to produce the crude ash and leaching and recrystallizing if this is desired. The quantities of water to be evaporated, however, are large, the necessary equipment costly, and such a procedure has commercial possibilities only during war prices.

Now it is true that almost any sugar factory could have paid for a potash recovery plant in one year with present potash prices, but the war may end any time and leave a lot of very costly equipment on hand, especially as the cost of such equipment, evaporators, boilers, etc., is abnormally high at present. Then also a beet sugar factory operates economically only the average length of the operating season, only about two days, and the earnings must be made during the short period. But at that some progress is being made, and at least one concentrating plant is under construction and several others under consideration and more of the values will be recovered during the next campaign than during the past.

However, in the case of a recovery of all the values in the liquor, it must at least be noted that only one of the values is touched directly by this.

Approximately the composition of the potash in the sugar beet crop grown in the United States at present is as follows:

Percentages	Moisture	Dry Substance	Potash K_2O
97.00	3.00	1.00	0.30

The K_2O is found in solution in the juice and in the molasses.

Percentages	Moisture	Dry Substance	Potash K_2O
97.00	3.00	1.00	0.30

This leaves under control of the manufacturers only about 40.0 per cent of the potash content of the beet which on the basis of a six million-ton crop amounts to between 6800 and 7500 tons of K_2O .

This quantity is now disposed of as follows:

Directly to the soil as factory sewage.....	20.0 per cent
Concentrated to 50-55 per cent dry substance and sold to fertilizer factories.....	5.0 per cent
Concentrated and calcined to a crude ash.....	5.0 per cent
Discharged into streams (representing the stock of values now lost).....	70.0 per cent

Thus far the subject has been considered from the angle of recovering the potash for the chemical industries or the potash and nitrogen as fertilizers only. That does not by any means exhaust the possibilities. Beet-sugar molasses and therefore the waste water contains a great number of substances which in themselves are valuable or may serve as the mother substance for valuable products. The possibilities can here be touched on only very briefly.

GERMAN TREATMENT OF WASTE LIQUORS

Even in the case of potash and nitrogen it appears from the experience of Europe that the general economy is served best by combining these into a more valuable product. From Germany it is reported that by the Bueb process of destructive distillation the waste liquor of molasses desugarizing processes operating by the strontium process, in that country, produce annually 5000 tons of potassium cyanide and 5000 tons of ammonium sulfate. Steffens waters can be similarly utilized and a United States patent has been granted for such a process.

The molasses waste liquors contain a whole series of organic acids which can be recovered and are valuable to industry.

The nitrogen of these waste liquors occurs in various forms, partly as a plant base of which the principle is betain, which has found some application in medicine. A large part of the nitrogen content exists in the form of amido acids. These it has been shown by Effront can, by suitable fermentation processes, be split into ammonia and a mixture of volatile fatty acids, acetic, propionic and butyric. Recent investigations in this country indicate that a mixture of the high boiling point ketones valuable in cellulose technology can be prepared from this liquor.

Ehrlich insists that the amido compounds present in considerable quantities in beet molasses waste liquors are the mother substances of fusel oil, more particularly amyl alcohol, and suggests extracting these compounds and utilizing them to increase the fusel oil production. This indicates only a few of the possibilities. While it is not claimed that beet molasses may yet prove another coal tar, chemically it may be almost as interesting.

But little has been done in developing the waste liquors values in this country. The reasons are various. Not the least lies in the fact that sugar is a sort of national and international political football. Between duties, bounties, premiums, special international agreements (as, for instance, the Brussels Conference) and competition with the tropics, the beet sugar industry in the United States has never felt sufficiently safe to venture in new directions.

At the outbreak of the present war the outlook was particularly dark. The tariff had been lowered, and a duty-free sugar clause enacted to go into effect May 1, 1916. Fortunately, this latter clause was repealed before going into effect.

What the development of the future may be will depend more upon legislation following cessation of hostilities than present high prices and in this respect the beet-sugar industry is not differently situated than most other chemical industries in this country.

THE INFLUENCE OF PIGMENTS ON RUBBER¹

By MAXIMILIAN TOCH

Rubber has a strange analogy to linseed oil and China wood oil, and although as far as we know the chemical compositions of rubber and the drying oils are totally different, this analogy holds good for reasons that we cannot explain. In 1904 I delivered a lecture on the chemistry of the rubber pigments before the American Chemical Society, and I published it privately, for I knew at that time that it should not be taken as final on account of my limited knowledge of the subject, but in thirteen years I have learned a little more on the subject so that I am able to-night to give you some facts which should be helpful.

The rubber industry thirteen years ago was insignificant, that is to say, if rubber and its compounds had been entirely destroyed from the face of the earth we would not have suffered very seriously for any great length of time because matters would have adjusted themselves, with perhaps some inconvenience, in less than a year. The loss of hard rubber would probably not have been felt for any great length of time, owing to the fact that celluloid and some of the lighter metallic alloys would have replaced it, but to-day, we face a different situation. Take the automobile industry alone, which I am informed ranks third in size and money invested in the United States, and the rubber industry sixth or seventh in size and investment in the United States, and you will plainly see that without rubber tires the automobile industry could not exist with the same measure of success.

At the Eighth International Congress of Applied Chemistry held in New York in September, 1912, Dr. Duisberg showed a piece of synthetic rubber, made in Germany, which weighed perhaps 20 kilos or more, and two automobile tires, made from this synthetic rubber, which had traveled 4000 miles, and apparently this rubber was as good or better than the natural. But if our information is correct, synthetic rubber is only a laboratory product, and the Central Powers are suffering tremendously for the want of rubber in warfare, for without it no staff officer can travel any great distance and ambulance work becomes a hardship and a menace with tires made of any other material, so that we must conclude that artificial or synthetic rubber is not yet a commercial success. The submarine that has been making several trips between Germany and the United States took back a cargo of platinum and rubber, indicating that rubber is an essential without which certain industries cannot hope to make much progress.

We accept the composition of rubber as being a terpene composed of C_5H_8 , but rubber as it is derived from the latex of the fig tree is much more complex and contains an appreciable quantity of oxygen; yet when the resins are extracted and we have a clean, elastic mass of the Para type there is no question of the composition of this mass being C_5H_8 , or perhaps $C_{10}H_{16}$.

The difference between hard rubber and soft rubber is a question of degree, vulcanization and percentage of sulfur. If we were to draw a hexagon of hard rubber and soft rubber we would have to conclude that the sulfur combination of rubber has two eutectics.

Rubber comes to the manufacturer now in a fairly pure state. Raw rubber contains moisture and foreign substances to a very large extent, all of which must be removed before the rubber is vulcanized. When cleaned rubber is mixed with from 3 to 5 per cent of sulfur and placed in a vulcanizer under pressure for several hours a soft rubber is the result, that is to say, it has a greater elasticity than the raw material from which it has been made and a distinct combination has taken place between the terpene and the sulfur. If, however, from 30 to 35 per cent of sulfur is added to the rubber and the pressure and heat con-

¹AMERICAN BEET SUGAR COMPANY,
ROCKY FORD, COLORADO

¹Address before the Syracuse Section of the American Chemical Society, Syracuse University, Syracuse, N. Y., April 13, 1917.

tinued for a longer period, a hard substance is the result which we know as hard rubber or vulcanite. The soft vulcanization to which I have referred is never a permanent material, that is to say, after the lapse of a few years, more or less, the rubber loses its elasticity and becomes brittle. The hard product, which contains from 30 to 35 per cent of sulfur, has been known to last for many years.

In 1912 the battleship "Maine," which had been lying in the mud 25 feet below the surface of the water in Havana harbor, was, as you remember, uncovered and the remains of the wreck were floated and taken out to sea and buried. The War Department and the Navy Department suggested at the time that I make an examination of the materials of which the ship was built to see the amount of deterioration that had taken place in 13 years. I duly reported on the condition of the metal and wood, and to my very great surprise all the rubber packing used in the pumps was as pliable and as perfect as the day on which the ship was sunk. I brought back several samples of this rubber packing, and they are still to be seen in the chemical museum of the College of the City of New York. It would therefore indicate that rubber in any form is perfectly preserved if kept away from oxygen, and this demonstrates a strange analogy: that rubber and many metals have the same characteristics and are preserved in the absence of oxygen.

There is a third method of vulcanization used for soft elastic articles such as toy balloons, rubber gloves, finger tips, dress shields and materials of that description. This is done by sheeting the rubber, cutting it or pressing it into the size of its ultimate shape and subjecting it to the vapor of sulfur chloride, but owing to the fact that the rubber will take up more sulfur and chlorine than it needs, articles of this type do not last as long as those that have a definite amount of either sulfur or chlorine in their composition. Bisulfide of carbon is used as a carrier for the chloride of sulfur, and unless the rubber article is thoroughly treated with ammonia or afterwards rinsed in some other dilute alkaline liquid, a mixed acid is formed, which tends to rot or destroy the rubber so made.

The rubber industry is still empirical to a large extent, and much of this has been due to the fact that the practical superintendent of the rubber factory, like many a practical man who has no fundamental education, resents the interference of the laboratory in his methods, but this will be overcome to a large degree when the practical superintendent will have been raised from the ranks of the research laboratory.

The rubber in pure form, that is to say, mixed only with sulfur and vulcanized, is not used to a very large extent in the arts. Of course, certain materials like dental dam, elastic bands, high-grade inner tubes, and a few such articles must be exempted. In fact, I can include the rubber portion of the football. As a rule, the rubber bladder which is enclosed in the leather case is generally made of a very high type of pure vulcanized rubber only, but all the other articles must of necessity be compounded with either fillers or reinforcing pigments.

Please observe carefully that there is a great difference between the ordinary filler of rubber and the reinforcing pigment. If you take an ordinary article of commerce like a rubber door mat this may be composed of only 7 or 8 per cent of pure rubber, the balance being reclaimed rubber and heavy fillers, but, on the other hand, if we take an automobile tire and inner tube it is quite important that fillers should not be used but reinforcing pigments should be used, for an automobile tire is now sold entirely on its merits and in many instances a guarantee is given as to its longevity. In due course I shall describe to you one of the reinforcing pigments which has so improved automobile tires as to increase their mileage from 2500 to 5000 miles.

The principal fillers used are barytes, whiting, Paris white, clay, ground slate, silicious hematite, silicious black oxide of iron, and many of the minerals of those types.

The principal reinforcing pigments are sulfide of antimony, litharge, precipitated barium sulfate, precipitated barium carbonate, vegetable black, carbon blacks free from grease or oil, alum-free ultramarine blue, red lead, sublimated zinc lead, zinc oxide, and lithopone. There are a number of others which I shall also describe.

FILLERS

Barytes is the natural sulfate of barium, which is crystalline and of itself has no chemical effect on any rubber composition as it is insoluble and infusible under ordinary conditions. It is, however, usually coarse, and there is some objection to it on account of its specific gravity, which averages 4.6.

Whiting and Paris white are the same, for they are both calcium carbonates. In time these materials are inclined to harden rubber, but one of the defects of the calcium carbonates is the amount of moisture that is adherent to them.

Clay is silicate of alumina and has the same defects as whiting if not more so, owing to the moisture which it contains and which is very likely to produce microscopic blowholes.

Ground slate as an earth consists of silicate of alumina containing iron and magnesia and is only to be recommended, after having been thoroughly dried, for coarse, cheap rubber materials.

Silicious hematite is a native oxide of iron containing about 30 per cent silica and 70 per cent iron oxide, Fe_2O_3 . Sometimes, depending upon the locality, the iron content may run lower or higher. It is not to be recommended on account of its high specific gravity and on account of its coarseness.

Silicious black oxide of iron is really a black slate which contains a fairly large amount of magnetic iron oxide. It is used only with materials as a "make-weight."

REINFORCING PIGMENTS

I am giving only a list of those that are used in large quantities, for there are many other materials with which this paper does not deal, as, for instance, the colors like chromium oxide, chromate of barium, chromate of zinc, sulfide of arsenic, and the blacks made from various carbonized materials.

Sulfide of antimony is one of the most important of the reinforcing pigments. This may contain no sulfur and be a pure antimony sulfide, or may contain as high as 17 per cent of sulfur. In this respect it has a great analogy to ultramarine blue, where the sulfur content and its stability as a chemical compound increases the life of the rubber rather than decreases it.

Litharge is the monoxide of lead, forms lead sulfide in the vulcanizing process, and, like antimony, produces a more or less soft rubber, practically the same as it does when used as a pigment with linseed oil. Red lead, which is a higher oxide of lead (Pb_2O_3), has a directly opposite effect on both rubber and linseed oil, for in time it produces a very hard, brittle rubber.

Precipitated barium sulfate, which is sold under various names, is either good or bad, depending entirely upon the method of its manufacture. If it is a straight barium sulfate made from a mixture of two materials which produce barium sulfate, and the precipitate washed and dried, it is one of the best reinforcing pigments which we have. If it is a by-product, however, it may contain oxide of boron and residual moisture, which in a rubber tire would be harmful material of producing good effects. This material is very largely known under the name of blaine fix, type lith or permanent white, and has almost entirely superseded, among the better manufacturers, the use of barytes.

Precipitated barium carbonate is the same as that of barium carbonate that is true of barium sulfate, except that barium carbonate can be decomposed. It is a good strengthening, but is not so good as barium sulfate.

The *carbon blacks* are of various qualities, from either the roasting and burning of soft or hard tars, shells of nuts, and the like, and have a very low drying effect on rubber, but in the case of the carbon black it happens a good deal from

grease or oil, and although it retards curing just as it retards drying in linseed or China wood oil, it inversely prolongs the life of the rubber.

Sublimed zinc lead has come into use only within the last ten or twelve years. It varies in composition from 5 per cent of sulfate of zinc and 95 per cent of oxide to 50 per cent of sulfate of zinc and 50 per cent of oxide of zinc. At all events, it has the great advantage over white lead that it contains no combined moisture and is not likely to produce blowholes, although it blackens in a heated mixture of sulfur and sulfur compounds even though some authorities claim that it does not do so.

Zinc oxide is one of the most valuable reinforcing pigments in the rubber industry and perhaps ranks higher than lithopone. It has a distinct hardening effect on rubber in time, but can be altogether regarded as a perfectly stable compound.

Lithopone is a mixture of zinc sulfide and barium sulfate and always contains a small percentage of zinc oxide. It is very largely used in the rubber industry to replace zinc oxide, although it is less of a reinforcing pigment. It has the unfortunate habit of turning gray when exposed to sunlight, but it turns white again when allowed to remain in the dark for a considerable length of time.

Magnesium carbonate is a spreader or extender, and when pure has no bad effect on rubber. It is used largely for making rubber more filmy and gives somewhat the effect of satin to sheet rubber.

Ferric oxide red, which is a pure Fe_2O_3 , is sold from a bright scarlet to a cherry color. When pure it has no effect on rubber, but when impure, containing a small amount of acid, it is deleterious.

Ferric oxide yellow is a hydrated oxide of iron and silicate of alumina, either natural or artificial. When absolutely dry and finely powdered it is very useful where a small percentage of rubber enters into the composition of the material made.

English vermilion is a sulfide of mercury largely used, and although its price is somewhat prohibitive in most articles, it is the only brilliant red color we have and is not injurious to rubber.

Graphite is a carbon, the purer forms consisting of 90 per cent carbon (graphitic) and 10 per cent silica and silicates. It cannot be regarded as a filler for it improves rubber for mechanical uses, exerts no bad influence and lengthens the life and usefulness of many rubber materials in which it is used.

I have not dwelt on the aniline dyes which are used, nor on the resinate and oleate colors, as this is really a separate subject and cannot be treated to-night. In a few words, however, I may say that the resinate aniline dyes have a decided use as a rubber coloring and are not as harmful as the oleate dyes. However, for toy balloon work and materials that are not supposed to last long, there is a decided use for some of the "lakes" in the so-called "cold-cure" method.

320 FIFTH AVENUE
NEW YORK CITY

INDUSTRIAL WASTE DISPOSAL¹

By HARRISON P. EDDY

While there are various waste materials resulting from the industries, the term "industrial wastes" has come to mean the liquid wastes from the processes employed in industrial establishments. In England they are called "trade wastes"—a term not quite as applicable in this country, although occasionally used. Neither the human excrement of operatives nor their wash waters are comprehended in this term, although in many cases there is no effort to prevent their admixture.

¹ Read at the Buffalo Meeting of the American Institute of Chemical Engineers, June 20, 1917.

ORIGIN OF INDUSTRIAL WASTES

Many industries employ great quantities of water for various purposes such as condensing, washing of raw stock, dilution of chemicals, transportation and application of materials and the washing and rinsing of finished products. Some of these uses do not defile the water and it can be discharged at will, as for example, many condenser waters. Other uses result in a very great change in the character of the water and render it unsuitable for discharge into some waterways.

In paper mills, after the digestion of the raw stock with strong chemicals, there remain the liquors, highly charged with mineral and organic substances, but for which the manufacturer has no further use. He therefore seeks to get rid of them in the most expeditious and least expensive manner. The fibrous stock is then washed and large quantities of wastes are discharged from the washers, more or less highly charged with substances like those already mentioned. From the paper machines come great quantities of water carrying fine fiber, clay, coloring matter and other substances depending upon the character of paper made and the processes employed.

In tanneries, pure water is indispensable, but after use it is highly colored, charged with spent chemicals and loaded with organic matter. Its burden of impurity is partly in suspension and partly in solution. Wastes from different processes within the same tannery often react upon one another, throwing out of solution substances which in their new physical condition may be deposited in waterways to their detriment. Some tannery wastes of themselves are so resistant to bacterial action that they do not readily putrefy, yet when diluted with the waters of a natural stream they may become most offensive.

The wastes of woolen mills vary radically from those of paper mills and tanneries, yet they may be the cause of just as serious complaints. The grease and soaps from the scouring of the wool, the spent dye liquors, the soaps from the cloth-washing and the rinse waters in the aggregate, are of great quantity, highly colored, turbid, charged with suspended matter and quite capable of transforming an attractive stream into an unsightly, foul-smelling and quite unattractive waterway.

Instances like the foregoing might be multiplied almost without end. Some of the other industries which have encountered difficulties in the disposal of wastes are wire-drawing and galvanizing works, carpet mills, dyeing and bleaching works, strawboard factories, slaughtering and packing houses, breweries, distilleries, gas works, chemical and explosive works and mines and coal washing plants.

EFFECTS OF WASTES UPON WATERWAYS

The ingredients of industrial wastes may be grouped in three main classes:

- (1) Floating and suspended matter.
- (2) Substances in solution, in colloidal condition and in an extremely fine state of suspension.
- (3) Bacteria.

Floating and suspended substances may render the waters into which they are discharged, unsightly, and cause deposits. Such deposits, if of organic matter, often deprive the overlying water of a large proportion of its natural content of dissolved oxygen which is necessary for the maintenance of biological equilibrium and the prevention of putrefaction. Decomposition is accompanied by the generation of large quantities of gas, some of which is entrained in the mud until it has accumulated sufficiently to enable it to buoy up large masses which may be seen floating for a time upon the surface of the water only to be broken up and redeposited upon the liberation of the gases.

Dissolved substances almost always accompany the suspended matter in industrial wastes. Sometimes they are much more troublesome. They, too, cause the depletion of the oxygen supply, usually through the action of the bacteria of decomposi-

tion. Particularly objectionable and difficult to treat are those wastes containing large quantities of very finely divided suspended matter and colloidal substances. Usually impurities of this class pass along with the waters of the stream into which they are discharged and do not form deposits. However, under some circumstances such ingredients are coagulated and thrown down, sometimes by the reaction of wastes of one process with those of another, and at others by natural physical, chemical and biological processes going on in the waters.

Most industrial wastes contain bacteria. These may not be pathogenic germs. In fact, they may be decidedly helpful in the problem of disposal, rather than harmful. There are abundant opportunities in some of the industries, however, for the pathogenic organisms to escape in the liquid wastes and thus contaminate the waters into which such wastes are discharged. One of the most dreaded organisms which may be spread about in this manner is the anthrax bacillus, sometimes present in hides, skins and wool. This organism is very hardy and appears to maintain its virility through its spores for many years.

Excrementitious matter from operatives is often combined with the industrial wastes and thus the entire flow may be rendered bacterially dangerous.

Wastes may cause objectionable conditions in many ways, depending upon their character and the size and condition of the waterway into which they are discharged. They may contaminate a water supply, render a stream unsightly and objectionable in appearance, cause putrefying deposits, render the natural waters putrid and offensive, poison or otherwise kill fish, and injure vegetation. Strange and contradictory as it may sound, complaint is frequently made that wastes are killing vegetation and about equally often that they are so encouraging the growth of vegetation as to do serious damage. If one complaint doesn't apply the other usually does.

It might appear that as the industries are the offenders in this field of activity, there would be few complaints from them of the conditions produced by the discharge of industrial wastes. Just the contrary is true. One of the most common complaints comes from the manufacturer to the effect that an upper riparian industry is rendering the water unfit for use in his plant.

SELECTION OF FACTORY SITES

Enough has been stated to show how wide-spread is the trouble in disposing of industrial wastes. When about to establish a new industry or plant, the proprietors usually make thorough investigation of the quality of the water available for their use. The extent of the supply is also generally investigated and often such collateral questions as the amount of power derivable from the passing stream. But how infrequently do they make even a superficial study of the problem of wastes disposal. Yet this may be a greater and more difficult problem than that of water supply.

Expenditures of \$100,000 or \$200,000 for wastes treatment plants and of \$25,000 to \$40,000 annually for the operation of such plants are becoming more and more frequent. Capitalizing the annual expenditure of \$25,000 at 5 percent and adding \$100,000 for construction cost, making no allowance for depreciation, it appears that the industry might have expended as much as \$160,000 in procuring a site which would not have entailed the necessity of wastes treatment.

The selection of a suitable site for an industry producing large quantities of wastes is a matter of much importance. Even though conditions at the outset appear to be favorable they may be materially altered by establishment of new industries down stream or by an increase of riparian population below the plant.

TREATMENT OF WASTES

When it is impracticable to afford the wastes sufficient dilution to prevent the production of unsatisfactory conditions, it be-

comes necessary so to modify the character of the wastes that they will not cause complaint.

One often hears that wastes cannot be so treated; that if a way were known the manufacturer would gladly adopt it. This impression that the wastes cannot be successfully treated is in many cases not true and it may be accepted that they can be so treated as to remove their objectionable and deleterious properties before their discharge into natural waterways.

On the other hand, such treatment may be and often is a very expensive undertaking and one from which the manufacturer naturally shrinks on this account and also because he personally is not familiar with the process or processes necessary to the accomplishment of the object.

Perhaps the most important step in the solution of this problem is the determination of the extent of treatment necessary to meet the requirements of the case. To answer this question intelligently it is necessary to know the character and quantity of the wastes produced, the character of, and conditions surrounding the waterway into which they are being discharged, and their effect upon the waters in question.

The next step is to determine how best to treat the wastes to accomplish the necessary results at a minimum cost and, in any event, one which is not prohibitive. There have been instances when the plant proposed for such treatment would have cost a sum about equal to the value of the entire industrial plant of which it was to become a minor part. Such a suggestion is absurd and tends to reduce or extinguish the respect of the manufacturer for the party making the suggestion, for the officials trying to enforce the laws and even for the laws themselves.

For the removal of suspended matter, screening may suffice under some conditions, while others may require the more complete removal by sedimentation. When the substances in suspension are of very light specific gravity and finely divided it may be necessary to resort to chemical precipitation.

Some dissolved matters may be removed by chemical precipitation, while others can be modified in character by chemical treatment without actual removal. If they are organic and subject to putrefaction, bacterial action may be required for their oxidation, as in sewage treatment.

Certain wastes are bacterially dangerous and it may be necessary to destroy the pathogens even where the suspended and dissolved matters would cause no harm. In such cases the treatment of the wastes may be all that is essential, while in others it may be necessary even to treat the raw material as has been suggested in the case of anthrax-infected hides.

It should not be inferred from this discussion that a single process can be selected for each case, for it often requires several to accomplish the desired result.

At one plant where the author's firm has supervisory charge of the wastes disposal department, no less than seven steps have been employed at one time. These are digestion of a portion of the wastes, sedimentation of the water, chemical treatment of the settled effluent, filtration of a portion and dilution of the remainder of the chemical effluent and finally the addition of chemicals to prevent the exhaustion of the supply of oxygen in the river.

VARIATION OF TREATMENT FROM TIME TO TIME

The process adopted should in many cases be varied from time to time to take advantage of favorable or unfavorable conditions. The volume of wastes produced and the composition affect the quantity of wastes produced and consequently make the conditions dictating treatment more or less variable. Industrial processes frequently are changed, requiring modification in the treatment methods.

In winter temperatures may be sufficiently low to retard or even prevent putrefaction under conditions which in summer

would transform a natural waterway into a stinking slough. In spring there are usually large volumes of diluting water which may make bacterial oxidation in filters unnecessary, at a time when the filters would be working under most unfavorable conditions.

All of these and innumerable other conditions must be taken into consideration if success is to be attained at a minimum cost.

ADVISABILITY OF ANTICIPATING COMPLAINT

In many cases industrial establishments which are now of great size have grown from very modest beginnings, often from merely a room or two adjacent to a water privilege which was the primary reason for the selection of the site. As the business has grown through the decades conditions have entirely changed. What was an abundant supply of water not only for industrial purposes but also for the dilution of the wastes, has now become barely adequate for industrial purposes alone and the entire flow now passes through the plant and perhaps through several plants more recently built. Thus the entire stream has become a river of industrial wastes rather than, as originally, a natural river into which a minor quantity of industrial wastes was discharged.

In all such cases there has been a collateral increase in the resident population. Now there are villages along the river where formerly were wooded lands and pastures. Such development has brought with it demands for parks and other recreation facilities, including the improvement of the natural stream for boating and perhaps for bathing purposes.

Under some conditions a proscriptive right may be acquired to make certain uses of the waters of the river, even though they be more or less hostile to the enjoyment of some privileges or to lower riparian owners. The proscriptive right is often advanced in defense of the practice of discharging untreated industrial wastes into waterways and their consequent pollution. Many of the industries, particularly in the eastern part of the country, are of very long standing. The continuous operation of an industrial plant devoted to the same general kind of work for more than a century, can be cited in numerous instances. In comparatively few cases, however, can it be shown that such industries are operating under conditions substantially identical with those of prior decades. Either the character of the business has changed so that processes are different and industrial wastes are greater, or less in quantity and decidedly altered in character, or the business as a whole has become much greater with a corresponding increase in the quantity of industrial wastes. These changes make it exceedingly difficult in most cases to establish a proscriptive right to the acts of which complaint is made.

It should be borne in mind that in no case can one acquire a right, by prescription or otherwise, to create a nuisance. This fact has been the stumbling block upon which many an effort to secure or maintain privileges, through court decisions, has been defeated.

The paramount lesson to be gained from experience in these matters is that it is wise to anticipate complaint of objectionable conditions whether from lower riparian manufacturers influenced by difficulties caused by the character of the water, from a community complaining because of odors and objectionable appearance of the stream, or from the farmer whose cattle will not drink the water, whose crops are killed because of inundation by polluted waters, or whose ditches and natural brooks have become so overgrown with vegetation due to the fertilizing ingredients of the water having their origin in industrial wastes, that they will no longer serve their purpose.

The prudent manufacturer will make it a part of his routine business to observe carefully the effect of the discharges from his plant upon the character of the water in the river, not alone in his immediate vicinity, but for a considerable distance downstream. When conditions become noticeably objectionable he

will take measures to remedy them, at the same time maintaining the valuable privilege of utilizing the stream for the disposal of his wastes, to as great an extent as is compatible with the public good and the reasonable use of the waters by lower riparian manufacturers. Such a policy, if intelligently pursued in many cases, will result in avoiding expensive litigation. More important than this, however, is the fact that by maintaining the waterway in a reasonably satisfactory condition the hostility of lower riparian dwellers may be avoided. Where such a feeling is aroused by objectionable conditions, it may exert itself through legislation or through litigation in such a manner as to require the establishment of exceedingly rigid restrictions as to the use of the river or even drive the industries away. Numerous instances of the latter can be cited.

NEPONSET RIVER CONDITIONS

One of the most interesting illustrations of the industrial wastes disposal problem is that of the Neponset River Valley near Boston in Massachusetts. This river rises about 22 miles from Boston Harbor, into which it discharges. Its natural drainage area is 114.14 sq. mi. and it also receives one-third of the flow of the Charles River at Dedham, equivalent to the drainage from 66.2 sq. mi. The total tributary area is therefore 180.3 sq. mi.

The normal yield of the drainage area is probably about as follows:

MONTH	Mil. gal. daily	Cu. ft. per sec.	MONTH	Mil. gal. daily	Cu. ft. per sec.
January	216	334	July	31	49
February	304	470	August	45	69
March	492	762	September	40	62
April	356	551	October	76	117
May	190	294	November	135	209
June	84	130	December	176	272
Monthly Average	178	276			

The actual flow is much more uniform than the natural flow would be because of the regulating effect of the storage reservoirs.

The State Department of Health reported at one time that there were about 30 mills discharging more or less wastes into this river. Before prohibitory statutes were passed, one wool scouring concern abandoned its location. Some manufacturers diverted a portion of their business to other plants and one abandoned the manufacture of one line of goods, thus avoiding the production of large quantities of liquid wastes which were very difficult to treat.

Eleven manufacturers have provided sedimentation tanks and ten have constructed strainers and filters of cinders, coke or sand. Some have adopted chemical precipitation as a means of improving the efficiency of natural sedimentation. Treatment plants have been provided in nearly all cases where the wastes require treatment, some of which have been described by the writer.¹

In 1902 the Massachusetts Legislature passed an act directing the State Board of Health,

".....to prohibit the discharge of sewage.....or every other substance which may be injurious to public health or may tend to create a public nuisance or to obstruct the flow of water, including all waste or refuse from any factory or other establishment where persons are employed, unless the owner thereof shall use the best practicable and reasonably available means to render such waste or refuse harmless.

"Section 2. The Board shall consult and advise with any such owner at his request or of its own motion as to the best practicable and reasonably available means of rendering such waste or refuse harmless, having regard to the circumstances and requirements of the situation and to the industrial interests involved." (Chap. 541, Acts of 1902.)

It is interesting to note that it was the intention at the time this original act was passed, to have reasonable regard for the manufacturing industries, not requiring them to go to extremes in the treatment of their wastes unless the exigencies of the

¹ "The Cleaning Up and Improvement of a Stream Polluted by Sewage and Trade Wastes," *Engineering & Contracting*, August 9, 1916.

situation required. In other words, incorporated into this statute was the "rule of reason."

At the time of the passage of this statute industrial wastes treatment in this country was in its infancy and progress in improvement of conditions in the Neponset Valley was naturally somewhat slow. In 1906 it appears that public sentiment had been so aroused that it was possible to pass an act in which the "rule of reason" was much less evident than in the earlier act. The only reference to it in the 1906 act was that the Board was to advise the owner of the factory as to the "*best practicable and reasonably available means of rendering the wastes or refuse harmless.*" The clause "having regard to the circumstances and requirements of the situation and to the industrial interests involved" was omitted from this act.

During the next 10 years many efforts were made to secure additional and usually more drastic legislation, in spite of the fact that the manufacturers expended large sums of money in an effort so to modify their wastes before their discharge that they should not endanger the public health nor tend to create a nuisance. Perhaps the culmination of these efforts may be said to have been embodied in a proposed act—Senate 113—presented to the Legislature for its consideration in the year 1916.

Section 1. Any person, firm, corporation or group of individuals who shall cause, either directly or indirectly, the pollution of the waters of any river in this commonwealth, shall be punished by a fine of not more than one hundred dollars for every day which said pollution continues after notice from the health commissioner that such nuisance be abated.

Section 2. A river shall be held to be polluted within the meaning of this act whenever by the introduction or discharge into its waters of any foreign or deleterious substance: (a) it shall give out any noxious or offensive smell, odor or vapor, which condition is a menace to the public health; (b) it shall become discolored in such a way as to be unsightly or offensive; or (c) it shall become poisonous or dangerous to fish or animal life subsisting therein, or to live stock using the same as a drinking place; (d) it shall become injurious to vegetation in its vicinity.

Section 3. The health commissioner of Massachusetts shall be charged with the enforcement of the provisions of this act and shall determine when the waters of any rivers are being polluted as aforesaid.

Section 4. All acts or parts of acts inconsistent herewith are hereby repealed.

There are several provisions in this act which would be exceedingly oppressive if applied with literal interpretation of the act and without reading into it the rule of reason. One of these is the provision for a fine not to exceed \$100, for every day which the pollution continues after notice from the Health Commissioner that such nuisance be abated. In some instances, even if prosecuted with diligence, plants for the elimination of those ingredients of wastes which caused the pollution, could not have been built in less than six months' time.

Aside from the broad scope of the specifications of a polluted river within the meaning of this act, the Health Commissioner was charged with its enforcement and apparently made the sole judge to determine when the waters of the river were being polluted, as specified by the act. Should such an act be found constitutional, which is subject to some doubt, it would apparently deprive the alleged offenders of their rights to a hearing before the courts of justice.

Happily, this act was not passed and is introduced here merely as an example of the extent to which industries or communities may go after they have become thoroughly aroused by long-continued objectionable conditions. It is confidently believed that such drastic legislation can always be avoided, and probably also its suggestion forestalled, by prudent foresight on the part of manufacturers in preventing objectionable conditions caused by the discharge of their untreated wastes.

PROGRAM FOR SOLUTION OF PROBLEM

In many cases where manufacturers have been confronted with a serious problem in connection with the disposal of their

industrial wastes, they have been inclined to attempt its solution without first acquiring a clear understanding of the scientific principles involved, either in the production of the conditions which caused the trouble or in the processes available for the treatment of the wastes to render them less objectionable. The treatment of industrial wastes usually is a subject entirely different from that with which the manufacturers have to deal in their usual business and in which they are primarily interested; all other matters, such as the treatment of waste liquors, being of only secondary interest and importance from their point of view. They have, therefore, often selected a plant poorly adapted to the use they desired to make of it. Sedimentation tanks, for example, are often found which are entirely inadequate for the purpose, although this process is most simple. All sorts of filters have been designed and constructed, but usually without the remotest conception of the scientific principles involved in the treatment which they were intended to accomplish.

Another fruitful source of misdirected energy has been the desire to recover from the wastes ingredients of value such, for example, as the grease and fertilizing ingredients in municipal sewage. Industrial wastes, like sewage, often contain ingredients which have a market value, and every encouragement should be afforded to the recovery of such products. As economic conditions change in the future there will be a greater need of economizing in this direction, and it is to be expected that processes will be devised for the profitable recovery of such ingredients. The fact that such processes may not be available at the time the problem first presents itself, but will probably be available at some future time, is not a justifiable reason for making no effort for its solution.

Whenever an industry is confronted with a problem of this kind, a program for its solution should be carefully worked out before making expenditures upon construction. In fact, the studies necessary to the preparation of such a program may disclose other means of solution, involving relatively small cost.

First a study should be made of the waterway, to note its condition and physical characteristics, such as size, velocity of flow, depth and temperature, and a similar study of wastes to determine their quantity and character. With the information gained in this manner it will be possible to form an opinion as to the extent of treatment required to meet existing conditions.

Next, the kind of treatment and the plant required to provide such treatment, should be determined. The methods selected should be those required to give the results which may be desired within a reasonable period of time in the future when perhaps conditions may have become decidedly different from those obtaining at the time the investigation is made. Such methods should always be selected and reported with the clear reservation that new and better processes may subsequently be devised.

Following the selection of methods should be the construction of plant. Here it may be wise to proceed progressively, building first the system of drains required for the collection of the wastes and for their discharge at a single point. After this has been done further investigations based upon the measurement and analyses of the combined wastes may be desirable. When the collecting system shall have been completed, it will be possible to provide the first part of the treatment process, such, for example as screening, or sedimentation. After this has been accomplished, still further investigations may be desirable to determine, first, the efficiency of the plant already installed and, second, the next process of treatment which should be installed and the probable results to be obtained.

However much or little may be progressed, it is important to build in accordance with an intelligently devised plan and in harmony with well defined processes as may follow. Thus many expensive mistakes will be avoided and advantage taken of all opportunities to provide an economical management of

plant. The following of such a course will often result in avoiding expensive pumping of the wastes, or the treatment of excessive quantities due to the inclusion of relatively clean waters which may not require treatment under the local conditions.

The final step, and undoubtedly the most important, is the intelligent operation of the plant. Whether the processes involved are simple or complex the supervision and control of operation should be based upon a knowledge of the conditions in the river, the character of the wastes and the scientific principles involved in their treatment. The object to be attained and extent of treatment necessary at the time of its accomplishment should be kept constantly in mind. Many thousands of dollars in the cost of operation may be saved in this manner.

METCALF AND EDDY
BOSTON AND CHICAGO

THE ECONOMIC RESOURCES OF THE KANSAS CITY ZONE¹

By ARTHUR J. BOENSTON²

Hardly more than half a century ago—and within the memory of many—the line indicated by the present eastern boundary of Kansas, Nebraska and Oklahoma marked the frontier of the Indian country. It is indeed difficult for the minds of the present generation to grasp the extraordinary transformation which has been made in this territory in such a comparatively short period of time.

Kansas City enjoys what might be called, for lack of a better term, extraordinary "nodality"—a natural center from which radiate or to which converge practically all of the important lines of trade and communication of the extensive southwest territory.

The population of the city since 1900 has more than doubled. To-day the population of the combined cities of Kansas City, Missouri and Kansas City, Kansas is estimated at nearly 400,000. Assessed valuations of property have increased from \$79,000,000 to over \$210,000,000.³ Post-office receipts have jumped from \$748,000 in 1900, to over \$3,589,318, and the mail matter handled in 1916 was nearly four times that of 1900.

Kansas City received from the adjacent territory during the last year over 115,649,800 bushels of grain of which wheat alone constituted 77,785,650 bushels. The State of Kansas alone in 1916 raised a wheat crop of 99 million bushels valued at practically \$135,000,000. This state ranks first in winter wheat production, and is only occasionally exceeded by North Dakota with the spring variety.

The shipments of live stock to the Kansas City stockyards from the surrounding country in the year just past total 131,812 car-loads,⁴ of 7,323,528 animals, of which 2,177,468 were cattle and nearly 3,000,000 were hogs. Over 5,000,000 packing animals were slaughtered in the local packing plants during the year 1916.⁵

Bank capital in 1900 was short of \$5,000,000 while to-day it exceeds \$26,000,000. No better index of the expanding business of a commercial center is to be had than that of bank clearings. These since 1900 have increased more than sixfold and for 1916 totaled the enormous sum of \$4,953,778,690. Kansas City to-day ranks sixth in bank clearings and is exceeded only by New York, Chicago, Philadelphia, Boston, and frequently surpasses St. Louis.

As a railway center Kansas City is second only to Chicago in the number of lines entering the city and the size of territory which these serve.

¹ Address delivered at the 34th Meeting of the American Chemical Society, Kansas City, April 11, 1917.

² Professor of Economics, University of Kansas, Lawrence.

³ Annual Statistical Report, Board of Trade, 1916, Kansas City, Missouri.

The Kansas City Zone is primarily occupied with what might be called the *extractive industries*, and among these, of course, stands agriculture as first in importance.

NUMBER AND VALUE OF LIVE STOCK
Report of Kansas State Board of Agriculture for 1916
Report of Oklahoma State Board of Agriculture for 1916
Missouri Red Book 1915

	KANSAS, 1916	OKLAHOMA, 1916	MISSOURI, 1915
	Number Value	Number Value	Number Value
Horses	1,056,124 \$120,398,136	742,750 \$63,133,750	1,084,000 \$77,560,000
Mules & Asses	296,007 37,000,875	282,347 27,670,006	329,000 32,571,000
Milk Cows	1,077,067 68,932,288	488,004 26,840,220	837,000 45,533,000
Other Cattle	2,200,848 94,636,464	1,143,245 43,443,310	1,555,000 60,490,000
Sheep & Goats	181,481 1,134,256	39,687 448,435	1,416,000 8,213,000
Swine	1,576,568 18,918,816	1,039,474 7,484,214	4,565,000 31,986,000
Total Value of Live Stock	\$441,020,835	\$169,019,935	\$276,353,000

A summary of these figures gives a total value of live stock for these three states alone of \$786,393,770 and their crops are valued at \$768,006,583. Thus the total value of crops and live stock based on the farm values (not the values at primary markets) reaches the huge sum of \$1,554,400,353. The gross value represented in crops and live stock on the farms of Kansas amounted to \$712,209,311.

This is the state's second best record in agricultural products, which was exceeded in 1914 by about \$5,000,000. The value of its live stock is the largest ever reported, exceeding the best prior year (1915) by \$30,000,000.

The wheat crop for this state in 1916 was the second largest in the history of the state and was worth \$134,615,300. Its quality was extra fine and the average price received by the growers is the highest reported since 1872.

The value of animals sold for slaughter in 1916 amounted to \$68,762,369. The income from poultry and eggs alone was \$12,466,694. Attention should be called to the great and increasing value in Kafir, milo, feterita, and sorghums and to the recently introduced grasses and fodders in the dry sections of the state, now amounting in value to nearly \$20,000,000. The alfalfa crop of 3,581,201 tons was worth \$30,907,618, and had it been marketed during the winter and spring would probably have brought nearly twice that amount. These forage crops, none of which were originally native to the state, and most of which have but recently been introduced, represent some of the striking achievements of the agriculture of this section.

The increase of dairy products is another hopeful sign pointing to more intensive agriculture. These products were valued at over \$14,460,000. A most notable gain is recorded in the figures for condensed milk during the past year, the amount and value of the product being nearly seven times larger than it was in 1915.

This section of the United States is still committed to the extensive system of cultivation. Commercial fertilizers, if indeed any fertilizers, are but little used. But little attention in a practical way is given to soil analysis and conservation. The farmer is, however, concerned with all those methods of cultivation aiming to conserve the moisture; with all the new crops suitable for the region; with improved machinery to reduce costs of farm operation and with the best and most profitable breeds of live stock. How long these virgin soils will respond with their natural fertility under present systems of cultivation remains to be seen. Already greater and greater demands are being placed upon the soil. For increasing yields, resort must be had to more and more intensive methods of cultivation.

The general opinion prevails that the wealth of the surrounding territory is embodied largely in the products of the wheat, corn, live stock and other agricultural belts. Few, unfamiliar with the region, appreciate the rapid industrial expansion which the district has made in the past ten or fifteen

	KANSAS, 1916		OKLAHOMA, 1916		MISSOURI, 1917	
	Yield (Bu.)	Value	Yield (Bu.)	Value	Yield (Bu.)	Value
Wheat.....	99,384,760	\$134,615,307	27,841,378	\$40,007,501	26,475,327	\$38,400,000
Corn.....	62,127,191	51,886,272	55,769,404	42,391,950	220,335,191	123,640,144
Oats.....	29,177,688	14,199,056	16,880,288	8,346,212	24,148,135	9,006,452
Barley.....	6,049,777	4,206,175		956,000	11,917	10,129
Rye.....	737,271	769,895			192,250	171,102
Cotton.....			628,685 Bales	\$1,011,955	23,478,492	2,512,199
Kafir.....	5,095,052	4,988,078	9,974,074	916		
Milo.....	1,188,482	1,163,996	4,316,597	3,214,630		
Sorghum.....	3,088,005	11,281,760	511,601	3,540,583		
Alfalfa.....	3,581,201 Tons	30,907,618	856,622	9,598,795		
Hay.....	1,648,965	11,280,422	182,223	1,430,042	4,386,385	39,117,508
Broom Corn.....	4,796 "	790,984	40,900	6,112,500	1,066,515	53,858
Irish and Sweet Potatoes.....	4,653,819	1,271,643		1,134,786	5,104,000	2,960,320
Peanuts.....			458,692	412,822		
Dairy Products.....		12,007,965				
Total Value of All Farm Products...		\$371,188,476		\$177,504,262		\$119,818,848

years. The increase in values of manufactured products has been stimulated by the development of great oil and gas fields and by those industries which have been made possible by cheap fuel.

INDUSTRIES

According to the last census, slaughtering and meat packing, with flour and grist mill products, made up about three-fourths of the total value of the manufactured products of the State of Kansas. The industry of slaughtering and meat packing owes its development chiefly to the fact that the district lies in the heart of the corn belt of the United States, to the low cost of winter-keep where live stock grazes on fields of winter wheat and cured grasses, and to the extensive introduction of alfalfa. This section accordingly is unsurpassed for stock-raising by any equal area in the country.

The census of 1910 credited 12.1 per cent of the total value of the slaughtering and meat packing products of the United States to the State of Kansas, and only one state, Illinois, ranked ahead of Kansas in this respect. The 35 establishments gave employment to 24 per cent of the average number of wage-earners and reported products valued at \$165,000,000. All of the principal packers have large establishments in Kansas City, Kansas. After Chicago, the local industries are the largest units in the United States. One of these concerns reports 45 edible and 24 inedible products in the category of their output.

An industry ancillary to that of meat packing with all its varied by-products, that of soap-making, is gradually becoming one of the most permanent and important of the immediate locality. Receiving their chief raw materials from adjacent packing and rendering establishments, the concerns engaged in this industry are to-day manufacturing a substantial output. Peet Brothers (manufacturers of soaps and glycerin) and Proctor and Gamble have both large, well equipped, up-to-date factories in Kansas City, Kansas. While no definite statistics are available, it is estimated that probably 15,000 to 16,000 boxes of soap are daily produced. Besides soap, glycerin should also be mentioned as an important product.

The flour and grist mill industry is second in importance among the manufacturing industries of the Zone. Due to its first rank as a winter wheat producing state, Kansas ranks third among the states of the Union in the value of flour mill and grist mill products. There are at present over 500 milling establishments in the state.

PETROLEUM

The preliminary estimates of the United States Geological Survey indicated the quantity of crude petroleum produced and marketed in the oil fields of the United States in 1916 at 292,000,000 barrels.¹ Later figures place the total production for 1916 at 297,000,000 barrels.

The Mid-Continent, or Oklahoma-Kansas field produced 122,671,767 barrels, consequently figures which are 41 per cent of the United States product for 1916. About 40 per cent of

assigned to California and the remainder (30 per cent) to the Appalachian, Lima-Indiana, Texas, and other fields. As nearly as can be ascertained, taking the amount of crude oil in storage, the average pipe-line runs and the estimated amount of oil shipped to scattered consumers, computations show the oil production of Kansas in 1916 to be 11,530,478 barrels. The potential production of Kansas at the present time is approximately 100,000 barrels per day.¹

PETROLEUM INDUSTRY OF THE UNITED STATES—PRODUCTION IN 1916 (Oil, Paint and Drug Reporter, Feb. 9, 1917, 91, No. 7, 85)

Fields	1916		1914	
	20 Million	20 Million	20 Million	20 Million
Eastern.....	20	20	22	22
Ohio-Indiana.....	16	15	15	15
Illinois.....	16	15	15	15
Kentucky-Tennessee.....	1	1	0.516	0.516
Mid-Continent.....	122,671,767	121,988,915	101,002,263	101,002,263
Gulf Coast.....	21	20	20	20
Texas Panhandle.....	8	8	8	8
Northern Louisiana.....	11	11	12	12
California.....	91	89	89	89
Wyoming.....	8	8	8	8
Other States.....	0.205	0.2	0.180	0.180
Total.....	306,297,760	298,187,631	287,119,667	287,119,667

Oklahoma's crude production for 1916 amounted to 111,741,280 barrels, or a total for the two states (as previously stated) of 122,671,767 barrels for the year.¹ Up to the present time the total production for the Mid-Continent field since its discovery on the introduction of pipe lines in 1900 has amounted to 762,174,158 barrels, of which 47,829,947 are credited to Kansas and 714,334,211 were credited to Oklahoma.

PRODUCTION OF THE MID-CONTINENT FIELD SINCE 1900 (Oil, Paint and Drug Reporter, Feb. 9, 1917, p. 107)

Pipe Lines	Kansas	Oklahoma	Total
Prior to 1900.....	438,000	4,125	452,125
1900.....	68,000	6,100	74,100
1901.....	165,000	10,000	175,000
1902.....	200,000	10,000	210,000
1903.....	941,000	140,000	1,081,000
1904.....	4,236,000	1,367,000	5,603,000
1905.....	3,892,000	8,441,000	12,333,000
1906.....	5,418,000	18,400,000	23,818,000
1907.....	5,311,000	41,800,000	47,111,000
1908.....	2,473,000	41,800,000	44,273,000
1909.....	1,011,000	41,800,000	42,811,000
1910.....	1,111,000	41,800,000	42,911,000
1911.....	2,907,000	41,800,000	44,707,000
1912.....	18,000,000	41,800,000	59,800,000
1913.....	11,000,000	41,800,000	52,800,000
1914.....	3,850,000	97,342,000	101,192,000
1915.....	4,115,000	112,817,000	116,932,000
1916.....	11,838,000	111,141,280	122,979,280
Total.....	47,829,947	111,741,280	159,571,227

The stock of oil in storage in the Mid-Continent field at the end of 1916 increased to 27,774,128 barrels, a gain of over 2 million barrels, practically the amount put in storage by the latter country prior to 1916. Oklahoma had increased her stock over 26 million barrels in storage at the end of the year.¹

CRUDE OIL

More oil wells were drilled in the Mid-Continent field in 1916 than in any previous year amounting to 10,000 in 1916.¹ It was

¹ Eng. and Min. J., Jan. 6, 1917, p. 30.

² Oil, Paint and Drug Reporter, Feb. 9, 1917, p. 85.

wells were drilled in the past year: 7601 in Oklahoma and 3640 in Kansas.¹ The rise in price of crude oil to \$1.55 led to rapid drilling and with market quotations such as these, extraordinary prices were paid for leases, wild speculation followed, and test holes were drilled immediately.

In the beginning of 1916 there were 3,848 producing wells in Kansas and at the end of the year there were 5,476 producing oil in the State, connected with pipe lines. Others should be added, including some of the large producers, which as yet have not been connected with any pipe lines. This increase of wells again shows the rapidity with which the Kansas division of the field has advanced during the past year.

In three years from January 1, 1914, to January 1, 1917, the number of producing wells in the Mid-Continent region has increased from 20,256 to 43,417 which graphically tells the story of the wonderful development of this remarkable oil field.²

Of the 11,241 wells drilled in the Mid-Continent field in 1916, 9,274 were successful oil producers, 476 were gas wells, and 1,491 were failures. This was the largest number of producing wells ever drilled in a single year in the Mid-Continent field. It is significant also that while the largest number of successful oil wells in the history of the field were drilled last year, the actual yield of the field was also the largest in its history.

WELLS DRILLED IN THE MID-CONTINENT FIELD
(Oil, Paint and Drug Reporter, Jan. 6, 1917, p. 109)

	In Kansas	In Oklahoma	Total for Mid-Continent Field
1905.....	1488	2535	4023
1906.....	730	3146	3876
1907.....	486	4234	4720
1908.....	473	3021	3494
1909.....	510	3340	3850
1910.....	486	4370	4856
1911.....	511	4445	4956
1912.....	1012	5982	6996
1913.....	2180	9314	11494
1914.....	2394	8259	10653
1915.....	1123	4725	5848
1916.....	3640	7601	11241
Total for the Field.....			81154

CHARACTER OF WELLS DRILLED IN 1916

	Oil	Gas	Dry	Total
Kansas.....	3167	116	357	3640
Oklahoma.....	6107	360	1134	7601
Mid-Continent Field.....	9274	476	1491	11241

One other feature of this remarkable field should receive our attention. Of the 81,154 wells drilled in this territory since the beginning of operations, 43,417 are still producing after fifteen years, indicating that 37,737 were either gas, dry, or have since become exhausted.³

When it is remembered that this field has been in active production for fifteen years or more, this is a remarkable record: 53.5 per cent of total wells still drilling and only 46.5 per cent gas, dry or exhausted.²

It is significant also that in 1916, with the vast amount of wild-cat drilling in all parts of Oklahoma and Kansas, 86.7 per cent of all wells drilled were successful oil or gas producers.

OIL REFINING

Of the 302 refineries in the United States—with a daily capacity of one million barrels crude oil—the Mid-Continent field has 74, or 24 per cent, 71 of these being independent companies and 3 Standard Oil companies.⁴ This is exceeded only by California with 76, 57 only of which are active and 19 idle. The Standard has invested \$8,000,000 or more in their three refineries at Neodesha, Kansas, Sugar Creek, Missouri, and Norfolk, Oklahoma. Their capacity of crude oil consumption per day is given at 60,000 barrels. The 71 independent refining companies, of which the Sinclair Syndicate, the Doherty Syndicate, Cosden & Co. and the International Refining Com-

pany are most prominent, have invested over one hundred million dollars in their plants. They utilize over 150,000 barrels of crude oil per day. The refining operations of the field represent then, for all concerns, an investment of \$111,099,720 in 74 plants, with a total daily consumption of 213,815 barrels of crude oil.¹

This gives the Mid-Continent field, in capital invested, plants, and output, about one-fourth of the refining business of the whole United States.

MID-CONTINENT REFINING, 1916
(Oil, Paint and Drug Reporter, Jan. 6, 1917, pp. 113, 115)

	Approximate Investment	Daily Average Crude Used in 1916 (Barrels)
71 Independent Companies (all since 1904-5)....	\$99,599,720	148,815
Independent Plants now Building.....	5,000,000	5,000
Total Independents.....	\$103,099,720	153,815
3 Standard Refineries (Standard Group).....	8,000,000	60,000
Final Total.....	\$111,099,720	213,815

	Built	Investment	Daily Consumption
STANDARD REFINERIES:			
Norfolk, Okla. (Carter Oil Company) 1916		\$3,500,000	40,000
Neodesha, Kans. (Standard Oil)..... 1892		1,500,000	7,500
Sugar Creek, Mo. (Standard Oil).... 1907		3,000,000	12,500
		\$8,000,000	60,000

Attention has been called to the profitability of refining this Mid-Continent oil due to the high yield of gasoline, often as high as 30 per cent, which percentage depends very largely on methods of distillation, whether oil is fresh or stored, and the variations in crudes of the same pool.

NATURAL GAS

Closely associated with the oil production of this territory is that of natural gas. The importance of this natural gas belt in localizing and developing the zinc, cement, and glass industries in a definite district cannot be overemphasized. The near-by supply of cheap gas has made possible and profitable these industries in Kansas and Oklahoma. These states, according to the latest authoritative figures available (1914), produced 22,627,507,000 and 78,167,414,000 cu. ft., respectively, a total of 100,794,921,000 cu. ft.²

The total natural gas production for the United States for the year was estimated at 591,866,733,000 cu. ft. This would credit the Oklahoma-Kansas field with about 18 per cent of the supply of the United States. Oklahoma and Kansas are exceeded only by West Virginia, Pennsylvania, and Ohio in the supply of natural gas.

The annual value of this important fuel in this district is placed at nearly \$12,000,000 and was utilized by 230,104 domestic consumers and 3030 industrial plants. A substantial portion of this gas was piped out of the states and consumed in Missouri.²

A recent state investigation by the Kansas Academy of Science made by Mr. W. W. Swingle—perhaps the most recent data available—shows that Kansas alone in 1916 produced over 25,000,000,000 feet of gas (25,402,521,000).³

NATURAL GAS PRODUCED IN 1914 (M. CU. FT.)
("Mineral Resources of the United States," 1914, pp. 751 to 781)

	M. Cubic Feet	Producers	Domestic Consumers	Industrial Consumers	Value
Total for U. S.....	591,866,733	555	187,714	1,079	\$94,000,000
Kansas.....	22,627,507	353	62,390	1,951	3,300,000
Oklahoma.....	78,167,414	437			8,000,000
Total for Kan. & Okla.	100,794,921	790	250,104	3,030	\$11,300,000

	Productive Dec 31, 1913	Gas	Dry	Total	Abandoned in 1914	Productive Dec 31, 1914
U. S.....	33,348	3,846	1,406	5,142	2,088	38,093
Kansas.....	2,227	448	249	664	481	2,261
Oklahoma.....	1,082	388	182	570	235	1,205

¹ *Eng. and Min. J.*, Jan. 6, 1917, p. 24.

² "Mineral Resources of the United States," 1914, p. 751.

³ *Topeka Capital*, March 8, 1917.

¹ *Oil, Paint and Drug Reporter*, Jan. 6, 1917, pp. 113, 115.

² *Ibid.*, Jan. 6, 1917, p. 109.

³ *Ibid.*, Jan. 6, 1917, p. 107.

⁴ *Eng. and Min. J.*, Jan. 6, 1917, p. 23.

PORTLAND CEMENT

Kansas ranks third in number of cement plants, there being 10 within the state, which is exceeded only by Pennsylvania with 20 and Michigan with 11. The output of these 10 active establishments in 1914 was 3,431,142 barrels, valued at \$3,180,669.

GLASS

The development of the glass industry in this part of the country is, like zinc and cement, due to the available supplies of natural gas, a cheap and particularly desirable fuel for this purpose. Starting about fifteen years ago the industry has gradually grown, in varying sized plants, throughout the gas belt. The last census placed Kansas eighth in rank in the value of its glass products.¹

GYPSUM

The demand for gypsum in the crude form for manufacturing Portland cement, and in other forms for paint, for land plaster, and for calcined plaster, is a steady and growing one. Kansas mined 80,774 tons of raw gypsum in 1914 and possesses four gypsum establishments or mills. Oklahoma mined 113,103 tons and had six establishments. The Kansas product is mostly calcined, the form of greatest value, and is utilized for wall plaster, plaster of Paris, etc.: 47,877 (short) tons of calcined plaster were marketed from Kansas in 1914, and the value of all gypsum products was estimated at \$278,343. Oklahoma's product was worth \$312,856 or a total value for the two states of \$591,199.²

SALT

Another resource, but of greater value, deposited with gypsum in this territory, due to the withdrawal or evaporation of the sea, is salt. Kansas is one of the four states credited with the production of salt, and has ranked fourth at the last three censuses in the value of this product.³ The state maintains this rank both in the quantity and value of salt marketed in 1915. Michigan, New York, and Ohio are the only states which exceed Kansas in production, with 12,000,000, 11,000,000, and 5,000,000 barrels, respectively. Kansas produced in 1915 3,765,164 barrels, valued at \$1,035,879, or about 10 per cent of the output, and approximately 20 per cent of the value of salt produced in the United States. (38,231,496 bbls. were marketed in the United States in 1915 valued at \$11,747,686.)⁴

The ten salt-producing plants, including brine and rock, are located in the central part of the state. Four of these mine rock salt. Evaporated salt production is centralized at the city of Hutchinson, with other establishments at Lyons, Anthony and Sterling. Deep wells are sunk to the salt beds often hundreds of feet below the surface, water is forced down to the beds and then pumped to the surface where the brine is evaporated. Open pans, grainers, and vacuum pan methods are used.

According to a recent report of the United States Geological Survey,⁵ 600 feet of rock salt have been encountered by the Short Grass Oil and Gas Company, in Clark County. The top stratum, 60 feet thick, was struck at a depth of 690 feet and was capped with 12 feet of limestone. The next lower bed 153 feet thick was separated from the first by a thin bed of limestone. Below these the beds varied in thickness from 5 to 30 feet. No water was encountered from 500 to 2900 feet. From 3300 to 3700 feet a great deal of strong brine was encountered, making casing necessary to that level.

Incidentally in this connection should be mentioned the Solvay Process plant located at Hutchinson, Kansas, the only establishment of this character in this part of the country. Sodium chloride, constituting of course the main raw material,

is converted into sodium bicarbonate or cooking soda. Present conditions and outlook seem to promise a substantial and increasing market for the output of this establishment. Mention should also be made of the demand for sodium carbonate in the adjacent territory for glass and soap manufacturing, for paper making, and for water softening processes.

CLAY PRODUCTS

Omission should not be made of the valuable clay products, and their potential possibilities, which this region affords. As time goes on these resources are destined to become more and more valuable. For Kansas alone their value, as last reported, was estimated at \$1,905,961.¹ Vitrified brick constituted the principal output, and was 31 per cent of the value of all clay products. Over 40 establishments, rather widely scattered, were producing vitrified, common, front, fancy, and fire brick; drain tile, sewer pipe, terra cotta, tile, and stoneware. The adaptability of the available fuels of the district, particularly gas, for this special form of industry, is apparent.

The desirability of these bulky and yet very valuable products in a commonwealth is evident to all. They are absolute essentials in the life of any settled community. Their great weight and bulk and relatively low value per unit precludes their shipment by rail unduly long distances. Instead of foregoing, in a measure, their consumption or being subjected to well-nigh prohibitive freight rates, the Kansas City Zone is abundantly supplied with all of these products which make for the increased diversification and satisfaction of material wants.

KANSAS CITY A LOGICAL MUNITION CENTER

In these belligerent times our attention is called to the fact that Kansas City is one of the logical munition centers of the United States.

The fats and oils derived from the packing plants and the cottonseed from adjacent states are making for the rapid development of soap manufacturing. Glycerin being a by-product of soap-making, one element, and a very important one, is here present for manufacturing of explosives. Close by, the roasting of zinc sulfide, the so-called blend or concentrates, leads, of course, to great possibilities in the production of sulfuric acid. It only remains to combine the two constituents thus produced here in increasing quantity, namely, glycerin and sulfuric acid, with nitric acid to furnish a substantial output of nitroglycerine, the basis for explosives and munitions.

For use in zinc and lead mining we observe these acids and glycerins produced locally, being shipped separately in bulk to the Joplin district, there to be combined into explosives suitable for mining operations. Glauber's salt is also sent in quantity to the glass factories of Kansas there to be mixed with sands, etc., in the making of glass.

POTENTIAL INDUSTRIES

A discussion of industries and resources would not be complete without at least passing reference to what many, qualified to judge, designate as potential industries of the Kansas City Zone.

The enormous quantities of wheat, corn, potatoes and canes, which are and can be produced, suggest the great possibilities of starch production in this territory. These same raw materials can also be made the foundation for enormous outputs of industrial alcohol, which is so rapidly becoming a basic and primary product the country over.

The great supply of hides from packing plants has suggested possibilities in the establishment of tanneries in various centers. It is maintained that tanning extracts or powders might profitably be shipped into this territory from bark-producing sections and at less expense than is incurred in transporting the heavy raw hides to the present tanneries. What the future holds for such an enterprise here remains to be seen.

¹ "Mineral Resources of the United States," 1914, p. 500.

¹ "Census of Manufactures," 1910, p. 681.

² "Mineral Resources of the United States," 1914, p. 261.

³ "Census of Manufactures," 1910.

⁴ "Mineral Resources of the United States," 1914, p. 291.

⁵ *Ibid.*, p. 265.

Similar suggestions are frequently made regarding the possibilities for cotton and woolen manufactures and the exceptional facilities for similar textile plants, due to unequaled railway connections which the district affords. Apparently their absence is primarily due to unavailable capital, and even more, perhaps, to a lack of the particular qualities and training of an industrial population adapted to these special industries.

With all the economic activities and possibilities which Kansas City territory possesses in the production of many concrete goods, partially or completely made ready for consumption, our survey would not be complete without attention being called to the facilities for moving and financing the products of these expanding enterprises.

The Kansas City Zone is served by a railway net which, with its management, is doing its part with deserving credit to facilitate the transportation of all these products from farms and mines and factories. Kansas City enjoys the schedules and rates of Missouri River basing points, and the radiating lines serve the territory and all interests concerned with uniform satisfaction. It can be maintained, I think, that in no section of the United States are the railroads doing more to cooperate with the legitimate enterprises of a territory than here in the Kansas City Zone.

Similar recognition should also be given to the banking facilities of Kansas City and the surrounding towns. Here is located one of the Federal Reserve Banks and also some of the strongest National Banks of the country. Here was early and successfully established a system of country clearings. The agricultural communities are particularly well supplied with banking facilities as evidenced by the exceptionally large number of state and national banks in all the smaller towns and cities and their universal patronage. Again, the vital connection and sympathetic cooperation of these financial institutions with the productive enterprises of the territory are fortunately one of the conspicuous features of our expanding economic life. Nowhere in the United States is banking on a more democratic basis.

In conclusion, one cannot refrain from here expressing and emphasizing the opinion that after all other explorers and exploiters have passed in review before us, last of all must come

warnings, all too little heeded. More and more we must call upon science to supplement the obvious gifts of nature and to reveal the wealth of materials and supplies which she has hitherto concealed.

But to apply scientific methods, funds, and increasing funds, of capital are necessary to utilize or make available the more productive, round-about methods of production. Contrary to the oft-repeated popular opinion, most industries are to-day undercapitalized. Scientific discoveries are outstripping the supplies of capital in the race of achievement. What sums of capital might not be utilized to-day were they only available!

The "hurtful forcing process" may be socially and economically undesirable if accompanied by wastes of natural resources, but the forging ahead of scientific discovery and utilization must ever be encouraged and kept far in advance in the procession.

The physical scientist and the economist unite, I am disposed or at least venture to think, in substantial agreement on this proposition: The world stands more and more in need of scientific discovery, while on the other hand nothing is more apparent than the necessity of increasing the funds of capital, coupled with intelligent business direction, to give life and effectiveness to these discoveries.

In the march of economic development, Science must blaze the way, and adequate supplies of Capital must support its programs. Assuming the brains to direct them, Science will determine the course of our future material achievements and Capital the degree of their realization.

UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

THE NEW ZINC FIELDS OF KANSAS-OKLAHOMA

By WINTHROP P. HAYNES

Received May 11, 1917

A short night trip by rail from Kansas City takes one into the heart of the largest zinc-producing district of the Central States, and of the United States too, for that matter, because statistics of production for 1915 credit the Central States with



FIG. 1. DEVELOPMENT IN THE LEADERS NEAR PIERCE

the greatest of all adventures. Science. Pioneering days of the old order are past. More and more the necessity of the methods of science become apparent in the exploitation of productive processes. The great, you please, rule of thumb, hit-or-miss method of knowing the artifice, with all their incidental wastes, are fortunately gone, here as elsewhere, and passing, we hope, forever. This present national crisis is but the last of

17 per cent of the smelter production of the United States, and places Missouri at the head of the list of the states producing pig-iron metallic zinc.

The Joplin district, located in eastern Missouri, produced 13.5 per

cent of the total production of the United States, and places Missouri at the head of the list of the states producing pig-iron metallic zinc.



FIG. 2—PICHER, OKLAHOMA: A BOOMING ZINC TOWN, JAN., 1917

its place in the front ranks of the zinc-producing region but public interest is now being diverted to the Southwest into the new field.

We shall, therefore, pass from the great dumps and extensive underground workings of the Webb City-Cartersville



FIG. 3—DRILLING RIGS PROSPECTING FOR ZINC ORE NEAR PICHER



FIG. 4—DEVELOPMENT NEAR ADMIRALTY, OKLA., JAN., 1917



FIG. 5—WELSH CONCENTRATING MILL, ADMIRALTY, OKLA.

regions, which have been so long established that there is only the routine development work on ore which does not interest us, and go by auto to the eastward from Joplin through Galena, Kansas, with its many old abandoned workings and great dumps, on to the South through Baxter Springs, Kansas, where we see many autos with parties of men driving about as if bent

on important business. Star drilling rigs are seen scattered over the country and they become more numerous as we approach the Oklahoma line. Near the State boundary are some new mills under construction. Others are already in operation, and we realize that we are in the new zinc fields at last. We go about two miles south into Oklahoma to what looks like a large city with many tall buildings, but find that it is really the town of Picher, which has had a wonderful growth in the past few months and is daily spreading out into the prairie. New concentrating mills of galvanized iron are being built, shafts being dug, and drilling going on (see Figs. 1 and 2). Small wooden shacks and prairie schooners cluster about the borders of the town, and have spread so far that they merge with the neighboring town of Admiralty, which shows the same mushroom-like growth.

It is a very inspiring sight to one who is used to seeing things old and stable, to get into a real boom town and observe the rush and hustle of all the people. We realize that this is part of the old Indian Territory where the Indians were given land at one time considered of little value. Now there is great effort to lease the land, and many of the Indians are very well off from their leases and royalties on production. The rows of small portable drilling rigs of the Star type first interest the visitor (see Fig. 3). They are prospecting the leases to determine the depth of the ore body and its thickness and extent. By systematic drilling a fairly accurate estimate of the amount of ore can be made, and thus this development work is removed from a gambling chance to a fairly safe mining proposition. The depth of drilling is comparatively slight, being in the neighborhood of 300 feet, and so the expense of this thorough prospecting is not great. The large number of concentrating mills indicates to a certain extent the number of small companies operating. It also indicates the great demand and high price paid for the zinc at the present time (see Figs. 4 and 5).

GEOLOGIC FORMATION AND STRUCTURE

The rocks which outcrop at the surface of this region consist of shales and limestones of late Paleozoic age. The western part of the district contains rocks of Pennsylvanian age which are represented on the map (Fig. 6) by diagonal shading. In the unshaded part of the map the rocks at the surface are of Mississippian age. Numerous wells, shafts, and drill holes have furnished data in regard to the strata below the surface. A vertical columnar section in northwestern Oklahoma¹ gives us the succession of strata shown in Fig. 7. The region lies on the northwestern flank of the Great Ozark uplift and therefore the strata have a general dip to the west and northwest.

ORES

The lead and zinc minerals which are being mined in this region are chiefly the sulfides: galena, PbS; and sphalerite, ZnS; but some of the oxidized ores, carbonates and silicates, nearer the surface, are also being used. In this district sphalerite is much the most important ore. These minerals are all

¹ Oklahoma Geological Survey, Bull. 9 (1912).

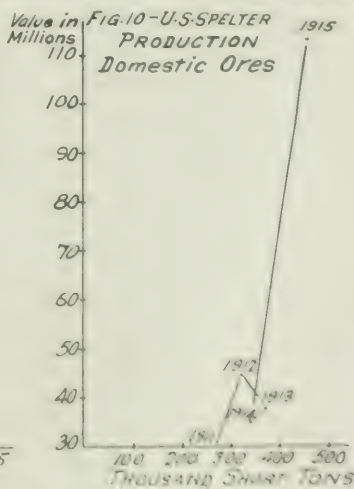
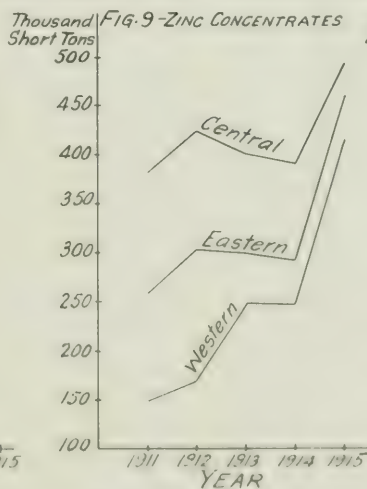
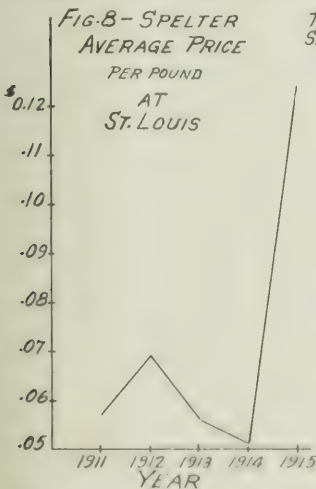


FIG. 6

found in the Boone formation (chiefly the cherty middle member), and occur in two forms: the common type being known as the "sheet ground" deposits, or "blanket veins," which are developed parallel to the bedding planes of the strata in which they occur, and often have great lateral extent; and the "runs" which are inclined and located in disturbed zones in the strata. The ore in the "runs" is usually of much higher grade than that in the "sheet ground," but the "runs" are of much less extent.

ORIGIN

A great many eminent geologists have worked on the problem of the origin of these ores, but no perfectly satisfactory theory



has been evolved as yet. The theories up to date may be grouped under three different heads. They are: (1) that the minerals were deposited by ascending waters; (2) that they were deposited by descending waters; and (3) that they were deposited by ascending and later concentrated by descending waters. The presence of small amounts of these minerals in the formations above and below the Boone chert would favor any of these

theories. The latest and most detailed work on this subject is by Mr. C. E. Siebenthal,¹ who believes that the circulation of the underground waters in this district has been upward, and that the ore minerals were concentrated from the scattered minerals chiefly in the Cambrian and Ordovician rocks.

PRODUCTION

The increased production of metallic zinc (spelter) in the United States since the outbreak of the war and its great increase in value is well shown by the accompanying diagrams: Fig. 8 shows the enormous jump in the average price of spelter from 1914 to 1915, and this high price has kept up to the present time. Fig. 9 shows the increased production of all of the groups of the states, with the beginning of the war, and the greater demand for zinc. Fig. 10 shows the relations of the production to the increased value for these same years. The figures on the production for the year 1915 show that the Joplin district produced 643,380,000 lbs. of zinc concentrates valued at \$23,419,103, and 329,088,000 lbs. of metallic zinc valued at \$40,806,912. The Joplin sphalerite concentrate ores average more than 57 per cent of zinc, while those from Montana average about 45 per cent; those from other places are lower than this. There was an increase of nearly 50 per cent in the quantity of zinc and zinc-lead ores treated in 1915.

CONCLUSION

Unquestionably this new zinc district has a much higher grade ore than that of the Joplin region, as seen from the ore being run through several of the large mills at Admiralty and Picher. It is from 15 to 20 per cent sphalerite. This means that great profit can be made even with rather expensive and careless handling of the ore.

When the price of zinc drops with the decrease in demand after this war, it will be necessary for these many small companies

with their multitude of mills to consolidate and go down to the maximum production and minimum cost, which will enable the older mines of the Joplin district to operate profitably with their rather low grade ore.

UNIVERSITY OF KANSAS
LAWRENCE, KANSAS

U. S. Geological Survey, No. 606 (1915)

THE LEGAL STATUS AND THE CHARACTER OF WORK DONE BY THE KANSAS STATE BOARD OF HEALTH WATER AND SEWAGE LABORATORY¹

By C. C. YOUNG

Since the foundation of the Chemistry Department at the University of Kansas, water analyses had been made by Professor Bailey and members of his department and considerable systematic work done by Professor Bartow and others, but it was not until 1906 that any real survey of the waters of the State of Kansas was attempted. At that time, an investigation of the quality of Kansas waters was prosecuted under a joint agreement between the Kansas State Board of Health and the United States Geological Survey, Horatio N. Parker representing the Geological Survey and Dr. E. H. S. Bailey, of the Chemistry Department of the University, representing the State Board of Health.

The funds available for this investigation were limited, but a very satisfactory report was made in *Water Supply Paper 273*.

As the organic law of the State provides that all scientific work of the State Board of Health shall be done at the University, the headquarters were naturally provided by the Board of Regents.

From October, 1906, to February, 1908, the work in the laboratory was carried on by Dr. F. W. Bushong and Archie J. Weith.

So much educational work had been done by Mr. Parker in the field with its coincident newspaper notices that a demand grew up among the people of the state for examinations of their water supplies. About this time, the Legislature passed the first of the water and sewage laws, which gave over to the State Board of Health supervision of water supply and sewage, including the purification of water and treatment of sewage. This necessitated some laboratory facilities for the Engineer of the State Board of Health. Consequently, it was found impracticable by the University to discontinue the Water Laboratory, which had been founded for the work done in conjunction with the United States Geological Survey.

When I came to the University in 1908, the water analysis was assigned to me as a portion of my work in the Chemistry Department. As in the history of all such organizations, the demand became so great that funds were not available to meet the wants of the citizens of the state. Although each year an increase was made in the appropriations, they could not keep pace with the demands. At the same time the work was growing in the Chemistry Department, the Bacteriological Department of the University was going through a similar experience with regard to bacteriological analysis of water.

In 1912, the United States Public Health Service and the State Board of Health instituted a joint survey of the Missouri River, calling upon both the Chemistry and the Bacteriological Departments of the University for laboratory studies. Following this work, a union was effected between the Chemistry and Bacteriological Departments forming a Water Laboratory of the University of Kansas, which was to do such work as the State Board of Health required and make a study of the sanitary water conditions of the state.

In a short time this organization was rendered ineffective on account of lack of sufficient funds to meet the ever-increasing demands for routine examinations of water supplies, so in 1915 a proposition was put before the Board of Administration of the University of Kansas whereby a bill was to be introduced founding a Water and Sewage Laboratory of the State Board of Health, and providing for the support of the Laboratory by fees collected for the analyses, and as it was intended to abandon the work on account of this condition, it was fortunate that this bill became a law.

The law as finally passed is as follows, with the rules and regulations that were drawn up and approved by the State Board of Health and Board of Administration.

RULES AND REGULATIONS OF THE STATE BOARD OF HEALTH FOR THE COLLECTION OF SAMPLES AND ANALYSIS OF WATER¹

Session Laws of 1915—House Bill No. 503

AN ACT giving the State Board of Health power to require analysis of waters furnished or sold to the public, and to provide rules and regulations for said analysis and collection of samples of water, and to prescribe penalties for the violation of said rules and regulations.

Be it enacted by the Legislature of the State of Kansas:

SECTION 1—That the State Board of Health shall make and publish, in the official state paper, rules and regulations for the collection of samples and analysis of water, either natural or treated, furnished by municipalities, corporations, companies or individuals to the public, and shall fix the fees for any services rendered under said rules and regulations to cover the cost of the services, which fees shall be approved by the State Board of Administration before they become operative.

SECTION 2—The analysis of all waters required in the rules and regulations shall be made at the Water and Sewage Laboratory of the State Board of Health in the University of Kansas, and the fees collected under the provisions of this act shall be turned into the state treasury for the benefit of said laboratory of the University of Kansas.

SECTION 3—That every corporation, railway, common carrier, company or individual that shall fail to comply with the rules and regulations prescribed by the State Board of Health under this act shall be deemed guilty of a misdemeanor and upon conviction shall be fined not less than \$50 nor more than \$500.

SECTION 4—This act shall take effect and be in force from and after its publication in the official state paper.

RULES AND REGULATIONS GOVERNING COLLECTIONS OF SAMPLES AND ANALYSIS OF WATER FROM CITY SUPPLIES FURNISHING GROUND WATER TO THE PUBLIC

1—A complete sanitary inspection of city supplies furnishing ground water shall be made by a representative of the Division of Water and Sewage of the State Board of Health at least once each year and samples collected for analysis. Samples so collected shall be subjected to a complete analysis at the Water and Sewage Laboratory of the State Board of Health, including microscopical, bacteriological, sanitary, chemical, and mineral examinations.

2—A second sample shall be collected, according to directions sent out by the Water and Sewage Laboratory of the State Board of Health, by city officials, waterworks officials, or other persons authorized by the Secretary of the State Board of Health, upon receipt of container from said Laboratory, and shall return said container within one week from date of receipt.

3—Results of these analyses with any pertinent remarks and advice shall be reported to the person whose name is signed to the information blank and to the Secretary of the State Board of Health.

4—As many additional analyses shall be made as are deemed necessary by the Engineer of the State Board of Health to show the quality of the water.

(1) Analyses of proposed city supplies shall be made upon request to the Water and Sewage Division of the State Board of Health.

5—Fees for service rendered under these rules and regulations for ground water supplies shall be payable July first of each year to the Director of the Water and Sewage Laboratory of the State Board of Health at the University of Kansas, Lawrence, Kansas.

¹ Presented at the Kansas City Meeting of the American Chemical Society, April 10 to 14, 1917.

¹ Published in the Topeka State Journal, June 14, 1915.

6—Fees have been fixed, based upon the population of the cities. The population of a city shall be taken from the preceding state enumeration:

POPULATION OF CITIES	FEES
Under 500.....	\$12.50
500-1,000.....	20.00
1,000-2,000.....	25.00
2,000-3,000.....	30.00
3,000-5,000.....	35.00
5,000-15,000.....	40.00
15,000 and up.....	50.00

RULES AND REGULATIONS GOVERNING COLLECTIONS OF SAMPLES AND ANALYSIS OF WATER FROM CITY SUPPLIES FURNISHING SURFACE WATER TO THE PUBLIC

(2) Analyses of chemicals used in water purification shall be analyzed upon request.

1—A complete sanitary inspection of city supplies furnishing surface water shall be made twice annually, and tests of the operation of the plant shall be carried on at the time of these inspections by a representative of the Division of Water and Sewage of the State Board of Health.

2—Samples shall be collected weekly, according to directions of the Water and Sewage Laboratory, by city officials, water-works officials or other persons authorized by the Secretary of the State Board of Health from the raw and finished treated water and sent to said Laboratory for analysis in containers furnished.

3—Results of these analyses, with any pertinent remarks and advice, shall be reported to the person whose name is signed to the information sheet, and to the Secretary of the State Board of Health.

4—City officials shall be required to keep any data on the operation of purification plants that may be required by the Division of Water and Sewage of the State Board of Health. This data shall be transmitted to the Engineer of the Division upon his request.

5—Fees for the services rendered under these rules and regulations pertaining to surface water supplies shall be payable July first of each year to the Director of the Water and Sewage Laboratory of the State Board of Health at the University of Kansas, Lawrence, Kansas.

6—Fees have been fixed, based upon the population of the cities. The population of a city shall be taken from the preceding state enumeration:

POPULATION OF CITIES	FEES
Under 1,000.....	\$30.00
1,000-2,000.....	50.00
2,000-5,000.....	70.00
5,000-10,000.....	100.00
10,000 and above.....	150.00

RULES AND REGULATIONS GOVERNING COLLECTION OF SAMPLES AND ANALYSIS OF DRINKING WATER SUPPLIED BY COMMON CARRIERS

1—Sanitary inspection of the sources of supply and methods of handling water furnished by common carriers to the public within the state at points where they have privately owned supplies shall be made twice annually by a representative of the Division of Water and Sewage of the State Board of Health.

2—Samples shall be collected at the time of inspection from the sources of supply and the place where trains are watered. Samples so collected shall be subjected to complete analysis in the Water and Sewage Laboratory of the State Board of Health in accordance with the standard adopted by the United States Treasury Department for drinking water supplied to the public by common carriers in interstate commerce.

3—Results of these analyses shall be reported to the proper railroad official, to the Secretary of the State Board of Health, and to the Surgeon General of the United States Public Health Service.

4—In case a water supply furnished by common carriers to passengers in the State does not meet the requirements of the

standard of the Treasury Department, and repairs or improvements on the supply are made with the approval of the Division of Water and Sewage of the State Board of Health, one additional analysis shall be made without cost to the common carrier.

5—Railroads or common carriers shall file with the Water and Sewage Laboratory of the State Board of Health a list of all places in the State of Kansas where passenger trains are furnished with water for drinking purposes, and the said laboratory shall be notified at once in case any change is made in the source of supply or method of handling the water.

6—The fees for the services rendered under these rules and regulations pertaining to railroads or common carriers shall be payable July first of each year to the Director of the Water and Sewage Laboratory of the State Board of Health at the University of Kansas, Lawrence, Kansas.

7—The fee for analysis shall be \$30.00 annually for each place where passenger trains are furnished with water to be used by passengers.

RULES AND REGULATIONS GOVERNING COLLECTION OF SAMPLES AND ANALYSIS OF WATERS SOLD OR FURNISHED TO THE PUBLIC FOR DOMESTIC CONSUMPTION IN BOTTLES OR OTHER CONTAINERS

1—All plants for the preparation of water for sale or distribution in bottles or other containers for domestic consumption and the sources of water supply shall be inspected twice annually by a representative of the Division of Water and Sewage of the State Board of Health and samples collected for complete analysis by the Water and Sewage Laboratory of the State Board of Health.

2—Bottles or other containers in which water is sold or furnished to domestic consumers must be sterilized before refilling. The method of sterilization shall be passed upon and approved by the Water and Sewage Laboratory of the State Board of Health, subject to approval by the State Board of Health.

3—Processes of purification of waters that are to be sold or furnished for domestic consumption must be passed upon and approved by the Water and Sewage Laboratory of the State Board of Health, subject to approval by the State Board of Health, before the water can be sold or offered for sale.

4—Any company, corporation or individual outside of the State of Kansas preparing water for sale or distribution within the State of Kansas shall file full information with the Water and Sewage Laboratory of the State Board of Health at the University of Kansas, Lawrence, Kansas, as to the sources of supply and methods of sterilization of bottles, and equipment for handling the water, and shall collect samples twice each year, according to directions, in containers sent out by the Water and Sewage Laboratory of the State Board of Health, and return same at once for complete analysis, carriage charges prepaid.

5—Reports of analysis shall be made to the person furnishing the information blank and to the Secretary of the State Board of Health, and permits shall be issued by the Secretary of the State Board of Health for the sale of water based upon the results of analysis and inspection and the recommendations of the Division of Water and Sewage of the State Board of Health.

6—The fee for the services rendered under these rules and regulations pertaining to bottles and bottled waters shall be payable July first of each year to the Director of the Water and Sewage Laboratory of the State Board of Health at the University of Kansas, Lawrence, Kansas.

7—The fee shall be \$10.00 annually for each source of supply from which water is bottled.

In case a person, company, corporation or individual is found guilty of selling or distributing water in violation of the provisions of the Water and Sewage of the State Board of Health, it is provided that the

matter pertaining to the administration of the rules and regulations herein contained, he shall within thirty days have the privilege of appealing to the State Board of Health as a whole, and said State Board of Health shall approve, set aside or modify the decision of the Division of Water and Sewage.

Fees collected under these rules and regulations shall be distributed over the expenses of collection and shipping of samples, and making of analyses, under the direction of the State Board of Health, subject to the approval of the Board of Administration of Educational Institutions.

RULES AND REGULATIONS GOVERNING COLLECTION OF SAMPLES AND ANALYSIS OF ICE SOLD FOR DOMESTIC CONSUMPTION¹

1—Corporations or individuals selling artificial ice for domestic consumption shall submit to the Water and Sewage Laboratory of the State Board of Health complete information concerning the source of water supply used for the manufacture of the ice and a detailed description of the process involved.

2—A fifty (50) pound cake of ice manufactured shall be shipped to the Water and Sewage Laboratory of the State Board of Health, Lawrence, Kansas, each year for complete analysis. Results of these analyses shall be reported to the person whose name is signed to the information sheet and to the Secretary of the State Board of Health.

3—Artificial ice shall contain less than 100 bacteria per cubic centimeter and no organisms of the *Bacillus coli* group in one cubic centimeter. If the ice does not meet these requirements it shall be sold for refrigeration purposes only and not for domestic consumption.

4—Corporations or individuals harvesting natural ice shall file full information with the Water and Sewage Laboratory of the State Board of Health with regard to the source of the ice and method of storage.

5—A fifty (50) pound cake of the ice shall be shipped to the Water and Sewage Laboratory of the State Board of Health during March or April each year for complete analysis.

6—Natural ice properly stored shall contain less than 100 bacteria per cubic centimeter and no organisms of the *Bacillus coli* group in one cubic centimeter. If the ice does not meet these requirements it shall be sold for refrigeration purposes only and not for domestic consumption.

7—County Health Officers and, in cities of the first class, City Health Officers, shall furnish the Water and Sewage Laboratory of the State Board of Health with lists of ice dealers in their districts.

8—Fees for the services rendered under these rules and regulations pertaining to ice supplies shall be payable by the manufacturer or owner of the ice plant January first of each year to the Director of the Water and Sewage Laboratory of the State Board of Health at the University of Kansas, Lawrence, Kansas.

9—Fee shall be \$15 annually for each source of supply of ice which is sold for domestic consumption.

We have been operating under this law and these rules and regulations since July 1, 1915, with the result that an organization has been built up that is handling expeditiously all of the work required and it has been possible to make several investigations of more or less importance.

In addition to the routine work, each member of the staff has been carrying on some research work, which was absolutely impossible under the old régime, as ample funds were never available.

The Board of Health and the University were agreeably surprised to find that there were very few complaints against the fee proposition and no organized opposition to the law in the Legislature that just closed.

County, City and Health Officers have felt free to call upon

the laboratory to make investigations in their districts and in some instances have submitted a large number of samples for examination. The Engineers of the State Board of Health have worked in conjunction with the city officials in collecting these samples, so that the field data have been accurately and scientifically collected.

During the first year, the laboratory made approximately 6,000 complete bacteriological and 800 chemical analyses. In addition to this, we have examined a large number of filter sands, alums, limes and hypochlorites and made any other special analyses that would tend to improve the operation of water purification plants.

WATER AND SEWAGE LABORATORY
LAWRENCE, KANSAS

SOME MACHINERY EMPLOYED IN THE MANUFACTURE OF GLUE¹

By ARTHUR LOWENSTEIN

In view of the fact that most of the improvements in the glue industry—at least so far as they pertain to distinctive improvements in equipment used in the manufacture of glue in this country—have taken place largely in that portion of the industry devoted to the chilling, cutting and spreading of glue, that which follows in this paper will be limited to this phase of the subject. In other words, it is not the purpose of the writer to treat on the preparing of raw glue stocks, the chemical treatment of such stocks and their subsequent cooking and evaporation, but rather on the product after it has left the evaporator.

The progress made in the glue industry in this country has been very gradual, and most glue manufacturers have been exceedingly conservative in adopting new equipment.

The old method of handling glue after it leaves the evaporator and this method is still in use to a considerable extent, consists in running the concentrated glue solution into wood, galvanized iron or zinc pans or "coolers" (such material being used to avoid staining the jelly with rust), and chilling these pans by means of running water, or usually in a refrigerated room, after which the product is removed either by cutting or by dipping the pans in hot water. The cakes formed in this manner are then either run against wires or knives. The Clyde cutting machine when originally invented marked a distinct advance in the method of cutting glue. The Clyde machine is of the wire-cutting type, made single or double, and is probably the most satisfactory machine of this type.

In some cases the chilled glue is chopped into blocks and then each block placed in a contrivance where, by the pressure of a lever, knives or wires descend on the cake of glue and cut the block into sheets.

Knife cutters will cut heavier jellies than the wire cutters, and this is desirable during the summer period. One of the objections raised against the knife cutters is that they "do not separate tops and bottoms."

Glue jellies when cut too stiff show a roughened surface, the appearance of which is unfavorable when dried.

After having been chilled and cut by any of the methods cited, the glue is spread by hand on nets.

The old system of chilling glue requires a chilling room sufficiently large to store several days' production of glue in coolers. It has frequently been found desirable in designing a glue plant using this method to arrange the chill-room so that outside temperatures can be used when suitable. The jellies must not be kept too long in these coolers, as even at low temperatures molds develop and depreciate the quality of the glue.

The principal objections to these methods of chilling and cutting glue have been that they require (1) considerable space for cooling room; (2) an excessive amount of refrigeration where

¹ Approved by State Board of Health, October 4, 1915. Published in the Topeka State Journal, October 15, 1915.

¹ Presented at the Buffalo Meeting of American Institute of Chemical Engineers, June 20 to 22, 1917.

only a limited surface of glue is exposed to the refrigerated air, and as a result most of the heat has to be conducted to the air through the medium of the metal pans; that if the coolers or pans are made of galvanized iron they rust badly and have to be replaced; that they frequently leak, with consequent loss of product; that one has "tops" and "bottoms" which prevent

paper. So far as he knows it is used only by this one company.

Some years ago when the Bureau of Chemistry of the United States Department of Agriculture started to investigate the gelatine industry with a view to decreasing the bacterial count of commercial gelatines and to prevent metallic contamination; some manufacturers found it necessary to adopt different methods of manufacture from the very beginning, in the selection of their raw materials and particularly in their method of handling the product from its inception until it reached the final stages. Inasmuch as gelatine is a particularly good culture medium for bacteria, it was found desirable to concentrate efforts on methods which would reduce the period of time after the gelatine left the evaporator until it was converted into sheets or other finished form. The object sought was to obtain a continuous method of chilling, cutting and spreading the product without having it come in contact with agencies carrying bacteria, such as employees' hands, etc. A method of this kind was worked out and later patented by Maurice Kind under United States Patent No. 1,046,307, issued in 1912. His method consisted in running the gelatine from the evaporators into a head tank located above a continuous belt, as shown in Fig. 1. A general idea of the principles involved in connection with this machine can best be gathered, perhaps, by quoting some of the objects of this invention directly from the patent, and from photographs shown herewith. A more detailed description can be readily obtained by reference to the patent itself.

"An object of the invention is to provide an apparatus wherein gelatin or other products where heat is necessary for extraction, may be converted from a liquid state, into a semi-solid state, by means of treatment with chilled air, and thereafter cut into the desired shapes for marketing purposes.

"A further object of the invention is to provide an apparatus of the above character with means for directing chilled air onto the upper surface of the semi-solid sheet, as it is formed and passed through a cooler on a conveyor.

"A further object of the invention is to provide a device of the above character with cutters for cutting the semi-solid sheets into strips.

"A further object of the invention is to provide an apparatus of the above character with a cutting means for cutting the strips into sections, together with a conveyor for receiving said sections which conveyor is so timed in its movements as to space the sections in trays carried by the conveyor."

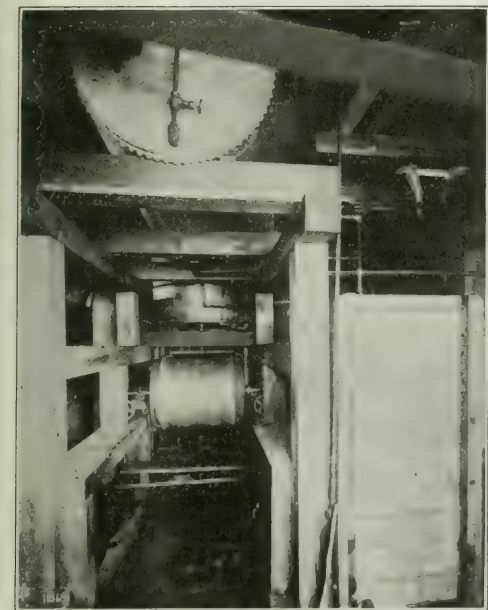


FIG. 1.—HEAD TANK AND DISTRIBUTING PIPE FEEDING THE GLUE SOLUTION ONTO THE BELT
(The large tank at the top is not part of the machine)

uniformity of product or make it necessary to put these parts into a lower grade or into some other commercial form; and that the product has to be kept so long in the coolers that in warm weather, particularly humid weather in summer, the quality of the glue is so affected by liquefying organisms that the glue maker has serious difficulty both in the cutting and drying of the glue; and finally, the labor in filling these pans and emptying them, cutting by the methods outlined, and finally spreading the product by hand on nets, is not only laborious but costly.

Because of these facts experiments have been carried on for years in the effort to secure mechanical or automatic devices of a continuous nature which would simplify the procedure and thus avoid so much loss and handling of the product. Various types of chilling rolls have been tried from time to time without success. The Cooper factory employed a chilling wheel years ago for this purpose, in which the wheel, chilled from within, picked up the liquid and chilled it, but somehow or other the process did not turn out to be practical. The writer has been informed within the last few years that one of the large glue companies had perfected a similar process, or at least to employing it commercially, in which a large wheel is employed. It is his understanding that this wheel may be 11, 16 or 18 ft. in diameter, with coned and flanged rim, using brine circulation in the rim which is supplied and circulated through stuffing boxes in the ends of the shaft. It is his understanding that the wheel spreads a sheet 30 in. wide. The writer wrote to the President of the company employing the machine, and had hoped to be able to include a cut and a more detailed description of it in this



FIG. 2.—CHILLING ROLL AND CONVEYOR SYSTEM FOR CHILLING THE PRODUCT IN A CONTINUOUS MANNER.

To sum up, this machine consists of a large wheel chilling the product in a continuous manner, the product being then spread on a net and finally spread on a tray, which is then carried by a conveyor.

and automatically cutting the gelatine into sheets of the desired size and spreading it automatically upon the usual screens employed for receiving it preparatory to drying.

This machine was perfected and was found to accomplish the desired purposes in the manufacture of gelatine. A number of glue makers learned of the use of this machine for gelatine, and about five years ago the first of these machines was installed for glue. It has been found well suited for this purpose, and capable of chilling, cutting and spreading any kind of glue which could be handled by the older methods previously outlined. As

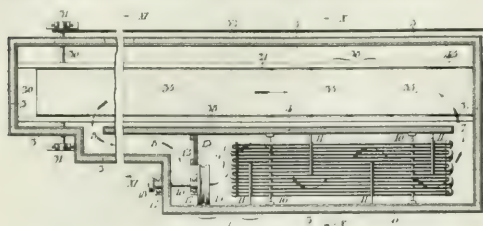


FIG. III - PLAN OF COOLING COMPARTMENT SHOWING RELATIVE POSITION OF BELT AND COILS, AND DIRECTION OF TRAVEL OF THE GLUE SPREAD ON THE BELT AND OF THE REFRIGERATED AIR

a result, a large number of both large and small glue manufacturers have adopted this machine. The manufacturers of this machine advise that it requires a floor space of about 85 ft. in length and 10 ft. in width for the installation of a single machine; that the power required to operate fan and belts is

about 10 horse-power; that it requires about 10 to 12 tons of refrigeration per machine, and that the capacity of each machine is about 4300 lbs. dry glue in a period of 20 hours, based on spreading the glue $\frac{1}{4}$ in. thick, and on a basis of glue fed to the machine containing 16 per cent solids. It is found in practice that the glue is spread on nets ready for drying, in not to exceed 15 minutes from the time the glue leaves the evaporator. Their claims for the machine are that it eliminates all of the disadvantages ascribed previously in this paper to the old methods of handling.

DRYING OF GLUE

Glue has been and is still ordinarily dried in straight tunnels with longitudinal circulation of warm air. There is a great difference of opinion among different operators as to the best length of glue tunnels, the size and kind of fan, the method of temperature regulation to be employed, whether a suction system or positive pressure system should be used, etc., but it is not the purpose of the writer to enter into a discussion of these points.

A number of other methods of drying glue have been attempted and some are being employed. Vacuum driers of one type or another have frequently been tried, but in most instances without meeting with commercial success. One company builds a drier with rotary air circulation, passing alternately over the coils and glue nets, which they recommend for glue drying.

In conclusion, the writer wishes to express his thanks to Mr. F. S. Williams; also to Mr. L. A. Kind for information relative to the Kind machine.

FIRST NATIONAL BANK BUILDING
CHICAGO, ILL.

CURRENT INDUSTRIAL NEWS

RUSSIAN METAL TRADE

Statistics recently published by the Russian authorities, says *Mining Journal*, 116 (1917), 149, shows that larger imports than ever of copper were necessitated by war demand. The supplies were got chiefly from the United States which contributed 11,728 tons and from Japan which supplied 8,517 tons. The figures for home production are not yet published.

RUSSIAN IMPORTS IN METRIC TONS

	1914	1915	1916
Aluminum.....	863	2,316	149
Antimony.....	1,343	2,325	3,636
Copper.....	4,576	10,778	23,548
Iron and Steel.....	2,236,345	1,787,041	1,752,660
Lead.....	36,691	25,059	23,128
Nickel.....	1,793	1,146	1,541
Tin.....	3,570	4,906	2,424
Zinc.....	14,328	14,137	11,840

Aluminum was only available in comparatively small amounts. Large supplies of antimony were available from Japan, and this metal shows a steady increase. As regards iron and steel, the imports are naturally small, Russia depending largely on her own domestic supplies.—A. MACMILLAN.

PLUMBAGO IN MYSORE

According to a Press message from Madras, an important discovery of plumbago is stated to have been recently made in Mysore by an expert prospector who is well known in the state. Graphite has been found in Bangalore before now but only in such small quantities as not to be paying. The present discovery appears to be a fairly rich deposit with the additional advantage that it is within three miles of the railway. Plumbago has been found in Travancore and Mysore previously, but the quality was not up to the standard of the Ceylon and Madagascar product, which is what the market requires. Whether the present kind is of better quality is not yet known.—M.

BLUE ASBESTOS

The annual report (1915) of the mining engineer for the South African Government, states that the only mines on which there are considerable reserves of blue asbestos actually developed and in sight, are those of the Cape Asbestos Company at Koegas and Westerberg. These mines have been developed underground on normal lines as also are the workings at Haauwpoort and Elandsfontein in the Hay district. At other places the asbestos is obtained from surface quarrying, but the seams that have been discovered and worked at the surface to more or less profit indicate supplies that will generally prove to be available for profitable extraction by underground methods later. The following analyses show the difference between blue asbestos (crocidolite) and chrysotile or white asbestos:

PERCENTAGES	BLUE ASBESTOS	WHITE ASBESTOS
Silica.....	51.1	39.3
Oxide of Iron.....	35.8	2.8
Magnesia.....	2.3	41.0
Alumina.....		3.6
Water.....	3.9	14.5

The blue variety contains also traces of lime and manganese oxide and a little soda. The presence of the large quantity of iron and the low content of water must account for whatever virtues and also faults the blue variety contains. There does not seem to be much question of the properties of white asbestos as a heat-resisting material, some varieties having been known to withstand a temperature of 5,000° F. without being affected. In addition, there can be no doubt as to its superior softness which enables it to be easily milled and reduced, and makes it specially useful for gland packing. On the other hand, blue asbestos has certain qualities peculiarly its own. The fiber, in addition to being lighter, is longer, stronger and more elastic, and its superior efficiency as an insulating material as regards heat, appears to be well known.—M.

KLENSURFACE—A COATING FOR TOOLS BEFORE HARDENING

We have recently received, says the *Engineer*, 123 (1917), 298, from the Brooke Tool Manufacturing Company, Birmingham, England, some particulars of a compound to which the name "Klensurface" has been given. This substance is for coating tools before hardening, so as to eliminate the waste of time and energy consumed in sand-blasting and to overcome the difficulties and risks due to oxidation of steel requiring a high temperature for hardening which may cause pitted and blistered surfaces on parts that cannot afterwards be ground. It is said to have no action whatever on the metal, being a protective agent only, and we gather that it preserves the smooth and bright finish which the cutter or tool has before hardening, thus preventing loss of size due to scaling whether the hardening be carried out in up-to-date appliances or in the open fire, while at the same time the need for sand-blasting is done away with. The method of using the substance is simple. The tool to be treated is first of all heated to visible red, and is then held in the compound for about ten seconds, withdrawn and then again plunged into the compound. It is then dried in the air. All that is now necessary is to heat the tool to the required hardening temperature and to quench it in the usual way. During quenching or air hardening, the protective film will, for the most part, peel off, and what remains can be easily removed, leaving, it is claimed, a clean white surface. The compound is also said to be very effective for annealing high-speed steel.—M.

GERMANY'S PRODUCTION OF IRON

At a recent meeting of the Union of German Iron and Steel Industries, some interesting information was given on the German production of iron during the war. The production of pig-iron in Germany during 1916 was about 13,000,000 tons as against 11,790,000 tons in 1915 and 14,380,000 tons in 1914. As regards this latter year, it should be borne in mind that, while the production for the first seven months was exceptionally high, it was the reverse for the last five months of the year, and the figure for 1914 does not afford any reliable basis for comparison. The following table shows Germany's production of pig-iron for the last ten years from which it will be seen that the industry has receded considerably from the preceding peace figures, in spite of strenuous efforts.

Year	Tons	Year	Tons
1907	13,010,000	1912	12,870,000
1908	11,810,000	1913	19,200,000
1909	12,920,000	1914	14,380,000
1910	14,790,000	1915	11,790,000
1911	15,530,000	1916	13,000,000

M.

ZEPPELIN ENGINE

A six cylinder, 160 horse power Benz engine used for enemy aircraft purposes has cylinders 130 mm. diameter and 180 mm. stroke. The cylinders are all cast separately and the weight of the engine complete comes out at 3,750 lbs. per brake horse power at the normal speed of 1,350 r. p. m. These particulars have been obtained by the British Naval and Military authorities from an engine taken from a captured Zeppelin.—M.

FUEL FROM PEAT

A Christiania paper reports the formation of a company in Norway for making fuel from peat by the Rosendahl method. The raw material for the new industry will be chiefly peat from the extensive Norwegian moors, but any other material may be used which is sufficiently abundant in the neighborhood of the factory, e. g., wood waste. The product is said to be readily combustible. Preliminary experiments have been conducted not only in the laboratory, but also under factory conditions on a small scale and the product is stated to have been satisfactorily tested in Christiania households. M.

GAS ANALYSIS BY ALPHA-RAYS

It is known that the highest conductivity in gases can be produced by exposing them to α -rays which ionize the gas. These rays, says *Engineering*, 103 (1917), 401, are absorbed by the gas, and if the absorption be complete, the ionization and the resulting saturation current are little affected by the nature of the gas. When the tube containing the gas is so long, however, that saturation is just secured by a heavy gas, the current would not be saturated if the gas were replaced by another less dense gas.

On this peculiarity, Professor F. Krüger, of Danzig, has based a new method of determining the proportion of two gases in a mixture, often a troublesome problem. The method is a current measurement, and, as the currents are very weak, of the order 10^{-9} ampere, very high resistances are required. At the winter meeting of the Bunsen Gesellschaft, Krüger explained how he produced high resistances for the purpose. He volatilizes platinum cathodes by the electric discharge and condenses the platinum vapor on little rods of amber. In this way, he has prepared a series of film resistances, ranging from 5×10 up to 3×10^{10} ohm. The analytical method is said to be expeditious and reliable within 0.1 per cent or less.—M.

QUALITIES OF STEEL

According to a paper published in the *Bulletin des usines de guerre*, the change in volume produced by hardening (quenching) steel is small if the hardening temperature is kept below a certain limit. Hardening in oil gives less variation in volume than hardening in water. Special metals, such as nickel-steel, show less diminution in volume than the carbon steels. Eutectic steels "crack" more frequently than carbon-steels, which latter undergo considerable changes in volume. Finally, from experiments carried out, in flat pieces the tension is distributed uniformly in every direction, while in cylindrically shaped pieces the ends contract and become hollow, the piece bellying out.—M.

BRITISH SUGAR BEET GROWING

An enterprise, estimated to cost \$2,500,000, for the production of home-grown sugar, has now been initiated. A grant of \$625,000 has been made by the Treasury by way of loan from the Development Fund towards the purchase of an estate of 5,600 acres at Kelham, England, where it is proposed to grow the sugar-beet and to erect a factory for its manufacture into sugar.

The undertaking is to be carried out by the British Sugar Beet Growers' Society, Ltd., of which Captain Beville Stainer is Chairman. The property has already been acquired and Mr. Alfred Wood, who is in charge of the home-grown flax, hemp and tobacco undertaking, is appointed to the Secretary.—M.

OIL SHORTAGE IN DENMARK

According to the *Ekstrabladet*, the oil mill at Aarhus, which supplies all the great margarine factories in Denmark with oil, is threatened with having to close unless sufficient oil can arrive in the near future, as the factories have only very small stocks in hand. It is stated that the oil mill will close if no oil arrives in Denmark. The American Embassy at Copenhagen, the navy of the United States and the war will have further difficulties in connection with Denmark's nearly exhausted demand for oil. The Danish navy requires a considerable quantity of oil, as not at all readily available, and the controlling authorities will exercise considerable restrictions on consumption. All electric power stations using oil are expected to close down and the use of petroleum for lighting purposes will probably be prohibited.—M.

A NEW SOURCE OF PLATINUM

According to a Bulletin of the Siberian Engineers' Society on the platinum fields of the Nizhni-Tagilsk Mining Circuit, the mining engineer, V. N. Tchorzhevsky, has begun the first experiments in the world on the extraction of platinum from dunite. The experiment promises to be extremely interesting. The platiniferous nature of dunite has long ago been observed and the presence of the metal is apparently connected with the existence of chrome iron ore in the rock, on the abundance of which the greater or lesser content of platinum in the whole dunite mass depends. All this was known before, but was rather of scientific interest and it is only now that the investigation of the dunites for platinum on a wide scale is being undertaken, in order to prepare a plan for utilizing the immense reserves of dunite rocks which in the Nizhni-Tagil district alone occupy an area of 11.7 sq. mi. The method of extraction adopted is the simple grinding under runners of the rock and the collection of the chromite slack, and then a fresh grinding of the latter in order to leach the pure metal finally from it. The chromite slack remaining after washing, the platinum sands being scrupulously cleared of all visible platinum, yielded with an experimental grinding by runners in the month of March, when it was impossible to deliver dunites to the factory, over 200 oz. of metal out of 9,720 lbs. The gray slack, which consists chiefly of undecomposed dunite obtained from the dredges when washing platinum, yielded 171 grains (Troy) of metal from 3,600 lbs.—M.

INDUSTRY IN CANADA

Last year a postal census was taken in Canada of all manufacturing concerns and constructive operations. The results of this investigation, classified under certain large groups of industries, are shown in the following table. The returns cover the year 1915:

Groups of Industries	Establishments	Capital	Cost of Material	Value
1 Food.....	6,470	\$198,246,942	\$291,997,953	\$377,811,758
2 Textiles.....	2,670	126,488,339	81,427,279	144,691,235
3 Iron.....	849	194,278,446	58,924,280	119,636,755
4 Timber.....	3,181	263,407,682	59,170,419	123,250,986
5 Leather.....	523	60,081,498	45,175,517	70,975,644
6 Paper.....	1,306	38,544,786	25,324,906	74,038,498
7 Liquors.....	341	52,148,837	10,129,252	34,859,927
8 Chemicals.....	255	52,148,588	24,930,308	45,410,486
9 Clay.....	771	96,371,573	10,962,041	27,228,413
10 Metals.....	1,173	174,621,994	45,931,080	90,943,278
11 Tobacco.....	166	23,060,898	16,017,707	28,987,250
12 Vehicles.....	464	125,965,499	40,547,113	73,878,212
13 Vessels.....	103	12,331,341	3,035,857	8,419,648
14 Miscellaneous.....	1,440	441,118,405	56,323,786	134,255,029
15 Handtrades.....	1,579	26,135,539	17,627,192	38,129,834
TOTAL.....	21,291	\$1,984,991,427	\$791,524,420	\$1,392,516,953
Per cent increase over 1905.....	34.8	134.5	93.8

The total salary and wage lists, respectively, in the 15 groups of industries shown amounted to \$60,144,000 and \$227,509,000 as compared with \$30,724,000 and \$134,376,000 in 1905. The only industries which have not shared in the substantial growth are sawmills, planing mills, brickyards, etc., and fruit and vegetable canneries.—M.

PURIFICATION OF ASBESTOS

A writer in a German paper says that commercial asbestos contaminated with iron compounds may be purified by treatment with a 2 per cent aqueous solution of oxalic acid for 48 hours, followed by washing with water. A band of asbestos 20 mm. wide showed at fourteen different places an electrical resistance of 600 to 700 ohms; after treatment as described, the resistance increased to 150,000 ohms. An alternative method consists in treating the asbestos for 20 to 24 hours in a current of hydrogen or carbon monoxide at 390 to 400° C. and then washing with very dilute hydrochloric or sulfuric acid and afterwards with water.—M.

FRENCH EXPORT PROHIBITIONS

A French Ministerial Decree dated March 19 abrogates the provisions of various earlier decrees by virtue of which the following articles were allowed to be exported or re-exported from France without special authorization when consigned to the United Kingdom, British Dominions, colonies and protectorates, Belgium (territory not in enemy occupation), Japan, Russia and the countries of America:

Acetone	Mica and micanite, worked
Cadmium in all forms	Monazite (ore of cerium, lanthanum, thorium)
Carbide of calcium	Nickel, metal, pure or alloyed, in all forms
Cement	Ores of manganese, molybdenum, titanium, vanadium
Cinchona bark	Radium and its salts
Cobalt in all forms	Saccharine and similar products
Copper, ore or metal, pure or alloyed, in all forms	Salts of chromium, copper, tin, mercury and molybdenum
Dextrine and soluble starches	Silica bricks
Fatty acids of all kinds	Silicon
Fats, animal (tallow, lard, margarine, oleomargarine and similar substances)	Sodium
Fats, fish, vegetable, alimentary	Starch
Lead: metal, pure or alloyed; pipes and other wares of all kinds	Stearic acid
Manures of all kinds (including chemical manures)	Tin, ore or metal, pure or alloyed, in all forms
Mica in sheets and plates	Tungsten metal in all forms
	Whale oil

—M.

BRITISH BOARD OF TRADE

During the month of April the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.:

CHEMICALS: Ammon'm sulfoeyanide	Anglite frames for ladies' handbags
Dinitrophenol	Brushes: tooth, hair, clothes, for Egypt
Dichloronitrobenzol	Buttons, all kinds
Potassium permanganate	Cast-iron lavatories
Silicate of sodium	Dog-collars, metal
Sodium permanganate	Fatty acids, cotton and corn oil
MACHINERY:	Fittings for manicure cases, in bone and ebony (cheap)
for combining thin sheets of tortoise shell to form thick sheets	Folding market bags, American cloth
for cutting out and sewing fabric gloves	Log-wood, black lake
for filling quilts by air pressure	Marine chronometers (2-day) chains and escape wheels, etc.
for making drawing pins	Micrometers with 3 verniers
for cementing or jointing tortoise shell	Moorson's measuring apparatus for ships
for making paper spoils	Poker-working needles, platinum points
for crushing and refining oilseeds	Shaving-soap, containing less than 1% of glycerine
for electrolytic production of hydrogen and nitrogen	Split rings, steel or iron
Flint glazing machines for pasteboards similar to "Grabl & Hoehl" machine	Swivel hooks, iron
Wire-stitching machines for box corners	Thimbles
Bread grating machines or nut mills	Varnish, black, for coating beer vats internally
Hand-branding machines fitted with petrol reservoir	Zinc oxide (40 tons)
Pebble grinding mills	

—M.

PHOSPHOR BRONZE

The characteristics of phosphor bronze in different forms are described in a publication by the Phosphor Bronze Company. Among other points, attention is drawn to the resistance it offers to corrosion and acid waters, to the small effect that rise of temperature has upon its mechanical properties, and to the fact that it does not yield a spark when struck. On this last account, tools and implements used in gunpowder mills, magazines and mines are advantageously made of it. In addition to being cast, it can be forged, drawn into rods, wire and tubes, and rolled into sheets, strips, tape and bars. When cold rolled or drawn, since its elasticity is absolute practically up to breaking stress, the metal can be exposed to strains only a few tons below the breaking weight without permanent set or deformation. The pamphlet also gives particulars of various other alloys—such as phosphor tin and copper, anti-friction metals of various kinds, and printing and stereotype alloys.—M.

THE MANUFACTURE OF IODINE

Reports from Quimper (France), says the *Oil and Color Trade Journal*, 51 (1917), 1469, speak of a new process for the manufacture of iodine and its derivatives. Iodine, of which the Department of Finistère is a great producer, was hitherto extracted from the soda produced by the incineration of certain kinds of marine algae. This method of operation, which necessitated the algae being first of all transformed, rendered the yield very poor and lacking in uniformity, as the incineration employed was very rudimentary. Mons. Vincent, Director of the Laboratory of Finistère, who has been studying the question for some time, has now discovered a process enabling iodine to be extracted by a direct treatment of such algae or seaweed. This process has been patented and is in use in the works at St. Pierre-Penmark and has given excellent results. A joint stock company has been formed for working the patent and utilizing the by-products.—M.

WOOD IN GAS-MAKING

In reference to the use of resinous wood for the production of gas, which has been adopted on a more or less extensive scale in several continental countries, a correspondent of the *Journal des Usines à Gaz* records his experience in the distillation of fir and oak in the Romorantin Gasworks. The wood, he writes, was distilled, unmixed with coal, in retorts of dimensions approximately 10 ft. × 25 in. × 14 in. in quantity to yield from 10 to 20 per cent of the make of gas from coal. Each charge was about 100 kilos of fir or 120 kilos of oak and it yielded about 25 cu. m. (900 cu. ft.) of gas. In working a bench of retorts, it was found necessary to adopt alternate days for the distillation of the wood. Continuous use of the same retorts for wood gave rise to stoppages in the ascension-pipes in the shape of a viscous grayish deposit, very troublesome to remove. The following figures were obtained for the cost of using the two woods: Fir,

price per ton, 40 francs.; labor, 4 francs.; furnace coke (200 kilos), 17.50 francs.; total, 61.50 francs.; deducting 50 francs. for sale of charcoal, the net cost is 11.50 francs. Oak, price per ton, 58.50 francs.; labor, 4 francs.; coke, 17.50 francs.; allowing for sale of charcoal at 70 francs., the net cost is 10 francs. The charcoal sells readily, the weight per hectolitre being 15 kg. in case of fir and 18 kg. for oak.—M.

TREATMENT OF TIMBER

Excellent results have been obtained with saponified creosote by simply soaking estate timber in an open tank, and the method seems to deserve a trial if the greater expense of creosoting pit timber under pressure cannot be faced, says the *Iron and Coal Trade Review*. The idea was first suggested by Mr. S. H. Collins, of Newcastle, England, in July 1914. According to him, the addition of a small percentage, say 0.25 per cent or less, of caustic soda to pure creosote improves penetration, even in the case of timbers like spruce, which take the oil with difficulty even when comparatively well seasoned. Moreover, saponification makes it possible to dilute the creosote with water and thus cheapens the impregnating process.—M.

SCARCITY OF SYNTHETIC PERFUMES

A number of synthetic perfumes are scarcely obtainable at the present moment. Among these is phenyl-ethyl alcohol, which is an absolutely necessary ingredient for artificial otto of roses. It is true, says the *Oil and Color Trade Journal*, that a certain amount is being offered, but a good deal of this is of indifferent quality, really fine grades being very difficult to obtain and then only at much enhanced prices. Amberpene is hardly to be found, the few makers complaining of lack of raw material. Benzaldehyde, free from chlorine, is exceedingly difficult to find, but the ordinary quality containing chlorine is offered fairly freely, although the price is very firm.—M.

OBITUARIES

JULIUS O. SCHLOTTERBECK

Once again the roll is called, and as the name of Julius Otto Schlotterbeck is reached, there comes the mournful yet triumphant response: "Gone forward."

Professor Schlotterbeck was born in Ann Arbor, Michigan, in 1865, the son of Hermann and Rosina Schlotterbeck. After attending the primary and high schools of Ann Arbor, he entered the pharmacy course at the University of Michigan in the fall of 1885, graduating from that institution as pharmaceutical chemist in June 1887. He continued his studies at the University, at the same time performing the duties of assistant in pharmacy and pharmacognosy, and in June, 1891, he was granted the baccalaureate degree in science.

His brilliant career in college won for him, as soon as he graduated, a position on the faculty of the University. In 1891 he was made instructor in pharmacognosy and botany, which position he retained until 1895, when he became a student of Tschirch at the University of Berne, where two years later he was awarded the degree of doctor of philosophy (*summa cum laude*). Returning to America, he was made assistant professor of pharmacognosy and botany, in 1901 he was junior professor and in 1907 he was promoted to the full professional position. On the death of Professor Prescott, in 1903, he was chosen Dean of the School of Pharmacy, and he retained that position until his death.

Professor Schlotterbeck was a tireless worker. In the publications of the American Pharmaceutical Association we find his papers from his pen, while he contributed three papers to the *Journal* of our own association. Of these, the most brilliant are his reports on his researches on the mineral alkaloids of the

Poppy family, particularly noteworthy being his painstaking investigation of protopine and his discovery in *Stylophorum diphyllum* of a new papaveraceous alkaloid, stylopine, $C_{19}H_{19}NO_6$.

It is needless to say that such a man was in demand in association work. In 1905 he was president of the State Pharmaceutical Association; in 1902 he was chairman of the Scientific Section of the American Pharmaceutical Association, while for two terms, 1910 to 1912, he was president of the American Conference of Pharmaceutical Faculties, after serving that organization for several terms as its secretary. In our own association, he was an active supporter of the division on pharmaceutical chemistry. He was a Fellow of the American Association for the Advancement of Science, and a member of the Committee on Revision of the United States Pharmacopoeia.

In his home life, Dr. Schlotterbeck was singularly happy. As one of his friends and recently about him: "He was a home man—the passion of science never built a barrier between him and his friends." Deep therefore is the loss that has come to his widow and his three children, Prescott, a freshman at the University of Michigan, Marian, a high school student, and Carl, a boy of eleven years. To these, our deepest sympathies go forth.

The writer will never forget his last meeting with Schlotterbeck. It was a delightful August evening in 1915, in the Golden Garden at Heidelberg, where we two who had respectively heard of each other in America, met accidentally, and instantly on foreign soil. He was then on his way to Illinois, full of spirit and enthusiasm for the work he was about to undertake, which he so brilliantly completed two years later. Since that time, our

meetings have been frequent, as our work has been along similar lines, and each meeting has brought a deeper appreciation of the many fine traits that Schlotterbeck possessed. Quiet and unassuming, yet conscious of his own powers and of the responsibility they brought to him, a deep student and yet a good comrade, Schlotterbeck was a man that American Pharmacy and American Chemistry can ill afford to lose.

COLLEGE OF PHARMACY, COLUMBIA UNIVERSITY H. V. ARNY
NEW YORK CITY

ALOIS VON ISAKOVICS

It was a terrible shock to all when we learned that our dear friend and colleague, Alois Von Isakovics, had passed away in the prime of his life on June 5 at his residence in Monticello, N. Y., after a comparatively short illness.

Alois Von Isakovics was born in Prag, Bohemia, July 20, 1870, the son of a distinguished military family. His father, an officer of high rank in the Austrian army, had mapped out for his only son a military career, and was greatly disappointed when the young son showed by his independent character that he did not believe army life would appeal to him. When a very small boy he started a little business of his own, collecting stamps and selling them, working at this after school and often late into the night, and before he left Europe this business, built up entirely by himself, had grown to such a size that he found it necessary to employ several of his school friends to help him with his correspondence and filling of orders. His aim already in early life was to have an international business and this he enjoyed even when a boy, as he received orders for his stamps from all over the world.

After finishing his general education, which comprised the regular curriculum of a young man of good European family, he came in the Spring of 1886 to America, the land of freedom and unhampered development. At first the battle was hard and the little money he brought with him soon gave out, but possessed with a grim determination to win and a never ceasing ambition, he accepted some very menial positions until he had mastered the English language and thus was started at the foot of the ladder, the top of which he so gloriously had reached at the time of his death.

In October 1888, he met Miss Marie Upshur, the daughter of a historic Southern family, which seemed to have been a real case of "love at first sight." They became engaged in July 1889, and after he was naturalized in 1892, in New York City, they were married in July 1895, at the Church of the Transfiguration, just twenty-five years after her parents were married there by the same minister, the Rev. Dr. Houghton. Their love remained ever young and devoted after twenty-two years of an unbroken union of happiness and bliss. They worked up

together what was the beginning of the Syndeur Scientific Laboratories and their lives were united in thought, purpose and ambition—the one was an inspiration to the other.

Von Isakovics was a genius in the particular field of chemistry to which he devoted his talents. He combined a high character, a lovable nature, with thorough scientific knowledge and exceptional commercial and executive abilities. It will be readily understood that it was uphill work to build up such a business monument as he left, in the face of severe competition which was backed by unlimited capital, but he always said it *could* be done and he would succeed.

The secret of his success has been his never failing business policy, to give his customers exactly what he said he would. There was never in his mind anything "good enough," only the "best" that science could produce would he offer his clients. He has thrown away many a pound of valuable materials because they did not comply with his idea of quality. He had often said he did not care how much the loss might be in dollars and cents so long as his conscience was clear and he gave his clients the very best possible value.

It was his cherished wish that should he ever be taken away his wife should go ahead in the same way as they had done together for the past 28 years and finally he hoped that his only son, Alois Von Isakovics, Jr., would take up the work. Mrs. Von Isakovics has been connected with the business from the day it was started by her late husband and it is her intention to take up the work where he has left off and to carry out his ideas in every detail.

Von Isakovics was endowed with those qualifications which go to make up an ideal man. His intelligence, honesty and fairness combined with his superior ability placed him in a position to be known all over the country and in many foreign lands. At the time of his death he was a member in the following Scientific and Social Societies: American Chemical Society, American Electrochemical Society (charter member), American Pharmaceutical Association, Manufacturing Perfumers' Association, Chemists' Club, Franklin Institute, New York Academy of Science (Fellow), American Association for the Advancement of Science (Fellow), Society of Chemical Industry, and Verein Deutscher Chemiker.

His great professional triumphs are recorded on the pages of scientific and practical literature such as: "Synfleur Heralds," Synopsis of Columbia University Lectures on "Perfumes and Flavoring Materials," and "Essential Oils, Synthetic Perfumes and Flavoring Materials," Chapter XXIX, in Rogers and Aubert's "Industrial Chemistry."

Von Isakovics was a devoted husband, a kind father and a sincere friend.

NEW YORK CITY

WILLIAM DREYFUS

NOTES AND CORRESPONDENCE

CALENDAR OF MEETINGS

American Pharmaceutical Association: Indianapolis, Indiana, August 27 to September 13, 1917.

American Chemical Society: Annual Meeting, Boston, Mass., September 10 to 16, 1917.

National Exposition of Chemical Industries (Third): Grand Central Palace, New York City, September 24 to 29, 1917.

American Electrochemical Society: Autumn Meeting, Pittsburgh, October 3 to 6, 1917.

National Paint, Oil and Varnish Association: Annual Convention, Chicago, October 8 to 10, 1917.

American Institute of Mining Engineers: Annual Meeting, St. Louis, Mo., October 8 to 13, 1917.

THE TEACHING OF ANALYTICAL CHEMISTRY

Editor of the Journal of Industrial and Engineering Chemistry:

To no one engaged in analytical chemistry, whether as practitioner, teacher, or original investigator, can the recent address by Dr. Hillebrand on "Our Analytical Chemistry and Its Future,"¹ fail to be stimulating and full of suggestion. It is not to be expected that the universities can turn out experienced analysts, but the chemical world has a right to expect our institutions to turn out men who have a capacity for becoming reliable analysts after reasonable experience. Dr. Hillebrand suggests that in this the universities have, in a large number of instances, failed; and those who have had opportunity of in-

¹ THIS JOURNAL, 9 (1917), 170.

investigating the conditions in the analytical laboratories of many of our industries will endorse that suggestion. In searching for a cause for this state of affairs one need not look very far, for a glance over the catalogues of a few universities will quickly convince one that other subjects in the curriculum are making rapid inroads on the time formerly devoted to chemical analysis. In view of the increasing number of topics which now find place in a chemical education this is not surprising, for not only must the claims of other chemical and related subjects be considered, but also the undeniable swinging back to a broader educational basis, which is becoming increasingly evident in many of our institutions, and which brings with it a less specialized curriculum.

Before taking up the discussion as to the best method of employing our reduced time in teaching analytical chemistry, it would be well to consider the true place of this branch in a chemical education. If training in this subject is restricted to the mere teaching of a number of procedures which can be more or less mechanically carried through, it is certain that it does not deserve much consideration; but there is no reason why the work should not be made a really useful end in itself—which it is not, if carried out in the manner just mentioned, and at the same time an educational factor of vital importance. There has been a decided tendency to raise the standard of qualitative analysis in the latter respect, as is evidenced by the tone and character of many of the recent books on the subject; but in quantitative analysis we are not yet quite so far advanced, and the few really modern books which have appeared have to make their way against much conservatism and prejudice. There is no branch better adapted to the presentation of elementary physico-chemical ideas than analytical chemistry, and in following this system of presentation there is the great advantage of keeping the student in vital contact with the indispensable modern ideas through the whole of his course, instead of allowing him, as is now too frequently done, to forget most of the real chemistry he has learned in advanced general chemistry and qualitative analysis, by plodding through a year in which his only chemical subjects may be old-style courses in quantitative analysis and organic chemistry. Surely the department of physical chemistry would be willing to let the analytical department encroach a little on its territory if, by so doing, students could be handed on for work in physical chemistry with a knowledge and enthusiasm which would materially lighten the burden of instructors in that department. With quantitative analysis taught on this basis, we whose hobby this subject is need not apologize for our interest.

There are two main points to be considered: *First*, students must be trained in exact methods of work, so that reliable results can be obtained; and *second*, the dignity of analytical chemistry must be maintained as a sound educational factor. A greater proportion of lecture work, even at the expense of some laboratory hours, seems to hold the greatest promise for the accomplishment of both ends. It is perfectly true that the student is more deeply impressed by what he learns in the laboratory than by the statements of a lecturer, and if unlimited time were at our disposal formal lectures might well be dispensed with altogether, and the whole instruction, even in the more abstract and theoretical phases, could be imparted by informal talks and discussions at the laboratory bench. Such a course, however, involves so great an expenditure of time, and necessitates so large a teaching force as to make it impossible under existing circumstances. The best thing we can do, then, is to give a far greater share of instruction in the lecture room than is now usually done, and thus free more of the laboratory time for the essentials that cannot be gained except by experience. Discreetness is a point frequently neglected, and it is common experience to find a student wasting time by weighing out a steel sample for the determination of phosphorus with the same

accuracy that he would employ in weighing copper foil for standardization. By more carefully planned lecture work, and by greater cooperation on the part of the laboratory assistants it should not be difficult to accomplish a third more in the average analytical course than is now done.

Dr. Alexander Smith¹ has called attention to the evils of overlapping courses, and my observation is that this is particularly true in analytical chemistry, both as regards lecture work and the analysis of samples in the laboratory. In the majority of institutions the departments of qualitative and quantitative analysis are entirely separate; text-books by different authors are used, the lectures are given by different instructors, and the instructor in one course is but little acquainted with the exact method of presentation used in the other course. In the qualitative course the student acquires, after much hard work, a faint glimmering of an understanding of the fundamental principles underlying the subject of analytical chemistry. The next year the study of quantitative analysis is begun, and the book of another author is used. The same ionic hypothesis is presented, the same mass law, in short, the same fundamental principles, for they are common alike to both qualitative and quantitative analysis; but in the work of this new author the student looks in vain for the familiar expressions, mathematical formulae, and symbolism which he has laboriously learned the year before; for the author of this new work has started again from the beginning, and, in his own way, and with his own peculiar terminology, he has presented the whole of the material which the student has learned before, with just a little in addition which applies exclusively to quantitative analysis. The result is that the student has to spend a good part of his second year in learning over what he is supposed already to know, simply because it is presented in a different way, with little thought of correlation with what has gone before.

This condition would be remedied by the adoption of a text-book, in two volumes, on analytical chemistry from the modern view-point by one author; or by having the lectures in both branches given by one instructor, any necessary changes in the terminology of the two books being made with a view to obtaining a unified system of presentation. If lack of suitable texts makes the first, and program difficulties make the second alternative impossible, it is still feasible to have both qualitative and quantitative analysis under the direction of the department of analytical chemistry, and to let the head of that department see to it that a unified system of instruction is established. In this way the quantitative course would take up the subject where the qualitative work left it, that is, without repetition of first principles, but with constant reference to those portions of the first course which deal with the knowledge prerequisite to the particular discussion in hand. The theoretical part of the second course would thus be really a continuation of the first, rather than a more or less confusing repetition of it, in which the seeming contradictions of the different writers tend to cast a haze of indistinctness over minds not yet sufficiently advanced to sift for themselves the chaff from the wheat. By this method of coordination much valuable time could be saved, and this could be devoted to extra drilling in the methods of securing exactness of results by added emphasis on those minor details which are so frequently hurried over for lack of time.

The curtailment of laboratory time makes expensive the optimum utilization of these hours, and a great saving can be made by avoiding undue repetition in advanced courses. The working through of the determination of phosphorus in iron ore in steel, in coke, in several types of fertilizers, and so on, is a slog, is doubtless splendid practice, but it is not economy. An extreme case has been cited, but it will serve to illustrate what in a lesser degree, or in a real contrast, is made manifest in instruction. Phosphorus should be determined in one class of

material gravimetrically, in another volumetrically; and in the lecture room the student should be taught the application of these methods to the most varied kinds of industrial products. There is no finer practice than the complete analysis of a rock, but for a student it consumes an immense amount of time. Even if there is not time, however, for the complete analysis, the fundamentals of rock analysis can still be taught, for the student will already have made a partial analysis of limestone, probably a silica by fusion, and a determination of sulfur in some form. In a one-hour lecture this work can be gathered into an organized whole, and correlated with the subject of a complete rock analysis. The student can then be required to determine ferrous iron, alkalis, titanium, and the other constituents which his previous experience has not covered. Thus by the organization of the laboratory work through the correlating influence of carefully planned lectures and theoretical study, a much broader foundation can be laid in the allotted time than is now usually done.

In summarizing, analytical chemistry should be taught as one subject, with the various branches closely correlated in a unified system. An unnecessary burden is placed upon students by using different methods in presenting the fundamental principles of qualitative and quantitative analysis. Much laboratory time can be saved by more lecture work, and by the avoidance of undue repetition in analytical exercises. This time should be spent in extra drill in the details of accuracy.

UNIVERSITY OF ARIZONA
TUCSON, February 14, 1917

PAUL H. M.-P. BRINTON

A CHEMICAL LETTER BY DR. ANDREW URE

Editor of the Journal of Industrial and Engineering Chemistry:

The following letter by Dr. Andrew Ure—the well-known author of Ure's Dictionary—has recently come into my possession and as it was written exactly 100 years ago and contains considerable matter of historical interest, its publication in the July issue of the JOURNAL may not be out of place. The letter, except for a slight tear due to breaking of the wax seal, is in perfect preservation. It bears the address, Dr. Granville, Hotel de Saxe, No. 12 Rue de Colombar, Faubourg St. Germain, Paris, and runs as follows:

GLASGOW, July 5th, 1817

MY DEAR SIR:

I avail myself with great pleasure of the opportunity offered by the visit of my ingenious friend, Dr. N. Hill, to Paris, to assure you of the grateful recollections which I shall ever entertain of your kindness, regretting only that the arthritic affection of my ankles prevented me from profiting so much as I would otherwise have done of your acquaintance with the French *Savans*. My journey homeward was tedious and uncomfortable; but soon after breathing my native Caledonian air my health returned to its former soundness, and the anomalous affections, connected, I believe, with the French wines, entirely disappeared.

Though far distant from you, I have followed with undiminished interest your useful labors and very interesting communications in the Institution Journals. Your tribute to Vauquelin is elegantly expressed, and very justly merited. It has found an echo in every man's heart who has, like me, had the good fortune to meet with this illustrious and benevolent philosopher. I hope soon to have a public opportunity of expressing my sentiments on the same grateful subject.

My winter occupations consist more in teaching pupils the general truths of science than in original investigations. Since the session ended, I have, however, been incessantly occupied in some researches which will make their appearance in monthly succession in our scientific journals—chiefly the *Annals of Philosophy*. In the *Medical and Surgical Journal of London* for this month you will find a paper of mine containing a description and analysis of a morbid intestinal concretion sent to me for examination by a physician in the vicinity of Perth. It differs entirely from any of which I have seen an account, resembling in chemical and physical properties pure ambergis, and containing no earthy phosphates or indeed any other saline matter.

By the analysis of Lagrange ambergis contains benzoic acid.

The substance in question yields none to any attempts at extraction which I have been able to make. And on examining with care two different specimens of ambergis, both reputed genuine, I have found the one to contain benzoic acid, but the other, and that the most characteristic, none. The paper itself will shew you that I have bestowed some pains on the subject, though I have by no means completed my investigations, being very much pressed for the account for this month's magazine. Some phenomena led me to fancy that the acid of ambergis was not benzoic but succinic acid; and I accordingly tried to discover a simple and certain criterion between them. Succinate of Ammonia sublimes without decomposition. Benzoate of Ammonia is decomposed in a gentle subliming heat; the Ammonia escaping partly in gas and partly combined with the water of crystallization. This fact, if you please, you may mention to M. Vauquelin; but very likely that excellent chemist may be already acquainted with it.

My first paper for the *Annals*, is on Ammonia, Muriatic Acid, Sal Ammoniac, the other Ammoniacal Salts, and the chlorides in general. It contains I believe several new facts, which I hope you will see next month. I should wish exceedingly to know the opinion concerning it of your distinguished friends at Paris. Will you write me? The whole deductions are from my own experiments. I point out some inaccuracies in Dr. Wollaston's Scale as well as in Dr. Thomson's Weight of the Atoms. I endeavor to show that Sal Ammoniac is not a chloride of ammonium, as Dr. T. has called it.

The bearer of this letter is author of a very ingenious paper on Laryngitis, and very deserving of being assisted in his views of seeing a little of Parisian Practice. As there is no person who is so thoroughly capable of promoting his views, may I beg you to give him a general system of directions for making the most of his time at the French Capital?

Present my respectful complements to your lady and believe me to be always, Dear Sir,

Your faithful and obliged servant,

ANDREW URE

Dr. Augustus Bozzi Granville, to whom the above letter is addressed, had one of the most adventurous careers which ever befell a man of science. He was the son of an Italian named Bozzi, a relative of Napoleon, but afterwards adopted the family name of his English mother. He studied under Volta at Pavia, from which university he graduated as a physician in 1802. Granville was an enthusiastic devotee of the new science of chemistry. At Paris he became acquainted with Countess Rumford, the widow of Lavoisier, who encouraged him in his chemical studies; Gay-Lussac, Vauquelin, and other well-known chemists were among his teachers. In 1814 and 1815 Granville taught chemistry at a medical school in London. His experiences, however, as a teacher of chemistry were unfortunate; an accident with chlorine gas completely destroyed his sense of smell and, the treasurer of the school absconding, the institution failed and Granville was never paid his salary. After this he returned to France and was studying in Paris at the time of Ure's letter.

Granville's extensive travels, together with his linguistic attainments, gave him a wider acquaintance with noted scientists than was the fortune of most other men of his day. He rendered no small service by helping to bring together English and Continental scientists who had been separated from one another by the Napoleonic wars for nearly 20 years. Granville¹ died in 1872 at the age of 88 and his long life forms a connecting link between the chemists of Lavoisier's time and those of the present day.

Although the imperfections of Ure's analytical methods throw little light upon the nature of his "morbid intestinal concretion," it seems probable that he was dealing with cholesterol or coprosterine, substances of which chemists are still striving to determine the exact constitution.

The allusion which Ure makes to his researches upon the composition of sal ammoniac recalls the famous "chloridic controversy" which occupied the minds of chemists a century ago. Ure's paper was published in Thomson's *Annals of Philosophy*

¹ Granville was well known as an authority upon mineral waters and sewage disposal. He also made important contributions to the study of the internal use of hydrocyanic acid in medicine. His two volume autobiography published in 1874 has all the fascinations of an exciting novel.

for Sept. 1917 (Vol 10, page 203), and in it he contends that sal-ammoniac is not a chloride of ammonium but a muriate of ammonia. According to the old view muriatic acid and ammonia both contained oxygen while hydrochloric acid and ammonium were oxygen-free. The muriates upon heating were supposed to be converted into chlorides by the expulsion of water.

Ure sublimed dry sal ammoniac over hot metals and obtaining water concluded that the latter was due to a combination of the hydrogen and oxygen in the sal ammoniac molecule. Sal ammoniac was therefore a muriate and not a chloride. The fallacy of this conclusion was pointed out by Thomson (in Vol. 12 of his *Annals*, p. 381) who by a natural intuition picked the winning side in the chloridic argument, as he did in the atomic controversy, years before most of his contemporaries.

Although Ure in after years realized the correctness of Thomson's view, he had the satisfaction of knowing that he went astray in good company. Berzelius believed up to 1820 in a hypothetical element *muriaticum*, which, upon combining with two atoms of oxygen, produced the anhydride of muriatic acid; this anhydride, upon further oxidation, as by means of manganese peroxide, yielded oxy-muriatic acid gas or chlorine. Berzelius also believed in another hypothetical element *nitricum*, the oxide of which was nitrogen and which oxide in combination with hydrogen gave ammonia. Relics of these old views still survive in chemical nomenclature.

The contribution of Ure, who was assisted in his experiments by Gmelin, a pupil of Berzelius, will always be worth reading, for it illustrates the difficulties with which early experimenters had to contend. As Kopp remarks in his account of the chloridic controversy, "it is interesting to note how correct observations led to incorrect conclusions."

The tributes which Granville and Ure both pay to Vauquelin only confirm what others have written about one of the best loved and most honored chemists of France. The readiness with which English scientists, after the bitter Napoleonic wars, could give expression to such feelings of admiration shows the strength of the bonds which unite the great international brotherhood of science, and at the time of the present crisis should fill us with hope for the future.

80 SOUTH STREET, NEW YORK CITY
May 16, 1917

C. A. BROWNE

TWO LETTERS ON THE INCOMPLETE HYDROGENATION OF COTTONSEED OIL

Editor of the Journal of Industrial and Engineering Chemistry:

In a very interesting article entitled "Incomplete Hydrogenation of Cottonseed Oil," by Hugh K. Moore, *et al.*, published in the May 1917 number of *This Journal*, the following statement occurs on page 461 under the caption "Response to Halphen Test." The amount of hydrogenation which is required to render the oil just incapable of responding to the test has not to our knowledge been investigated. A very limited amount of experimental data is given and a conclusion is drawn on page 462. "The degree of hydrogenation necessary to destroy the response of Cottonseed Oil to the Halphen test has been shown to be a drop of about four units in the iodine number." There are so many variable factors which would have an effect on this conclusion that it seems a rather broad statement to make on the limited evidence submitted.

It is rather interesting to the writer that the statement is made in the article that "the amount of hydrogenation which is required to render the oil just incapable of responding to the test has not to our knowledge been investigated" in view of United States Patent 1,187,999, application for which was filed by the writer on August 15, 1913, and issued on June 20, 1916, in which the following statement appears in the specification:

In carrying out my new process for the manufacture of the

product, a fatty oil, for instance, choice or prime yellow cottonseed oil, is placed in a closed vessel and caused to be chemically combined with hydrogen in the presence of a catalyst. Any of the known processes of hydrogenation, or any active catalyst may be employed, which does not leave any residual catalytic impurities in the product after careful filtration. A temperature of 150 to 200° C. has been satisfactorily employed, and the time required to produce the desired result after attaining this temperature, is from five to thirty minutes, depending upon the activity and proportion of the catalyst employed. In practice the time or degree of hydrogenation desired are determined by preliminary experiment on the oil and catalyst used in an experimental apparatus. In carrying on such preliminary test the hydrogenation process is continued until a sample of the oil fails to respond to the Halphen reaction and the desired degree of crystallization takes place when the oil is chilled.

"Depending upon the particular oil treated by the process, the iodine value of the finished product varies from about 90 to 102. Its titre (as determined by the Wolfbauer method) has been slightly increased during the process to the extent of from about 0.1 to 0.5° C. over that of the original oil treated. The color of the treated product is usually somewhat lighter than the original oil. On cooling the product it in part readily crystallizes, thereby making separation of the stearin from the oil much easier and more effective for 'winter pressing' for salad oil than is the case with ordinary cottonseed oil. The new product responds negatively to the Milliau test for cottonseed oil."

Other parts of the specification and also the claims of this patent treat further on this subject.

Inasmuch as a copy of this patent was sent to the Berlin Mills Company and was investigated by their patent attorney, it is somewhat surprising to the writer to find at this time an article published by the research laboratory of this company over the name of the company, in which the above quoted statement occurs.

CHICAGO, June 6, 1917

ARTHUR LOWENSTEIN

Editor of the Journal of Industrial and Engineering Chemistry:

In reply to Dr. Arthur Lowenstein's criticism of a section in our article on "The Incomplete Hydrogenation of Cottonseed Oil," we wish to state that U. S. Patent 1,187,999 was familiar to us at the time the section in question was written; neither at that time nor at the present time, however, could we regard the disclosures of the patent as constituting anticipation of our work.

The fundamental statement of the patent, as quoted above by Dr. Lowenstein, is as follows: "..... the hydrogenation process is continued until a sample of the oil fails to respond to the Halphen reaction and the desired degree of crystallization takes place when the oil is chilled." There is no warrant for assuming from the language of the patent that when the Halphen test is just destroyed the proper amount of crystallizable material has just been produced; in fact it would appear that a considerable degree of choice may be exercised in the production of this stearine after the Halphen test response is gone.

The iodine number of the product of the patent is not stated to be that of a product in which the response to Halphen test has just been destroyed but is that of a product in which both conditions have been met. The breadth of the range given, 99-102, indicates that "the desired degree of crystallization" upon chilling is subject to considerable variation according to the product in view.

The other distinguishing mark given in the patent, namely, a range of increase in titre, likewise fails to disclose any definite knowledge of the degree of hydrogenation necessary to destroy the response to the test. Its inclusion in the Halphen test, like that of the iodine number, is a rather arbitrary statement with the Wolfbauer method, since the only measurement in this method is that it is certain that the range of 0.1 to 0.5° C. represents a very

large range in actual hydrogenation, as measured by change in iodine number. It is noteworthy that our experiments invariably showed a decrease in titre, as measured by the A. O. A. C. method, before any increase began, so that to increase the titer 0.1 to 0.5° C. above that of the original oil required a drop of iodine number to about 70.

We wish to point out that if, as Dr. Lowenstein asserts, there are "many variable factors which would have an effect on this conclusion," there exists no published evidence to that effect. It seems probable to us that temperature is the only factor which would have such an effect, and the temperature 150 to 160° C. was specified in the experiment in question.

We are therefore unable to agree with Dr. Lowenstein's implication that U. S. Patent 1,187,999 anticipates our disclosure. It is quite possible that other investigators have carried out the same work at an earlier date, but we believe ourselves to have been the first to publish the results of such work.

BERLIN
NEW HAMPSHIRE
June 12, 1917

H. K. MOORE
G. A. RICHTER
W. B. VAN ARSDEL

AN EXPLOSION OF AN ANILINE STRIPPER

Recently a stripper employed on aniline waters exploded and as the cause has not been ascertained, it is thought that a description of same may be of interest to manufacturers of aniline and similar compounds.

DESCRIPTION OF STRIPPER

The stripper is a $\frac{3}{8}$ -in. steel tank 7 ft. in diameter and 8 ft. $\frac{3}{8}$ in. deep, flat bottom and plate cover on top, all $\frac{3}{8}$ -in. steel. To stiffen the cover, two 6-in. I-beams ($12\frac{1}{4}$ lbs.) 16 in. between centers were riveted on the cover. The cover was bolted to the flange with about forty $\frac{3}{4}$ in. \times $\frac{1}{2}$ in. bolts. The bolt holes are spaced about 6 in. apart on three-quarters of the circumference and 12 in. on centers on the remaining quarter. The bottom has a $2\frac{1}{2}$ -in. outlet with a plug cock which runs to the sewer. The top has a $2\frac{1}{2}$ -in. inlet with a cross. The cross has a 2-in. inlet with a valve and a $1\frac{1}{2}$ -in. inlet with a valve. On the top of the cross was a $\frac{3}{4}$ -in. level safety valve and a gauge.

The stripper has a closed coil of 2-in. pipe, for the purpose of heating, 8 turns, welded, connected in through the side with cast-iron elbows and nipples to the coil.

There is a $1\frac{1}{2}$ -in. valve and line feeding the top of the coil with steam and the bottom drains through a $\frac{3}{4}$ -in. steam trap.

On the cover was a manhole and a 6-in. vapor line outlet running up vertically for 6 ft. to a $2\frac{1}{2}$ -in. coil in a 4 ft. \times 6 ft. wooden tank. The vapor line, coil and coil-outlet have no valve. The coil discharges into a steel separator, 5 ft. \times 6 ft. The aniline is drawn off the separator.

OPERATION JUST PRIOR TO THE EXPLOSION

The stripper was filled with aniline waters up to just 30 in. from the top of the stripper, by means of a steam siphon from the wooden tank in the yard which is used as a reservoir for aniline waters. At 4:30 P.M., April 21, 1917, the cover was placed on the manhole of the stripper and the steam turned on the coil between 4:45 and 5:15 P.M. by a workman. The stripper is operated by simply distilling the aniline waters, condensing the aniline and water in a coil and running same into a separator. About 5:45 P.M. the stripper exploded. A workman was 10 to 20 ft. from the stripper when it went up and was splashed with water, undoubtedly from the stripper; the water was warm, not hot, and he was not burned.

RESULTS OF THE EXPLOSION

The cover of the stripper was blown off with considerable force, breaking all the bolts which held it on by tension. The cover was bent and the flange of the stripper bent. The cover landed on the edge of the floor beside the stripper.

The entire contents of the stripper (1600 gallons) were thrown out, leaving a layer of $1\frac{1}{2}$ in. of iron sludge in the bottom of the stripper. A hole 20 ft. \times 25 ft. was torn through the roof and an 8-ft. I-beam bent 18 in. out of line. The wire glass windows which were near were broken. The stripper was not damaged very much. The same cover was replaced and except for a few fittings was satisfactory for service again.

After the explosion the inlet valve to the coil was found wide open $5\frac{3}{4}$ turns. The condenser was clear. The two valves on inlets to the cross on the cover were closed.

COMMENTS

The aniline waters were analyzed with the following results:

SAMPLE:	Feed Water as put into Stripper	Liquid from Bottom of Stripper after Explosion
Aniline.....	3.13 per cent	3.07 per cent
Acidity (as H ₂ SO ₄)..	0.005 per cent	0.09 per cent
Nitro Compounds...	None	None

The explosion behaved as though a layer of explosive had been placed on the bottom of the stripper. It is almost inconceivable that the explosion could have been caused by steam because the $1\frac{1}{2}$ in. steam inlet is the only supply. If this were led into the stripper through a break in the coil, the contents of the stripper would probably have been heated to boiling before exploding. Even then, it is difficult to see how the steam at 115 lbs. would create such a sudden and violent explosion, entering as it did, and with the exit condenser coil wide open.

We would be pleased to receive opinions as to the probable causes of this explosion, which we are at present unable to explain.

NEWARK, NEW JERSEY
April 30, 1917

MARDEN, ORTH & HASTINGS CO., INC.,
per RICHARD S. BICKNELL

BUREAU OF STANDARDS' ANALYZED SAMPLES

The Bureau of Standards, Washington, D. C., now has ready for distribution its High Phosphorus Standard Analyzed Iron E No. 7, which is typical of the irons from the Alabama area. The analysis is: carbon, 2.17; graphite, 1.82; combined carbon, 0.38; silicon, 2.21; titanium, 0.095; phosphorus, 0.862; sulfur, 0.051; manganese, 0.444; copper, 0.021; chromium, 0.014; nickel, 0.016; and vanadium, 0.073. The renewal No. 12-b, of the Basic Open Hearth Steel approximately 0.4 Carbon, is also ready. Until printed certificates can be secured, the above samples will be issued with provisional certificates without details of analysis, or description of methods. A new sample of Bessemer steel with approximately 0.1 per cent carbon to replace No. 8-a is now in process of analysis.

DECENNIAL INDEX OF CHEMICAL ABSTRACTS

The intention of offering the Decennial Index of Chemical Abstracts in bound form has been reconsidered. There has been so little demand, and members who are binding their volumes have so many different bindings, that it was considered unwise, and, in fact, almost impossible to offer a binding which would suit the members of the Society.

June 8, 1917

CHAS. L. PARSONS

ALCOHOL AND WATER IN ETHER—CORRECTION

In the article under the above title, *THIS JOURNAL*, 9 (1917), 521, in the table on page 522, the first "0.25 per cent Water" in the last group of figures should read "0.025".

R. L. PERKINS

NITROGEN INDUSTRIES LITERATURE—CORRECTION

In printing the "Literature of the Nitrogen Industries, 1912 to 1916," in the April issue of *THIS JOURNAL*, pages 424 to 438, we omitted to state that this material was reprinted from the January, February and March, 1917, issues of the *General Electric Review*.—[EDITOR]

WASHINGTON LETTER

By PAUL WOOTON, Metropolitan Bank Building, Washington, D. C.

That the United States is fully alive to the important part chemistry plays in modern warfare is indicated by the vast amount of chemical work which is being done by government agencies or under the direct supervision of the government. Practically every one of the many chemical laboratories in the city is devoting a considerable portion of its time to war work.

Much of the chemical work which is in progress in Washington, or is being directed and controlled from the capital, is of a nature which precludes any public discussion. This applies particularly to the work being done under the direction of the Committee on Chemicals of the Council of National Defense, of which Dr. Wm. H. Nichols, of New York, is chairman. It also applies to the very extensive experimentation by the Bureau of Mines with poison gases. It has not been deemed good judgment to disclose many facts with regard to the work being done by the Carnegie Geophysical Laboratory and the Bureau of Standards on optical glass. Some of the problems being worked upon at the Bureau of Chemistry are of such a nature as to preclude even the mention of the class of work being conducted.

It is agreed that splendid judgment was shown by Van. H. Manning, director of the United States Bureau of Mines, by Dr. Chas. L. Parsons, the chief chemist of that bureau, by George E. Hale, chairman of the National Research Council, and by Prof. Marston T. Bogert, chairman of the Committee on Chemistry of the same organization, in undertaking several months ago a census of all chemists in the United States. As a result of the foresight shown, more than 10,000 names have been classified. This long list, which is thought to include a large proportion of the chemists of the United States, has been card indexed under the personal direction of Albert H. Fay, statistician for the Bureau of Mines. The chemists have been classified under no less than forty heads, so that ample sources of information on any subject are available to any one working in the government interest. It is also anticipated that it will be necessary to draw many men from this list for Federal Service, as Congress comes to realize the need for more chemical aid and appropriates for this work.

Speaking generally, however, Dr. Nichols' committee is canvassing the requirements of the country for chemical supplies and is matching this information against available supplies. Its efforts will be directed largely toward keeping the requirements and the production on a parity. Diligent work is under way to make available adequate supplies of such chemical materials as may show a deficiency. The importance of the work is more clearly understood when it is said that many of these materials are essential to our national life. The Nichols committee will give preferential attention to general industrial and munitions chemistry. A full understanding has been had with all government and many private agencies, so as to coordinate the work and to eradicate duplication.

Means by which poison gas attacks may be combatted form one of the principal problems being considered by the Chemistry Committee of the National Research Council, of which Marston T. Bogert, professor of organic chemistry at Columbia University, is chairman. It may be stated that definite results have been accomplished and that the assistance which the Committee is rendering is being increasingly recognized by the government.

Research, looking to betterments in non-corroding alloys also has been given preferential attention by Prof. Bogert's committee. The importance of these alloys has been increased tremendously during this war by the necessity of providing more lasting linings to lengthen the life of big guns, by the demand for guns to be mounted on submarines and by the need for non-corroding alloys in submarine and torpedo construction. Fixation of atmospheric nitrogen, problems involved in treating balloon envelopes, and the means of detecting hydrogen escaping from a gas bag give an idea of the varied problems which are under active investigation by the Chemistry Committee.

The development of industries, totally new to the United States, and the working out of certain standards for munition manufacturers and for those directing other businesses, give an indication of the tremendous scope of the work in hand. In fact, Prof. Bogert's committee is the clearing house for the chemical research work of the country. The organization is comprised of the main committee and some thirty subcommittees. Each of the subcommittees in turn function as a clearing house. The whole chemical field has been subdivided and each division placed in charge of a subcommittee. The returns of the census of the chemists taken by the National Re-

search Council, including replies from more than 10,000 chemists, have been classified carefully. Each sub-committee will be supplied with a list of the experts handling the class of work to which the sub-committee is assigned.

The Chemistry Committee is mainly coordinating and supplementing work being done by the various government bureaus. No work is undertaken until it is certain that efforts can be combined to advantage and care is taken to see that there is no duplication of effort. As a result of the stress of the existing war situation, investigations being conducted by the government, by universities and by privately conducted enterprises, are being forced into a much closer coordination. The old barriers of secrecy are being broken down. What had been impossible of attainment in times of peace is being accomplished quickly now, as a result of a great increase in efficiency. It is expected that this entente will be maintained after the close of the war.

Recently a ship carrying a cargo worth \$10,000,000 was sunk by a submarine. Prof. Bogert points out that a fraction of this sum would be sufficient to mobilize all the scientific brains of the country, and he is strongly of the opinion that more financial assistance should be given the scientific agencies which are at work on problems of the utmost importance to the welfare of the nation. As it is, much of the scientific work is being carried on by volunteers and their immediate friends at very heavy expense to themselves.

Due to the strain being placed upon the transportation facilities of the country, Dr. Carl L. Alsberg, chief of the Bureau of Chemistry of the Department of Agriculture, is making every effort to reduce to a practical basis the drying of fruits and vegetables, thereby eliminating ninety per cent of their weight and facilitating their transportation and preservation. Another great advantage of the drying process is the important difference in the expense between this and other methods of preservation.

High prices being demanded for copper sulfate have set the Bureau of Chemistry to a thorough checking up of the Pickering method of preparing Bordeaux mixture. The noted English chemist maintains that the amount of copper sulfate in Bordeaux mixture can be reduced materially without impairing its efficacy. In addition to laboratory work in this connection, actual field experiments are being conducted on an extensive scale.

Due to the fact that the chemical properties of lead arsenates never have been studied exhaustively, the Bureau of Chemistry is conducting important work with these compounds. It has been found that the common lead arsenates in many cases are not compounds, but mixtures instead. Since tri-lead arsenate is not formed by the ordinary processes of manufacture, work on this chemical is receiving special attention. Study is being made of the action of water upon the lead arsenates. Natural waters have been found with such chemical content as to break up a lead arsenate. Since arsenic in a soluble form is highly injurious to foliage, this problem is a very important one. It also has been found that some other spray materials, when combined with lead arsenates, also break up the compound. Calcium arsenates are being studied in the hope of providing a cheaper substitute for lead arsenates.

Rapid progress has been made by the congressional committees on the Trading with the Enemy Bill. The House Committee on Interstate and Foreign Commerce has ordered the bill reported favorably. Representative Montague, of New Jersey, was authorized to write the report and is now engaged in this work. A subcommittee of the Senate Committee on Commerce, consisting of Senators Randall, Vardaman, Vardaman and Fernald, is now engaged in the study of the bill. It probably will be reported to the full committee before the end of the present work. The subcommittee has found no objection to that portion of the bill which provides for the manufacture within the United States of such products as may be protected by a patent owned by an enemy of the nation. The bill authorizes the Federal Trade Commission to control the manufacture of such products if it is found to be in the public welfare. The bill provides that the patent, concerning the production of an article covered by such a patent shall be with the Federal Trade Commission and that the Secretary of the use and enjoyment of the invention that has been made. Five per cent of the gross sum received by the inventor from the sale of these inventions are to be reported with the government for the protection of the owner of the patent.

PERSONAL NOTES

The Franklin Institute made the annual presentation of its Franklin Medal on May 16, 1917. The medal was presented to Admiral David Watson Taylor, Chief Constructor, Chief of Bureau of Construction and Repair, United States Navy, in recognition of his "fundamental contributions to the theory of ship resistance and screw propulsion, and of his signal success in the application of correct theory to the practical design of varied types of war vessels in the United States Navy," and to Prof. Hendrik Antoon Lorentz, President Royal Academy of Sciences, Amsterdam, Professor of Mathematical Physics, University of Leiden, in recognition of his "researches which have so largely contributed to laying on a new foundation our knowledge of the nature of light and in developing our ideas concerning the ultimate constitution of matter." Chevalier W. L. F. C. van Rappard, on behalf of the Royal Netherlands Government, received the Franklin Medal for Prof. Lorentz, and addressed the Institute. Admiral Taylor addressed the Institute on the subject of "The Science of Naval Architecture."

Memorial services were held in Lawrence, Kansas, June 7, in honor of the late George E. Patrick, who, at the time of his death, was Chief of the Dairy Laboratory of the Bureau of Chemistry, U. S. Department of Agriculture. Following the service the ashes of Professor Patrick and of his wife were deposited in the cemetery at Lawrence. Professor Patrick was from 1874 to 1883 head of the Chemistry Department of the University of Kansas. In connection with the memorial services addresses were made on different phases of his life and work by Dr. Erasmus Haworth, Dr. E. H. S. Bailey, Hon. J. D. Bowersock, Dean L. E. Sayre and Chancellor Frank Strong. Professor Patrick left to the University a fund of something over \$7,000 in memory of his wife. The interest of this fund is to be used for a series of prize essays by students on "The Application of the Teachings of Jesus to the Practical Affairs and Relations of Life."

Dr. C. G. Storm has resigned his position as directing chemist of the Aetna Explosives Co., Inc., New York City, to accept a position as consulting explosives chemist with the Ordnance Department of the War Department, at Washington, D. C.

Dr. Wm. L. Gomory has discontinued practice in New York City as a consulting chemical engineer and is now associated with the Wabash Refining Company as general manager at their refinery in Robinson, Illinois.

At the May meeting of the Rhode Island Section of the A. C. S., a Chemical Section of the Providence Engineering Society was formed, which will have its meetings in conjunction with the Local Section of the A. C. S. It is expected that this affiliation will awaken greater interest in chemistry in that locality and be of benefit to both the chemists and the engineers.

The National Academy of Sciences gave a reception at the Smithsonian Institution, Washington, D. C., in honor of the members of the French Scientific Mission to the United States, on Thursday evening, June 14, 1917.

The Industrial Sites Association of America has been recently organized and incorporated, with offices at 115 Broadway, New York City. The purpose of the I. S. A. A. is to serve as a clearing house for data concerning the properties, sites, buildings, railroad and water facilities, labor conditions, population, etc., of all towns and cities where manufacturing plants could be advantageously established. This information will be given free.

William C. Carnell, chemical director for Harrison Brothers Co., Philadelphia, has resigned to become associated with Charles Lennig & Co., manufacturers of chemicals, Philadelphia.

Dr. T. R. Ball, of the University of Illinois, has been appointed assistant professor in chemistry at Washington University, Saint Louis, Mo.

Mr. Edward L. Pierce, vice-president of the Semet-Solvay Company, has been elected president of the Solvay Process Company to succeed the late Mr. Frederick R. Hazard.

Beta Rho, a local chemical fraternity of Washington University, Saint Louis, was installed on June 9, as Alpha Epsilon Chapter of Alpha Chi Sigma, the national chemical fraternity. The installation was conducted by Dr. L. I. Shaw, of Northwestern University, and Dr. L. F. Nickell, of Washington University, assisted by members of the Saint Louis Alumni Chapter. The members of the active chapter are Messrs. L. F. Nickell, E. E. Fickett, F. B. Langreck, I. C. Walker, E. J. Ulbricht, A. E. Goldstein, J. S. Logan, W. C. Adams, P. G. Marsh, J. F. Stickley, H. M. Van Horn, G. F. Dreimeyer, A. W. Roth, M. E. Schwarz, J. S. Boulden, C. W. Studt.

A Committee on Research to cooperate with the National Research Council has been appointed at Washington University, St. Louis, consisting of B. M. Dugger (Chairman), J. Erlanger, E. Flad, W. W. Horner, A. S. Langsdorf, E. Mallinckrodt, R. McCulloch, L. McMaster, G. T. Moore, E. L. Opie, L. Pyle, P. A. Shaffer and J. L. Van Ornum.

Dr. E. C. H. Davies, of the University of Chicago, has been appointed instructor in chemistry at Washington University.

Mr. F. A. Lidbury, manager of the Oldbury Electrochemical Company, Niagara Falls, N. Y., has been elected president of the Engineering Society of Buffalo.

Mr. B. A. Foley has terminated his connections as assistant manager of the Palo Co. and is now associated with the Lenx Apparatus Co., Inc., 9-11 East 16th Street, New York City.

Mr. Clifton Taylor, until recently general sales agent of the Electric Reduction Company, has been elected assistant treasurer. Mr. Taylor is located at the Washington plant office.

Drs. J. R. Bailey, H. W. Harper and E. P. Schoch, of the University of Texas, have recently taken over the solution of all chemical problems in connection with the largest army camp in this country, situated at San Antonio, Texas.

A complimentary dinner was given to Mr. Thomas J. Parker by some of his friends, at the Chemists' Club, New York City, on the evening of May 19th. The speakers were Dr. Milton C. Whitaker, Prof. Chas. F. Chandler, Dr. Charles H. Herty and Dr. Hugo Schweitzer.

Prof. C. E. Davis has resigned as professor of chemistry at the Utah Agricultural College at Logan, and accepted a position as research chemist for the National Biscuit Co., with headquarters in the Havesmeyer Laboratory, Columbia University.

Dr. R. P. Rose, until recently with the Mellon Institute and the General Coal Products Company, is now in Saint Louis in connection with work on a phenol plant.

Dr. William R. Cathcart has been appointed technical director of the mill and paper division of the Corn Products Refining Company, succeeding the late George M. MacNider.

James Mason Crafts, formerly president of the Massachusetts Institute of Technology (1898-1900), died at his summer home in Ridgefield, Conn., on June 20, aged 78 years.

The U. S. Civil Service Commission announces the following open competitive examinations: *Organic Chemist* (male), for filling two vacancies in the Bureau of Science, Manila, P. I., at entrance salaries from \$1800 to \$2250 a year; *Laboratory Aid and Junior Chemist* (male), at entrance salaries of \$3.28, \$3.84, \$4.48, and \$5.04 per diem.

Mr. Edward R. Taylor, charter member of the American Electrochemical Society, and for several years on the Board of Directors as manager and vice-president, died at his home in Penn Yan, N. Y., on May 28th. He was best known for his electrical carbon bisulfide furnace.

Platinum ware, consisting of two dishes, eight crucibles, and covers, and ten feet of wire, was stolen from the chemistry department of Miami University, Oxford, O., about May 26th.

Prof. Lloyd Van Doren, of Earlham College, Richmond, Ind., has been cooperating with The McIntosh Stereoscopic Co., Chicago, in the compilation of a series of lantern slides suitable for illustrating topics in general chemistry and in industrial chemistry.

The Technical Section of the Canadian Pulp and Paper Association held its Summer Meeting, June 14-16th, in the course of a visit to the plants of the Belgo-Canadian Pulp and Paper Co., The St. Maurice Paper Co., and Laurentide Co., Ltd., all situated in the province of Quebec. The Technical Association of the Pulp and Paper Industry sent delegates headed by President H. P. Carruth.

Dr. Allerton S. Cushman, president of the Institute of Industrial Research, with headquarters at Washington, D. C., has been commissioned a major in the Officers' Reserve Corps, and will do special research work under the ordnance section on the chemistry of high explosives.

The Blaw Steel Construction Company, Pittsburgh, Pa., announce the appointment of Mr. G. E. Land as advertising manager. Mr. Land was recently connected with the advertising department of the National Tube Company.

Miss Helen S. French, instructor of chemistry in Wellesley College, has been advanced to an assistant professorship.

Mr. James F. Couch has been elected president of the Des Moines Chemical Society.

Prof. G. H. Clevenger, of Leland Stanford University, has been appointed research professor in metallurgy and will relinquish his elementary and routine teaching.

Dr. E. C. Worden is in Texas directing the development of a new oil and sulfur property near Houston.

Mr. John C. Summers has recently been appointed as head of the Baking Department of the Dunwoody Institute at Minneapolis. He will sever his connections with the Operative Miller and Baker School and Laboratories July 1st and take up his new duties at that time in Minneapolis. Mr. Summers has previously been connected with the experiment stations in the Louisiana State University, Purdue University, Colorado Agricultural College, and Kansas Agricultural College, and has also filled the position of chief chemist with the Holley Sugar Company, Denver, Colorado.

The Fourteenth Annual Meeting of the American Leather Chemists' Association, held in Atlantic City, N. J., June 7-9, 1917, was the most successful ever held, both in point of attendance and the character of the papers presented. One hundred and thirty-five of the less than four hundred members of the association were present, Westerners predominating.

The following members of the Philadelphia Section A. C. S. are chairmen of subcommittees of the Chemistry Committee of the National Research Council, of which Dr. M. T. Bogert is chairman: Mr. Arthur H. Thomas, president Arthur H. Thomas Company, Philadelphia; Dr. A. E. Taylor, Rush professor of physiological chemistry, University of Pennsylvania; Dr. Arthur M. Comey, director of the Eastern Research Laboratories, E. I. du Pont de Nemours & Company.

Mr. James J. Bajda, formerly chief dye chemist and chemical engineer for B. Heller & Company, will have charge of the dye plants, now under construction, of the Block Chemical Laboratories.

W. E. Tottingham, assistant professor of agricultural chemistry, College of Agriculture, Madison, Wis., is on leave of absence and is working at Johns Hopkins University with Prof. Livingston, on special problems in plant chemistry and physiology.

Mr. C. D. Geidel, chemist and bacteriologist in the state food laboratory, Madison, Wis., has accepted a position in the miscellaneous laboratory, Bureau of Chemistry, Washington, D. C., and assumed his new duties on June 15.

FOREST PRODUCTS LABORATORY

Mr. C. P. Winslow has been appointed director of the Forest Products Laboratory to succeed Mr. H. F. Weiss, now in charge of the Division of Forest Products of the C. F. Burgess Laboratories.

Dr. A. W. Schorger, who for seven years has been connected with the Forest Products Laboratory, has resigned to take charge of organic chemistry with the C. F. Burgess Laboratories. The Burgess Laboratories are actively engaged at present upon problems of national preparedness and defense and are represented on both national and state committees. Dr. Schorger's immediate duties will be in connection with some of these problems, especially those relating to foodstuffs.

Mr. R. C. Palmer resigned as chemist in charge of wood distillation to become chief chemist of the Newport Resin & Turpentine Co., with headquarters at Pensacola, Fla. Dr. L. F. Hawley has succeeded him.

Dr. S. F. Acree severed his connection as chief chemist at the laboratory on April 1st. He is now with the National Wood Chemical Association, with headquarters at Syracuse University.

Dr. F. W. Kressman is now manager of the Standard Lesse Co. plant at Fullerton, La.

Mr. Sidney D. Wells has left the paper and pulp division to become superintendent of the Chesapeake Pulp & Paper Co. plant at West Point, Va.

INDUSTRIAL NOTES

The Marden, Orth & Hastings Company has recently opened a new branch office in the Hoge Building, Seattle. This is the fifth American branch of the firm, which has its main office at 61 Broadway, New York City.

The Bayer Company is suing the United Drug Company for alleged infringement of the trade mark "Aspirin."

A fire in the Barrett Manufacturing Co.'s chemical plant at Philadelphia, destroyed the naphthalene building and damaged several others, loss \$40,000.

A new company has recently been organized at Stockholm, Sweden, for the manufacture of nitric acid and other chemicals. The works will be erected at Trollhattan and will be supplied with electric energy by the "Royal Waterfalls Committee." The company intends to use the Birkeland-Eyde process and will produce about 7000 tons annually of concentrated nitric acid and a large quantity of nitrates as a by-product. It is planned to commence operations this year.

Experimental laboratories of the Aetna Explosives Company, at 1387 Sedgwick Avenue, Bronx, New York City, were partially wrecked by explosion on Tuesday night, May 29, 1917.

Harrisons, Inc., who recently became affiliated with the du Pont Chemical Works, Wilmington, have purchased the plants of Cawley, Clark & Company, large paint and color manufacturers, Newark, N. J., and the lithopane plant of the Beckton Chemical Company in Newark and Philadelphia. The deal is said to involve over \$2,000,000.

Walter Birge, president of the Air Reduction Company, has confirmed previous reports that negotiations were in progress looking to a merger of his Company with the Union Carbide Company. He stated that should any form of exchange of stock be agreed upon he would offer only the oxy-acetylene business of the Air Reduction Company. "The Company has been devoting much time to the development of the nitrogen end of its business," and Mr. Birge reported expected to be working its nitrogen plant on a commercial basis within a few days.

The American Association of Pharmaceutical Chemists at their annual convention in Atlantic City, N. J., adopted on June 15, resolution urging Congress to suspend the patent rights of alien enemies of the United States during the war.

The Synthetic Manufacturing Co., of North Tonawanda, N. Y., of which Mr. A. E. Summey is general manager, has recently engaged as production manager one of the production engineers of the Scoville Manufacturing Co. This was necessitated by the large demand on the Synthetic Co. for their products ortho and para nitrophenol and salicylic acid.

The American branch of the Treibacher Chemical Works of Treibach, Austria, contemplates the erection of an American plant. One of their chemists, Mr. Goldfogel, has recently returned from Austria where he spent several months familiarizing himself with the German process for the manufacture of rare earth metals. It is understood the Central Empires are using rare earth alloys in place of tungsten steel.

Contracts have been awarded by the Powers-Weightman-Rosengarten Co. for the erection of a shed at their factory, Ridge Ave. and Calumet St., Philadelphia, and for repairs to the factory. The shed will cost \$5,500 and the repairs \$9,000. The repairs are to replace the damage done in a recent fire at the plant.

The National Amine & Chemical Company, located for more than twenty years at 100 William Street, have leased three floors in the new Heckseher Building at 244 Madison Avenue, New York City, for executive offices.

Through a cooperative agreement with Cornell University, representatives of the Bureau of Mines have been stationed at Moore Hall, where the electric arc apparatus of the Department of chemistry has been utilized for some experimental work of the Bureau. Representatives of the Bureau, meeting at Cornell, have indicated that a suitable electric furnace might eventually reduce the metal losses from a carbonization and avoid the use of costly crucibles. The Harvard chemists have constructed a furnace with special attention to the efficiency of use in terms of heat contained and with special attention to the temperature problem caused by the Bureau. The Bureau is interested in the use of the furnace for the production of carbon monoxide from the reaction of carbon and steam, and in the extraction of metals from ores. Arrangements to install a suitable electric furnace for the Bureau are being made. It may be the result of the work at Cornell that the Bureau will be able to produce carbon monoxide from the reaction of carbon and steam, and avoid the use of costly crucibles. The Harvard chemists have constructed a furnace with special attention to the efficiency of use in terms of heat contained and with special attention to the temperature problem caused by the Bureau. The Bureau is interested in the use of the furnace for the production of carbon monoxide from the reaction of carbon and steam, and in the extraction of metals from ores. Arrangements to install a suitable electric furnace for the Bureau are being made. It may be the result of the work at Cornell that the Bureau will be able to produce carbon monoxide from the reaction of carbon and steam, and avoid the use of costly crucibles.

GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

BUREAU OF STANDARDS

Rules and Regulations for the Enforcement of the Lime-Barrel Act. ANONYMOUS. Circular No. 64, 5 pp. Issued April 20. Paper, 5 cents.

Structure of the Coating on Tinned Sheet Copper in Relation to a Specific Case of Corrosion. PAUL D. MERICA. Technologic Paper No. 90, 17 pp. Paper, 5 cents.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS

Annual Report. This report includes the following five supplements which contain the principal technical findings as developed by the Board during its two years' work: General specifications covering requirements of aeronautic instruments; nomenclature for aeronautics; mufflers for aeronautic engines; gasoline carburetor design; experimental researches on the resistance of air.

GEOLOGICAL SURVEY

Zinc in 1915. Production and Resources. C. E. SIEBENTHAL. From Mineral Resources of the United States, 1915, Part I, pp. 851-981. Published April 30.

SPELTER PRODUCED AND CONSUMED IN THE UNITED STATES IN 1915	
Production of primary spelter (a)	(Short tons)
From domestic ore.....	458,135
From foreign ore.....	31,384
	489,519
Production of secondary spelter (a).....	29,764
Redistilled.....	23,136
Remelted.....	542,419
Apparent consumption of primary spelter.....	364,494

(a) "Primary spelter," which is produced directly from ore, is here distinguished from "secondary spelter," which is obtained by refining zinc ashes, skimmings, drosses, and old metals. The statistics of secondary spelter are given on page 856.

Fuel Briquetting in 1916. C. E. LESHNER. From Mineral Resources of the United States, 1916, Part II, pp. 1-4. Published May 4. "The production of fuel briquets in 1916 was 295,155 net tons, valued at \$1,445,662, an increase, compared with 1915, of 73,618 tons, or 33 per cent, in quantity and \$409,946, or 40 per cent, in value. The production in 1916 was the greatest recorded and exceeded that of 1914, the previous high record, by 44,520 tons."

Gypsum. R. W. STONE. Bulletin 666-E. 3 pp. "The three years 1913-1915 saw no marked fluctuation in the gypsum industry. For some time the annual output has been near 2,500,000 tons of raw material.

"This particular industry could not suffer from restraint of ocean traffic, because the imports, which come wholly from New Brunswick and Nova Scotia, are normally only about one-fifteenth as much as the domestic production, and gypsum is so abundant and widespread in the United States that the nation is easily industrially independent in this respect.

"In 1915 there were 77 active mines or quarries which supplied 69 gypsum plants. A number of plants are standing idle. In case of greatly increased demand for gypsum products

the idle plants could quickly be put into commission, and the active plants that are working only one or two shifts could be put on a 24-hour schedule, thus making a large increase in the output. The production of gypsum boards probably could not be so quickly increased as that of other products, because they are made on machines which are not on the market.

"As the deposits of high-grade gypsum in the United States are widespread, practically inexhaustible, and in many places close to present lines of transportation, and as the milling part of the industry can easily be made to increase its output, the outlook for this popular structural material is fair even in times of world-wide unrest.

"The principal uses of gypsum are as structural material and as ingredient in Portland cement. Gypsum wall plaster is in common use, and gypsum boards, blocks, and tile are fast making a market because of their light weight, convenience, and fire-resistant qualities. Because of the rapidity with which the plaster sets, permitting carpenters to follow the plasterers within a few hours, and because of the size and shape of the gypsum block, tile, and board units, which favor quick construction, these materials are especially adapted to the hurried emergency building operations occasioned by great industrial activity."

Grinding and Polishing Materials. F. J. KATZ. Bulletin 666-K. 3 pp. "The American industries requiring millstones, grindstones, pulpstones, oilstones, whetstones, scythestones, corundum, garnet, silica, feldspar, diatomaceous earth, and tripoli, have long been independent of foreign supplies, and the developed domestic sources of supply are capable of greatly increased production. The imports of these materials have been small in comparison with domestic production and have very probably been fostered only by a natural preference and conservatism in favor of articles that had long been used before the American supplies came into the market.

"American emery seems to be inferior to and unable to supplant the emery from Naxos, Greece, imports of which have been very largely shut out. Artificial carbide and aluminum oxide abrasives can be substituted, but some manufacturers, particularly lens grinders, seem to be reluctant to make a change, probably because it would involve changes in technique. Necessity must overcome such reluctance.

"Corundum for a number of years has been supplanted by the artificial abrasives. Very recently, however, there has been a small revival in corundum mining.

"No domestic source of satisfactory lump pumice has been exploited commercially.

"The country remains dependent on foreign sources for diamond dust and bort, imports of which in the last three years have been about 25 per cent less than the average during the previous three years.

"The pottery industry, however, is in need of siliceous pebbles for grinding quartz and feldspar in tube mills. Substitutes that contain even small quantities of iron cannot be used.

"Metallurgic plants and cement mills have used a far larger quantity of flint pebbles than the pottery industry. The pure silica pebble is not required for them, the only essentials being toughness and hardness. For these purposes there are large quantities of suitable granite and porphyry pebbles in many localities along the New England coast which have not yet been drawn upon.

"Dimension blocks cut from quartzites in Florida, Tennessee, and Iowa, have appeared on the market during the last two years and seem to be satisfactorily supplanting foreign flint lining."

Potash. HOYT S. GALE. Bulletin 666-N. 4 pp. "The output of potash salts and potash products in the United States during 1916 has been reported to the amount of 35,739 short tons, having a mean potash content of about 27 per cent K_2O and a total potash content of 9,720 short tons of K_2O . This is almost exactly 10 times the production reported for 1915, although it is still perhaps less than 5 per cent of the normal potash consumption. In 1913 the only potash known to have been produced within this country was made from wood ashes.

"The almost entire stoppage of supplies from abroad and the meager stocks on hand with which to meet the requirements have at times carried the price of potash from a normal figure of 50 to 75 cents to \$5 or \$6 a unit (1 per cent of potash per ton of material).

"The forms in which potash has been produced and marketed are so diverse that it is difficult to make a summation of actual tonnage that will have any real significance. Therefore the tonnage reports of all forms have been reduced to terms of available or water-soluble potash (K_2O) contained in the product, which is the standard commercial unit by which the potash value of these materials is usually expressed.

SUMMARY OF POTASH PRODUCTION IN 1916

SOURCE	Available potash (K_2O) (short tons)	Value of point of shipment
Natural salts or brines.....	3,994	\$1,937,600
Alunite and silicate rocks, including recoveries through furnace dust.....	1,850	715,000
K_2CO_3	1,356	781,100
Wood ashes (potashes, pearl ash).....	412	270,000
Distillery waste (molasses).....	1,845	500,900
Miscellaneous organic sources.....	63	38,130
	9,720	\$4,242,730

"The foregoing list does not include many fertilizer materials previously on the market, such as cottonseed meal and tobacco stems, some of which are largely or chiefly valued for their potash content and whose price has accordingly risen in the present market. These materials, being by-products of other industries, are not produced primarily because of their content of potash. The total given therefore represents the marketed production of potash salts and products manufactured especially or chiefly for their potash value.

"The present situation of this country concerning potash, with a view to possible emergency requirements, though not ominous, requires most careful consideration. It may be assumed that the stocks of high-grade salts of German origin remaining in the United States and, indeed, throughout the world except in the central allied countries are now practically exhausted. The actual domestic production of high-grade salts, moreover, is still very small and is limited to a very few sources, and the difficulties in the way of refining the large bulk of low-grade potash materials would probably be great."

Bauxite and Aluminum. JAMES M. HILL. Bulletin 666-O. "The consumption of bauxite in the United States has increased steadily because of increase both in the consumption of aluminum and in the output of other products made from bauxite. It is particularly gratifying to know that although the consumption of bauxite in the United States in 1916 amounted to 425,130 long tons, an increase of 41 per cent over the consumption in 1915 and of 74 per cent over the consumption in 1914, practically all domestic requirements were met by the American producers. This bears out the forecast made by the Geological Survey in 1914, that the domestic deposits would be more actively developed to supply the demand formerly met by French bauxite.

"Deposits of bauxite in Pulaski and Saline Counties, Ark., have yielded the larger part of the domestic output. The deposits in the bauxite field of northern Georgia and Alabama have contributed a considerable quantity, and in recent years

the fields in central Georgia and Tennessee have made additions to the output.

"The growth of the American aluminum industry has been steady heretofore, but it is probable that the production in 1917 will show a pronounced increase, owing to the operation of the new plant at Badin, N. C., which is practically completed and which made a small output in 1916. This project, started by French capital, was taken over by American interests in 1915 and pushed to completion.

"The uses of aluminum are myriad, but as some are more essential than others, it is likely that the minor articles formerly made from aluminum will for the present be made in smaller quantity, because the available supply of aluminum will probably be diverted to more urgent uses.

"In statistics for years prior to 1916 published by the United States Geological Survey, the output of aluminum abrasives has been included with that of other artificial abrasives and cannot now be separated, but the domestic production in 1916 amounted to 30,708 short tons, having a value of \$2,139,230."

PUBLIC HEALTH SERVICE

Vaccine Virus. ANONYMOUS. Public Health Reports, 32, 687-9 (May 11). Virus of various manufacturers purchased at drug stores has been found, though within the stamped expiration date, to give less than 50 per cent of "takes," but when obtained direct from the manufacturer, "takes" were nearly 100 per cent. Vaccine virus at pharmacies is often kept in the cellar or in the soda fountain cooler, and the temperature of these places, both winter and summer, has been found to be in the neighborhood of 15° C. (59° F.) or higher. This is by no means satisfactory. Ice-box temperature is not freezing temperature, but usually several degrees above freezing. Vaccine virus should be kept in a metal container in constant contact with the ice itself. If it can be kept at or below the freezing point, so much the better. There is no danger of keeping it too cold.

Conference of Health Authorities. United States Public Health Service in Annual Conference with State and Territorial Health Authorities, Washington, April 30 and May 1, 1917. Public Health Service, 32, 689-91 (May 11). This is a summary of the proceedings.

Drinking Fountains. Investigation of Fountains at the University of Minnesota. H. A. WHITTAKER. Public Health Reports, 32, 691 (May 11). "This investigation included the 77 drinking fountains in use at the University of Minnesota. These fountains represented 15 different types, all of which were found to be improperly constructed to prevent them from contamination by the consumer. The bacteriological examinations conducted on these fountains showed that 80 per cent were infected with streptococci, and that the water from 11 per cent of these fountains contained organisms of this type when they were not found present in the water supplied to the fountains. These results indicate that drinking fountains may be a factor in the transmission of communicable diseases, a condition which should be remedied.

"Experiments were conducted with various fountain nozzles to supplant those in use, and a type was designed which is economical to construct and safe from a sanitary point of view."

Public Health Administration in South Bend, Indiana. C. E. ROHL FOX. Public Health Reports, 32, 694-5 (May 11). Of interest to municipal and state health officials.

The Public Health Service in Time of War. Executive Order Making the United States Public Health Service a Part of the Military Forces of the United States. Public Health Reports, 32, 695 (May 11). Under the authority of the Act of Congress approved July 1, 1916, and subject to the limitations therein expressed, it is ordered that hereafter the members of the

ened or actual war the Public Health Service shall constitute a part of the military forces of the United States, and in times of threatened or actual war the Secretary of the Treasury may, upon request of the Secretary of War or the Secretary of the Navy, detail officers or employees of said service for duty either with the Army or the Navy. All the stations of the Public Health Service are hereby made available for the reception of sick and wounded officers and men, or for such other purposes as shall promote the public interest in connection with military operations.

(Signed) WOODROW WILSON

THE WHITE HOUSE, 3 April, 1917."

Maintenance of Health in Industries. Its Relation to the Adequate Production of War Materials. J. W. SCHERESCHESKY. Public Health Reports, 32, 835-839 (June 1).

COMMERCE REPORTS—MAY, 1917

Owing to the cutting off of the Austrian supply, exports of **magnesite** from Greece to the United States have greatly increased. Details of its mining, calcimining and uses are given. (Pp. 411-415.)

Several plants in Switzerland are preparing to manufacture **synthetic alcohol** and **acetic acid**, starting with **calcium carbide**. The proposed annual output is 7,500 to 10,000 tons of alcohol. (P. 426.)

Tests made at the Bureau of Standards upon "palau" as a **substitute for platinum** in crucibles, have shown that it compared favorably with platinum. It is, however, much more attacked by fused pyrosulfate than is platinum. (P. 427.)

The output of **porcelain** from Bohemia in 1916 was about half the normal amount. Fears are expressed as to future trade in the United States owing to American and Japanese competition. (P. 480.)

The Norwegian production of **whale oil** is about 58 per cent of the world's production. The oil obtained by boiling the flesh and bones is of inferior grade, containing as much as 50 per cent of free fatty acids. **Fertilizer** and cattle food are obtained as by-products. (P. 454.)

Investigation of **platinum** deposits in Spain has shown that platinum is present in the sands of 12 or more rivers, in amounts up to 2 or 3 g. per cubic meter. The investigation is to be continued and will also include study of associated iron chromium and nickel deposits. (P. 476.)

Export of **argols** from Argentina is decreasing on account of increased production and consumption of **tartaric acid** in Argentina. (P. 484.)

Production of **rubber** in the Dutch East Indies shows a large increase. (P. 497.)

A factory for the manufacture of "**kraft**" paper has been established in British Columbia. (P. 498.)

Great efforts are being made to increase the production of **camphor** in Formosa. (P. 500.)

Details of the cultivation of coconuts and production of **copra** in East Africa are described. (P. 502.)

Japan is now suffering from an over-supply of **potassium chlorate**, the price of which has greatly declined. (P. 553.)

Imports of **copra** and **coconut oil** into the United States for 1917 are nearly twice those of 1916. The three principal sources are the Philippines, Australia and the Dutch East Indies. (P. 556.)

Plans are being made in Russia to increase the production of **cement** to four or five times the present annual production (25,000,000 barrels). (P. 574.)

Hull, England, is now the world's greatest center for the **vegetable-oil** industry, based on the quantity of oil-yielding materials handled. Marseilles is first in yield of oil. The principal materials used are linseed, rape-seed, cottonseed, castor seed, soya beans, illipe, mowra, poppy seed, sesame seed, palm kernels, peanuts, and copra. The oils are in demand for marga-

rine, and as a source of glycerine; and the "cake" for cattle food. (Pp. 580-588.)

A list of **dyestuff manufacturers**, prepared by the Bureau of Foreign and Domestic Commerce, contains the names of 158 manufacturers. (P. 590.)

Lignite is to be used as fuel in Australian power plants. (P. 603.)

Statistics are given for the Japanese production and export of **antimony**, **molybdenum**, **tin**, and **tungsten**. (P. 647.)

Production of **platinum** in Russia in 1916 was 86,800 troy ounces, about 75 per cent of the 1915 production. (P. 647.)

Export of **nitrate** from Chili has again decreased, owing to the shortage of vessels and to strikes. (P. 678.)

A company has been formed in Norway for developing the extensive deposits of **titanium iron ore**. (P. 709.)

The use of coal gas for firing furnaces for the **heat treatment of metals** is increasing greatly in England. (P. 715.)

Exports of **copper** from Chile in 1916 are higher than ever before, being 20,000 tons greater than in 1915. (P. 725.)

Production of **mica** in India is over 50 per cent greater than usual. (P. 734.)

Plans are being made in British Guiana to manufacture **alcohol** instead of rum (import of which into the United States has been forbidden). An annual production of 4 or 5 million gallons of alcohol is anticipated. (P. 751.)

New deposits of **copper** and **gold** are reported from Central Asia. (P. 769.)

Large deposits of **chrome iron ore** and **molybdenite** are reported from Australia. (P. 794.)

Any appreciable export of **soya beans** from Manchuria to the United States is unlikely, owing to the local demand and to the lack of shipping. Details of the production and handling of the beans are described. (P. 796.)

Large **iron works** are to be erected at Ekaterinburg, in the Urals. (P. 799.)

Russia furnishes practically the world's whole supply of **licorice** which is used in medicines, candy and tobacco. The industry is described in some detail. (P. 806.)

The mineral output of British Columbia in 1916 was over 40 per cent greater than in 1915. It includes **gold**, **silver**, **lead**, **copper**, **zinc**, **coal**, and **coke**. Some **manganese** was obtained as a by-product of zinc smelting; about 40 ounces of **platinum** were recovered in placer mining; and small amounts of **antimony** and **molybdenum** ores were also produced. (Sup. 23b.)

SPECIAL SUPPLEMENTS ISSUED DURING THE MONTH

DENMARK—4a	DOMINICAN REPUBLIC—26a
SWEDEN—16a	HAITI—30a
CANADA—23b and c	ADEN—49a

STATISTICS OF EXPORTS TO THE UNITED STATES

LONDON 642	DENMARK—Sup. 4a	BRITISH COLUMBIA—
Rubber	Chalk	Sup. 23b
Tin	Chemicals	Bullion
Hides	Diamonds	Cassara
Indigo	Flint pebbles	Coal
	Fusel oil	Explosives
NOTTINGHAM 686	Hides	Fertilizer
Leather	Ink	Firebrick
Paints	Leather	Hides
Hides	Paper	Lime
Stoneware	Porcelain	Copper ore
	Rags	Gold ore
	Rennet	Rubber
VERA CRUZ 702	SWEDEN Sup. 16a	Tin
Chicle	China	NOVA SCOTIA Sup.
Vanilla	Classware	23b
Hides	Enamelled ware	Cod oil
Rubber	Hides	Fertilizer
Lead	Iron and steel	Grindstones
Mica	Iron ore	Gypsum
Mercury	Matches	Hides
Silver	Fusel oil	Lime juice
	Cresote oil	Manganese ore
DOMINICAN REPUBLIC	Paper	Paper stock
Sup. 26a	Potash	HAITI Sup. 30a
Hides	Soda	Beeswax
Molasses	Wood pulp	Castor beans
Copper ore	WINNIPEG—Sup. 23c	Coconuts
Rosin	Hides	Fustic
Sugar	Paper	Guano
Wax	Senega root	Hides
Fustic	Wood pulp	Logwood
Logwood		

NEW PUBLICATIONS

By IRVING DE MATTEY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- Agricultural Geology.** R. H. RASTALL. 8vo. 331 pp. Price, \$3.25. C. P. Putnam's Sons, New York.
- Agriculture: Productive Agriculture.** J. H. GEHRS. 12mo. 436 pp. Price, \$1.00. The Macmillan Company, New York.
- Analysis: A Brief Outline of Qualitative Analysis.** J. O. FRANK. 8vo. 22 pp. Price, \$0.50. Castle Pierre Press, Oshkosh, Wis.
- Applied Mechanics: Cours élémentaire de mécanique industrielle.** E. GOUARD and G. HERNIAUX. 2 Vol. 8vo. 549 pp. Price, 7 fr. H. Dunod et E. Pinat, Paris.
- Cement Industry: A Practical Treatise on the Building, Equipping and Running of a Portland Cement Plant.** W. A. BROWN. 8vo. 158 pp. Price, \$3.00. D. Van Nostrand Company, New York.
- Chemical Tests for Minerals.** A. J. BURDICK. 12mo. 93 pp. Price, \$1.25. Gateway Publishing Company, Beaumont, Cal.
- Chemistry: Experimental General Chemistry.** J. H. RANSOM. 2nd Ed. 12mo. 191 pp. Price, \$1.00. McGraw-Hill Book Company, New York.
- Chemistry: Historical Introduction to Chemistry.** T. M. LOWRY. 12mo. 581 pp. Price, \$2.50. The Macmillan Company, New York.
- Chemistry: Les Sciences physiques du brevet élémentaire. Notions de physique et de chimie.** A. BRÉMANT. 16mo. 374 pp. Price, 8 fr. E. Arault et Cie, Paris.
- Chemistry of Farm Practice.** T. E. KEITT. 12mo. 265 pp. Price, \$1.25. John Wiley & Sons, New York.
- Compressed Air for the Metal Worker.** C. A. HIRSCHBERG. 8vo. 321 pp. Price, \$3.00. Clark Book Company, New York.
- Engineers' Manual.** R. G. HUDSON and OTHERS. 12mo. 310 pp. Price, \$2.00. John Wiley & Sons, New York.
- Food Analysis: A Course in Food Analysis.** A. L. WINTON. 8vo. 252 pp. Price, \$1.50. John Wiley & Sons, New York.
- Gasworks: Modern Gasworks Practice.** ALWYN MEADE. 4to. 529 pp. Price, \$7.50. D. Van Nostrand Company, New York.
- Hydrodynamics.** HORNER LAMB. 4th Ed. 8vo. 708 pp. Price, \$6.25. C. P. Putnam's Sons, New York.
- Hydroelectric Practice: American Hydroelectric Practice.** W. T. TAYLOR. 8vo. 439 pp. Price, \$5.00. McGraw-Hill Book Company, New York.
- Inorganic Chemistry: Experimental Inorganic Chemistry.** ALEXANDER SMITH. 5th Ed. 12mo. 171 pp. Price, \$1.00. The Century Company, New York.
- Marine Engineering.** W. F. DURAND. 8vo. 982 pp. Price, \$6.00. Marine Engineering, New York.
- Materials: Résistance des matériaux appliqués aux constructions.** E. ARAGON. 8vo. 662 pp. H. Dunod et E. Pinat, Paris.
- Mechanical Movements, Powers and Devices.** G. D. HIRSCH. 15th Ed. 8vo. 409 pp. Price, \$3.00. Norman W. Henley Publishing Company, New York.
- Scientific Works: Bibliographie des travaux scientifiques.** J. DENIKER. 4to. 206 pp. Price, 5 fr. Ernest Leroux, Paris.
- Sewage: The Activated Sludge Process of Sewage Treatment. A Bibliography of the Subject with Abstracts.** J. E. PORTER. 8vo. 40 pp. Price, \$0.25. General Filtration Company, Rochester, N. Y.
- Solution: The Nature of Solution.** H. C. JONES. 8vo. 380 pp. Price, \$3.50. D. Van Nostrand Company, New York.
- Storage Batteries Simplified; Operating Principles, Care and Industrial Applications.** V. W. PAGE. 12mo. 208 pp. Price, \$1.50. Norman W. Henley Publishing Company, New York.
- Sulfuric Acid: The Manufacture of Sulfuric Acid and Alkali; a Theoretical and Practical Treatise. Supplement to Vol. I.** GEORGE LING. 4th Ed. 8vo. 347 pp. Price, \$5.00. D. Van Nostrand Company, New York.
- Tube Milling.** A. DUMAS. 8vo. 159 pp. Price, \$2.00. McGraw-Hill Book Company, New York.
- White Coal (Tasmanite). La Houille blanche.** A. BERGER. 8vo. 74 pp. Price, 6 fr. Joseph Barthe, Grenoble.

RECENT JOURNAL ARTICLES

- Acetylene: Cutting Steel Risers with Oxy-Acetylene.** A. KREBS. *The Acetylene Journal*, Vol. 18 (1917), No. 12, pp. 661-666.
- Ammunition: Problems in Ammunition Manufacture.** A. J. HEMMEL. *The Iron Trade Review*, Vol. 60 (1917), No. 33, pp. 1127-1133.
- Chemical Reactions of Ore Smelting.** W. C. HARRISON. *The Iron Trade Review*, Vol. 60 (1917), No. 23, pp. 1034-1036.
- Coal-Tar Dyestuff Industry.** J. P. STINE. *The Chemical Engineer*, Vol. 25 (1917), No. 3, pp. 110-117.
- Coke Briars and Its Utilization.** W. A. HAYES. *Coal*, Vol. 14 (1917), No. 18, pp. 80-84.
- Compressed Air.** C. E. HERRICK. *Industrial Management*, Vol. 53 (1917), No. 7, pp. 55-56.
- Electric Furnace: A Convenient and Inexpensive Electric Furnace for High Temperatures.** A. W. FAHRENWALD. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 10, pp. 565-566.
- Flax Straw as a Material for Papermaking.** E. B. BIGGAR. *Paper*, Vol. 20 (1917), No. 9, pp. 13-14.
- Flotation: The Cascade Flotation Machine.** C. R. WILFLEY. *Engineering and Mining Journal*, Vol. 103 (1917), No. 20, pp. 871-873.
- Flow of Water over Triangular Weirs.** H. E. BROUGHTON. *Technology Monthly*, Vol. 4 (1917), No. 2, pp. 21-25.
- Furnace: Non-Reversing Regenerative Furnace for Copper Smelting.** W. G. PERKINS. *Mining and Scientific Press*, Vol. 114 (1917), No. 22, pp. 759-762.
- Glass Analysis.** E. W. HAGMAIER. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 10, p. 604.
- Industrial Chemists and the Fertilizer Crisis.** H. C. LINT. *The Chemical Engineer*, Vol. 25 (1917), No. 3, pp. 86-89.
- Industrial Scales and Weighing.** H. T. WADR. *Industrial Management*, Vol. 53 (1917), No. 2, pp. 252-271.
- Leaching of Low-Grade Copper Ores.** JOSEPH IRVING. *Engineering and Mining Journal*, Vol. 103 (1917), No. 21, pp. 932-933.
- Lead Mining in Derbyshire.** L. C. STUCKEY. *The Mining Magazine*, Vol. 16 (1917), No. 4, pp. 193-200.
- Metallurgy: Five Years of Metallurgical Progress.** F. A. THOMSON. *Mining and Scientific Press*, Vol. 114 (1917), No. 19, pp. 654-656.
- Metallurgy of Ferro-Silicon.** R. J. ANDERSON. *The Iron Trade Review*, Vol. 60 (1917), No. 19, pp. 1025-1029.
- Metals: The Scientific Cutting of Metals.** A. L. DELBEEU. *The Iron Trade Review*, Vol. 60 (1917), No. 22, pp. 1178-1180.
- Microscopic Paper Fiber Analysis.** G. K. SPENCE and J. M. KRAUSS. *Paper*, Vol. 20 (1917), No. 11, pp. 11-13.
- Milk: The Composition of Milk.** P. S. ARUP and OTHERS. *The Analyst*, Vol. 42 (1917), No. 493, pp. 118-124.
- Nitrogen: Relation of the Transformation and Distribution of Soil Nitrogen to the Nutrition of Citrus Plants.** I. G. McBERTH. *Journal of Agricultural Research*, Vol. 9 (1917), No. 7, pp. 183-252.
- Oil and Gas in Southwestern Texas.** A. J. HAZLETT. *Oil Trade Journal*, Vol. 8 (1917), No. 6, pp. 92-94.
- Ore Treatment at the Perseverance Mine, West Australia.** W. R. CLOUTMAN. *The Mining Magazine*, Vol. 16 (1917), No. 4, pp. 202-208.
- Paper: Handmade Paper and Its Watermarks; A Bibliography.** DARD HUNTER. *Paper*, Vol. 20 (1917), No. 12, pp. 20-26.
- Paper: Folding Endurance of Paper.** F. P. VITCH and OTHERS. *Paper*, Vol. 20 (1917), No. 12, pp. 13-19.
- Petrography as an Aid to Flotation.** D. G. CAMPBELL. *Engineering and Mining Journal*, Vol. 103 (1917), No. 21, pp. 929-931.
- Plumas Copper Belt.** G. H. GOODHUE. *Engineering and Mining Journal*, Vol. 103 (1917), No. 22, pp. 969-970.
- Potash "Noose."** THOMAS H. NORTON. *The Chemical Engineer*, Vol. 25 (1917), No. 3, pp. 84-86.
- Radioactivity.** W. I. HARKINS. *Radium*, Vol. 9 (1917), No. 2, pp. 30-39.
- Refractories: The Deterioration of Refractories.** H. B. CROSSHAW. *The Iron Trade Review*, Vol. 60 (1917), No. 20, pp. 1086-1088.
- Refrigeration: Operating the Absorption Refrigeration Machine.** D. L. EVANS. *Refrigerating World*, Vol. 52 (1917), No. 8, pp. 15-17.
- Salt Manufacture by Solar Evaporation of Sea Water.** L. A. PALMER. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 9, pp. 317-319.
- Science and Commercialism.** R. G. PICKINSON. *Engineering Magazine*, Vol. 4 (1917), No. 7, pp. 26-28.
- Silica: Accurate Silica Determination in Commercial Analysis.** F. G. HAWLEY. *Engineering and Mining Journal*, Vol. 103 (1917), No. 18, pp. 841-843.
- Silica as a Component of Furnace Slags.** W. G. IMHOFF. *Steel, Pig Iron and Scrap*, Vol. 5 (1917), No. 4, pp. 133-136.
- Silicate: A New Silicate of Lead and Zinc.** P. A. VAN DER MEULEN. *Bulletin of the American Institute of Mining Engineers*, Vol. 123 (1917), No. 123, pp. 183-185.
- Slags: Characteristics of Electric Furnace Slags.** W. G. IMHOFF. *Steel, Pig Iron and Scrap*, Vol. 5 (1917), No. 5, pp. 163-170.
- Specific Gravity in Rubber Compounding.** A. C. ELLIS. *Mechanical Engineering*, Vol. 146 (1917), No. 1114, p. 1114.
- Starches: Properties Useful to Mills.** L. M. M. STARK. *Paper*, Vol. 20 (1917), No. 1, pp. 16-17.
- Steam: Oil Engines for Small Light Plant.** C. H. MURKIN. *Paper*, Vol. 45 (1917), No. 2, pp. 2-3.
- Steam Distillation: Studies in Steam Distillation.** H. B. HARRINGTON. *Chemical Engineering*, Vol. 42 (1917), No. 3, pp. 3-4.
- Steel for Architectural Engineers.** A. J. HARRINGTON. *Paper*, Vol. 45 (1917), No. 2, pp. 2-3.

MARKET REPORT—JUNE, 1917

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON JUNE 20

INORGANIC CHEMICALS

Acetate of Lime.....	100 Lbs.	4.50	@	4.55
Alum, lump ammonia.....	100 Lbs.	4.00	@	4.25
Aluminum Sulfate, high-grade.....	Ton	70.00	@	80.00
Ammonium Carbonate, domestic.....	Lb.	11 1/2	@	12
Ammonium Chloride, white.....	Lb.	15	@	15 1/2
Aqua Ammonia, 26° drums.....	Lb.	6 1/2	@	7
Arsenic, white.....	Lb.	18	@	19
Barium Chloride.....	Ton	80.00	@	90.00
Barium Nitrate.....	Lb.	11	@	11 1/2
Barytes, prime white, foreign.....	Ton	30.00	@	40.00
Bleaching Powder, 35 per cent.....	100 Lbs.	1.75	@	2.00
Blue Vitriol.....	Lb.	9 1/2	@	10
Borax, crystals, in bags.....	Lb.	7 1/4	@	8 1/4
Boric Acid, powdered crystals.....	Lb.	13	@	13 1/2
Brimstone, crude, domestic.....	Long Ton	45.00	@	
Bromine, technical, bulk.....	Lb.	55	@	60
Calcium Chloride, lump, 70 to 75% fused.....	Ton	30.00	@	32.00
Caustic Soda, 76 per cent.....	Lb.	6.75	@	6.85
Chalk, light precipitated.....	Lb.	4 1/2	@	4 1/4
China Clay, imported.....	Ton	18.00	@	30.00
Feldspar.....	Ton	8.00	@	15.00
Fuller's Earth, foreign, powdered.....	Ton	35.00	@	
Glauber's Salt, in bbls.....	100 Lbs.	70	@	75
Green Vitriol, bulk.....	100 Lbs.	1.00	@	1.05
Hydrochloric Acid, commercial, 18°.....	Lb.	1 1/2	@	1 1/2
Hydrochloric Acid, C. P., conc., 22°.....	Lb.	1 1/4	@	2
Iodine, resublimed.....	Lb.	3.50	@	3.55
Lead Acetate, white crystals.....	Lb.	15	@	15 1/4
Lead Nitrate.....	Lb.	15 1/2	@	16
Litharge, American.....	Lb.	11	@	11 1/4
Lithium Carbonate.....	Lb.	1.25	@	
Magnesium Carbonate, U. S. P.....	Lb.	20	@	22
Magnesite, "Calcined".....	Ton	60.00	@	65.00
Nitric Acid, 36°.....	Lb.	6 1/2	@	6 1/4
Nitric Acid 42°.....	Lb.	7 1/2	@	8 1/2
Phosphoric Acid, sp. gr. 1.710.....	Lb.	3 1/2	@	3 1/2
Phosphorus yellow.....	Lb.	1.45	@	1.50
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, casks.....	Lb.	36	@	37
Potassium Bromide (granular).....	100 Lbs.	1.00	@	1.10
Potassium Carbonate, calcined, 80 @ 85%.....	Lb.	65	@	75
Potassium Chlorate, crystals, spot.....	Lb.	54	@	56
Potassium Cyanide, bulk, 98-99 per cent.....	Mixture	2.30	@	2.40
Potassium Hydroxide, 88 @ 92%.....	Lb.	82	@	83
Potassium Iodide, bulk.....	Lb.	2.90	@	
Potassium Nitrate.....	Lb.	30	@	32
Potassium Permanganate, bulk.....	Lb.	4.00	@	4.25
Quicksilver, flask.....	75 lbs	85.00	@	
Red Lead, American, dry.....	Lb.	11 1/2	@	13
Salt Cake, glass makers'.....	Ton	19.00	@	20.00
Silver Nitrate.....	Oz.	47 1/4	@	
Soapstone in bags.....	Ton	10.00	@	12.50
Soda Ash, 58%, in bags.....	100 Lbs.	2.70	@	2.80
Sodium Acetate.....	Lb.	9	@	10
Sodium Bicarbonate, domestic.....	100 Lbs.	2.10	@	2.25
Sodium Bichromate.....	Lb.	15 1/4	@	16 1/2
Sodium Chlorate.....	Lb.	23 1/2	@	24 1/2
Sodium Fluoride, commercial.....	Lb.	12 1/2	@	13 1/2
Sodium Hyposulfite.....	100 Lbs.	1.75	@	1.85
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	4.05	@	4.15
Sodium Silicate, liquid, 40° BÉ.....	100 Lbs.	1.60	@	1.70
Sodium Sulfide, 60%, crystals, in bbls.....	Lb.	2 1/4	@	3
Sodium Bisulfide, powdered.....	Lb.	.05	@	.05 1/2
Strontium Nitrate.....	Lb.	28	@	30
Sulfur, flowers, sublimed.....	100 Lbs.	3.05	@	3.45
Sulfur, roll.....	100 Lbs.	2.85	@	3.25
Sulfuric Acid, chamber, 66° BÉ.....	Ton	29.00	@	30.00
Sulfuric Acid, oleum (fuming).....	Ton	40.00	@	42.00
Talc, American white.....	Ton	10.00	@	12.00
Terra Alba, American, No. 1.....	100 Lbs.	85	@	90
Tin Bichloride, 50°.....	100 Lbs.	19.75	@	
Tin Oxide.....	Lb.	66	@	68
White Lead, American, dry.....	Lb.	11 1/2	@	12
Zinc Carbonate.....	Lb.	23	@	25
Zinc Chloride, commercial.....	Lb.	16	@	17
Zinc Oxide, American process XX.....	Lb.	15	@	15 1/2

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	47	@	48
Acetic Acid, 56 per cent, in bbls.....	Lb.	10	@	10 1/2
Acetic Acid, glacial, 99 1/2% in carboys.....	Lb.	37	@	42
Acetone, drums.....	Lb.	27	@	29
Alcohol, denatured, 180 proof.....	Gal.	1.00	@	1.01

Alcohol, grain, 188 proof.....	Gal.	3.24	@	3.30
Alcohol, wood, 95 per cent, refined.....	Gal.	1.00	@	1.02
Amyl Acetate.....	Gal.	4.25	@	4.50
Aniline Oil.....	Lb.	29	@	30
Benzoic Acid, ex-toluol.....	Lb.	5.00	@	5.50
Benzol, 90 per cent.....	Gal.	55	@	58
Camphor, refined in bulk, bbls.....	Lb.	89	@	90
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	40	@	42
Carbonyl Bisulfide.....	Lb.	6	@	6 1/2
Carbon Tetrachloride, drums, 100 gals.....	Lb.	16	@	17
Chloroform.....	Lb.	60	@	61
Citric Acid, domestic, crystals.....	Lb.	74	@	75
Cresote, beechwood.....	Lb.	1.90	@	2.00
Cresol, U. S. P.....	Gal.	1.25	@	1.30
Dextrine, corn (carlows, bags).....	100 Lbs.	6.35	@	6.40
Dextrine, imported potato.....	Lb.	15	@	16
Ether, U. S. P., 1900.....	Lb.	23	@	30
Formaldehyde, 40 per cent.....	Lb.	18	@	18 1/2
Glycerine, dynamite, drums included.....	Lb.	58 1/2	@	59
Oxalic Acid, in casks.....	Lb.	46	@	47
Pyrogallol Acid, resublimed bulk.....	Lb.	3.25	@	
Salicylic Acid.....	Lb.	1.35	@	1.40
Starch, cassava.....	Lb.	—	@	—
Starch, corn (carlows, bags) pearl.....	100 Lbs.	5.05	@	5.10
Starch, potato.....	Lb.	12 1/2	@	13
Starch, rice.....	Lb.	10	@	12
Flour, sago.....	Lb.	6	@	6 1/2
Starch, wheat.....	Lb.	5 1/2	@	6 1/2
Tannic Acid, commercial.....	Lb.	45	@	50
Tartaric Acid, crystals.....	Lb.	80	@	81

OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	60	@	65
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil, No. 3.....	Lb.	25	@	26
Ceresin, yellow.....	Lb.	14	@	18
Corn Oil, crude.....	100 Lbs.	15	@	16
Cottonseed Oil, p. s. f. o. b. mill.....	Gal.	1.10	@	1.11
Cottonseed Oil, crude.....	Lb.	16 1/2	@	16 1/2
Menhaden Oil, crude (southern).....	Gal.	—	@	—
Neat's-foot Oil, 20°.....	Gal.	1.70	@	
Paraffine, crude, 118 to 120 m. p.....	Lb.	7 1/2	@	7 1/4
Paraffine Oil, high viscosity.....	Gal.	29 1/2	@	30
Rosin, "F" Grade, 280 lbs.....	Bbl.	6.40	@	
Rosin Oil, first run.....	Gal.	37	@	
Shellac, T. N.....	Lb.	60	@	
Spermaceti, casks.....	Lb.	24	@	
Sperm Oil, bleached winter, 38°.....	Gal.	nominal	@	
Spindle Oil, No. 200.....	Gal.	24	@	25
Stearic Acid, double-pressed.....	Lb.	24	@	25
Tallow, acidless.....	Gal.	1.50	@	1.60
Tar Oil, distilled.....	Gal.	31 1/2	@	
Turpentine, spirits of.....	Gal.	43	@	

METALS

Aluminum, No. 1, ingots.....	Lb.	59	@	61
Antimony, ordinary.....	Lb.	19 1/2	@	20
Bismuth, N. Y.....	Lb.	3.00	@	3.10
Copper, electrolytic.....	Lb.	33	@	
Copper, lake.....	Lb.	31	@	
Lead, N. Y.....	100 Lbs.	11 1/4	@	12
Nickel, electrolytic.....	Lb.	55	@	56
Platinum, refined, soft.....	Oz.	77 1/2	@	
Silver.....	Oz.	28	@	
Tin, Straits.....	Lb.	64	@	64 1/2
Tungsten (W/O).....	Per Unit	20.00	@	
Zinc, N. Y.....	100 Lbs.	9 1/2	@	9 1/2

FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	5.85	@	6.00
Blood, dried, f. o. b. Chicago.....	Unit	5.50	@	5.60
Bone, 4 and 50, ground raw.....	Ton	35.00	@	
Calcium Cyanamid.....	Unit of Ammonia	4.00	@	
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	
Castor Meal.....	Unit	—	@	
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	nominal	@	
Phosphate, acid, 16 per cent.....	Ton	14	@	15
Phosphate rock, f. o. b. mine.....	Ton	1.75	@	2.00
Florida land pebble, 68 per cent.....	Ton	4.75	@	5.00
Potassium "muriate," basis 80 per cent.....	Ton	350.00	@	365.00
Pyrites, furnace size, imported.....	Unit	nominal	@	
Tankage, high-grade, f. o. b. Chicago.....	Unit	5.10	@	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

AT EASTON, PA.

Volume IX

AUGUST 1, 1917

No. 8

Editor: CHARLES H. HERTY

Assistant Editor: LEOLA E. MARRE

Advertising Manager: M. A. WILLIAMSON

ADVISORY BOARD

H. E. BARNARD, H. K. BENSON, F. K. CAMERON, B. C. HESSE, A. D. LITTLE, A. V. H. MORY, M. C. WHITAKER

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly; single copy, 60 cents. Price per single copy to American Chemical Society members, 50 cents. Foreign postage, seventy-five cents. Canada, Cuba and Mexico excepted. Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

All communications should be sent to The Journal of Industrial and Engineering Chemistry,

Telephone: Vanderbilt 1930

35 East 41st Street, New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

War Service of Chemists	730
Licenses for the Preparation of Synthetic Drugs Subject to Foreign Patents	730
Government Nitrogen Fixation Plans	730
British Control of Platinum	731
Status of Chemists in Hospital Units	731
Neglected Resources	731
The Color Trade Journal	732
The New Advertising Manager	732

EXPORTS PROHIBITED BY GREAT BRITAIN—TO JULY 14, 1917. 732

ORIGINAL PAPERS:

Art of Coloring Glass. H. Rosenthal	734
The Chemical Control of Ammonia Oxidation. Paul J. Fox	737
The Effects of Exposure on Some Fluid Bitumens. Charles S. Reeve and Richard H. Lewis	743
The Oxidation of Mineral Oils by Air. I. The Effect of Sulfur on the Oxidation of Hydrocarbons with Particular Reference to Asphalt. Benjamin T. Brooks and Irwin W. Humphrey	746
The Chemistry of Wood. III—Mannan Content of the Gymnosperms. A. W. Schorger	748
The Preparation of Ethylene Glycol. Benjamin T. Brooks and Irwin Humphrey	750
Iodometric Determination of Chlorine in Chlorides. Gregory Torsosian	751
A Method of Ashing Organic Materials for the Determination of Potassium. P. L. Blumenthal, A. M. Peter, D. J. Healy and E. J. Gott	753
Sources and Composition of Some Commercial Invert Sugar Syrups with Notes on Sorghum Syrup. Stroud Jordan and A. I. Chesley	756
Vinegar Investigation. A Study of the Changes that Cider Undergoes during Fermentation and Prolonged Storage and Its Subsequent Conversion into Vinegar in Rotating Generators. B. G. Hartman and L. M. Tolman	759
The Acid Content of Fruits. W. D. Bigelow and P. B. Dunbar	762
The Determination of Nitrate in Sewage by Means of Ortho-Toluidine. Earle B. Phelps and H. L. Shoup	766
A Comparison of American and Oriental Stoleas. Stroud Jordan	770

LABORATORY AND PLANT

Nitric Acid Sophistication, A Serious Production Menace. James R. Withrow	771
---	-----

Determination of the Explosibility of Pyrites as Well as Its Available Sulfur and the Sulfur Content of Its Cinders. C. R. Gyzander	770
A Convenient Apparatus for Electrometric Titration Depending on the Change of Oxidation Potential, and Its Application to the Determination of Small Quantities of Chromium in Steel. G. L. Kelley, J. R. Adams and J. A. Wiley	780
The Photomicrography of Paper Structure. Millard B. Hodgson	782
A Photometer for the Measurement of the Translucent Effect of Paper. C. Frank Sammet	784
A Practical Revision of the Cobalti-Nitrite Method for the Determination of Potash. R. C. Hall and E. H. Schwartz	788
Determination of Carbonates in Limestone and Other Materials. J. F. Barker	786
Carbonation Studies: I—A Mechanical Stirrer for Carbonation Direct in the Bottle. Harrison E. Patten and Gerald H. Mains	787
A Sampling Press. W. Blair Clark	788
Determination of Gas Density. Junius David Edwards	789
A Simple Improvised Apparatus for Hydrogen Sulfide Precipitation under Pressure. Aubrey Vail Fuller	790
A New Filter Flask. Jos. A. Shaw	790

ADDRESSES

The Chemical Development at Berlin. N. H. Hendrick	791
The Professional Status of the Chemist. Raymond F. Bacon	792
The Inspection and Testing of Titanium. K. K. Stevens	801

CURRENT INDUSTRIAL NEWS

SCIENTIFIC SOCIETIES	802
Calendar of Meetings. Boston Meeting. American Chemical Society. Autumn Meeting. American Electrochemical Society. Pittsburgh Conference. 1917. American Institute of Chemical Engineers. Ninth Semi-Annual Meeting. Houston. 1917.	802

NOTES AND CORRESPONDENCE	803
WASHINGTON LETTERS	804
PERSONAL NOTES	805
INDUSTRIAL NOTES	806
GOVERNMENT PROCEEDINGS	808
BOOK REVIEWS	809
NEW PUBLICATIONS	810
MARQUE DÉPOSÉE	811

EDITORIALS

WAR SERVICE OF CHEMISTS

To the Members of the American Chemical Society:

In accordance with the resolutions passed by the Society at the Kansas City Meeting, the officers of your Society have been urging the government that chemists, as in England, Canada, and France, be used for chemical service in the war, either in the employ of the military branch, of the other government branches, or of necessary industries. A special committee was organized by your President, consisting of Dr. W. H. Nicholas, *Chairman*, Drs. M. T. Bogert, A. A. Noyes, your President and your Secretary, to lay definite recommendations before the authorities. These recommendations have been published in the July number of *THIS JOURNAL*.

The government, it appears, has decided that there will be no general exemption of any class of men as a class—for reasons which are eminently wise and necessary at the present moment. At the same time, no doubt, it is anxious to see every man used in what appears to it to be the right place for him. It has seemed perhaps best to make no general ruling whatsoever, except to the effect that there will be no class exemptions, and to leave all individual cases to the federal district exemption boards, to which exemptions for industrial, agricultural and professional reasons are left by law.

Under the circumstances, in the absence of instructions from the government and in view of the general desire on the part of our members for guidance and advice in this matter, we would recommend to you *unofficially* the following procedure:

1—Chemists of military age selected by draft for service and accepted by the local boards to which the physical examination, etc., is committed are advised to submit to their federal district boards:

1—An official certificate of their employers, or of the university or college from which they have received degrees or with which they have been or are connected, certifying as to their education and experience as chemists.

2—An official statement by their employers of the nature of their work as chemists.

3—A recommendation, if such seems right, from their employers, or their university or college, that they be assigned to continue their work as chemists.

4—A request that in default of such assignment, they be detailed to serve as chemists in the military branch of the government.

II—If enlisted in any capacity, inform the Secretary of the Society by postal card of the company, regiment, and corps in which you are enrolled, in order that a record may be kept of the fact and the War Department advised from time to time of chemists in the Army should their services as chemists be required.

The purpose of this recommendation is to put into the possession of the government authorities all the facts necessary for it to decide exactly for what service a given man is most fitted. We believe this to be in accordance with the resolutions adopted at the Kansas City Meeting and in accordance with the patriotic duty of every American chemist to serve his country under the selective draft in the capacity the government itself, with a full knowledge of the circumstances, selects for each individual.

WASHINGTON, D. C.
July 24, 1917

JULIUS STIEGLITZ, *President*
CHARLES L. PARSONS, *Secretary*

LICENSES FOR THE PREPARATION OF SYNTHETIC DRUGS SUBJECT TO FOREIGN PATENTS

One of the evils resulting from the war is that the supply of important synthetic drugs, such as salvarsan, novocaine, veronal, atophan, etc., has been largely cut off in this country and a dangerous shortage is threatened. A provision in the Adamson Bill before Congress is intended to bring relief to this situation by providing for the licensing of manufacturers to make patented synthetic drugs under certain conditions and guarantees. In order to be in a position to assist manufacturers who may be interested in applying for licenses to the Federal Trade Commission, the National Research Council has organized a special committee on synthetic drugs, whose duties will be, on the one hand, to secure information as to shortages in given drugs, and, on the other hand, more especially to assist manufacturers as far as possible by advice and, if necessary, by research work, in getting the manufacture under way without loss of time. The chairman of the committee is Professor Stieglitz of The University of Chicago and manufacturers interested in a given product are requested to communicate with him without delay. Other members of the committee will probably be Dr. M. Gomberg of the University of Michigan, Dr. Adams of the University of Illinois, and Dr. W. A. Puckner, Director of the Chemical Laboratory of the American Medical Association.

GOVERNMENT NITROGEN FIXATION PLANS

On account of the general interest of chemists in the matter and on account of the participation of the American Chemical Society in the formulation of the policy recommended to the national government regarding the expenditure of the fund appropriated by Congress for fixation of atmospheric nitrogen, there is reproduced here the authorized statement on the subject issued by the Secretary of War on July 16, 1917.

By direction of the President, certain plants will be immediately constructed for the production of nitrates from atmospheric nitrogen. The plants to be constructed do not involve the use of water power, but use a process which is a modification of processes previously known; and the total expenditure involved in these projects is about four million dollars. Nothing further can be said at this time about the process or the location of the works which are to be constructed. Of the total amount appropriated by Congress, namely, twenty million dollars, substantially sixteen million dollars remains undesignated as to its expenditure by the President. The Committee, consisting of the Secretaries of War, Interior and Agriculture, to which the President referred the question of the selection of a site or site for the development of water power, has made no report to the President on that subject, but is engaged in the making of further engineering studies, and the subject is temporarily closed to further discussion by localities and communities desiring to be considered as possible sites for the plants.

In this connection we had expected to comment at some length upon a speech on this subject recently delivered on the floor of the Senate. In view, how

ever, of the carefully guarded nature of the statement of the Secretary of War, we shall withhold our comments until such time as the details of the report of the "Committee on Nitrate Supply" are made public. Then we shall feel at liberty to express freely the thoughts suggested by that speech.

BRITISH CONTROL OF PLATINUM

The following letter from Mr. G. Shaw Scott, secretary and editor for the British Institute of Metals, has been received by Secretary Parsons in reply to a letter inviting coöperation with the American Chemical Society towards conservation of platinum.

MR. CHARLES L. PARSONS,

Secretary American Chemical Society:

I had the pleasure of presenting to my Council at their Meeting on June 20th, your letter and enclosures of April 30th, relative to the use of Platinum in Jewelry.

The Council were in entire harmony with all you say, but it would now appear that any action on the part of this Institute, on lines such as appear to have been taken in your country, would now seem to be unnecessary, seeing that the British Ministry of Munitions of War has taken over the entire control of all the Platinum in this country. This means that in future the Ministry will be the sole purveyor of Platinum, and, naturally, none of it will go to the jewelers, the whole of the valuable metal being utilized for national purposes.

No doubt your Government will take similar steps, if it has not already done so, for, obviously, Platinum plays such a vital part in the war that it is nothing short of a crime to allow its use for purposes of personal adornment.

(Signed) G. SHAW SCOTT,

Secretary and Editor

STATUS OF CHEMISTS IN HOSPITAL UNITS

A correspondent, under date of July 17, 1917, writes us in part as follows:

"I was in the position last June of some uncertainty as to a choice of work for the following year. I had just been granted the degree of Ph.D. in chemistry from one of our leading universities, and, although several months past the registration age, was desirous of serving in a capacity most useful to my country. This left me undecided as to a choice of positions open to me. At this time the chief of a large hospital unit then in course of organization for service in France, called up the head of our chemical department, requesting a chemist for the unit, specifying a Ph.D. man capable of tackling any original problem that might arise at the base. The faculty selected me to see the physician in charge. In short, I was asked if I was a Ph.D., whether I had done any original research, and whether I would accompany the unit as chemist—one of the enlisted men. My question as to a commission was met with the reply that only physicians and dentists were given commissions, but the possibility was mentioned that I might be offered a civilian appointment at fifty dollars a month.

"I refused, although I wanted very much to go. I had minored in bacteriology and had six years experience in health department laboratory work, and felt able to do good work with the unit. My refusal was for two reasons. The money borrowed for my education had to be repaid as soon as possible and that was impossible on a small salary with unknown expenses. Also, I felt that expecting to get a university trained chemist and in return offering enlistment with orderlies, cooks and barbers was insulting to the dignity of the profession, when men no more highly trained—physicians and dentists—were

granted a higher rank. I have written thus at length, partly on the urging of chemist friends. I am now adjunct professor of chemistry at the University of ———.

"Although disappointed at the lack of recognition accorded chemists by the army officials, I am writing you not in a spirit of complaint, but that you may have the facts of such a case, in the event that it should become advisable later for chemists to seek recognition.

"Another very similar case has just come to my attention here at ———, where a unit is now being organized."

The situation here revealed is amazing. We incline to the belief that this does not represent the deliberately formulated policy of the War Department, but that in the rush of unusual organization the matter has simply been overlooked. If, however, these surmises are incorrect, then we respectfully urge an early review of the subject by the officials in charge.

NEGLECTED RESOURCES

Two articles by Dr. Stroud Jordan in this issue, the one on Sorghum Syrup, the other on American Storax, present questions of economic import whose consideration we would like to urge particularly upon the chemists of the southern states.

Much work was done nearly thirty years ago by the U. S. Department of Agriculture to develop the sorghum industry as a source of sugar. The work was not successful because of difficulty of crystallization due to presence of invert sugar, starch, dextrin and gums. This very difficulty, however, is changed to an advantage if the product be considered from the standpoint of invert sugar syrups, such as are used in the manufacture of tobacco, in baking and in confectionery, for in these lines a non-crystallizing syrup is needed. Moreover, as a "softener" this sorghum syrup will take up about 14 per cent of water, practically the same as glycerine. To-day the price of glycerine is very high because of munitions demands; so, too, we are paying high prices for sugar, and Mr. Hoover is calling upon us to conserve in every way possible the sugar supply. For the continually increasing quantities of invert sugar syrups demanded by industries, raw or granulated sugar has been artificially inverted, although in sorghum syrup we have a natural product ready-to-hand, which, if made in abundance and properly marketed, would find a normal use in the industries mentioned and would thus conserve an equivalent quantity of cane sugar.

There are other features in such a development which bear strongly on the all-important food question at the present time. The fodder of the cane has value as a food for cattle, while the scrubland and constitute an important factor in the raising of pork. The fact that this crop can be planted in much thicker stands than corn adds all the more to the value. Any for acre it is estimated that one acre is worth approximately twice as much as corn. If we are not interested in long range there is the further possibility of utilizing the seed as raw material for alcohol manufacture, again increasing the food supply of the war belt.

We have seen many places in southeastern Georgia, in the old denuded turpentine belt, where land is very, very cheap, and where agriculture does not seem to thrive, and yet alongside of every home was the sorghum patch. In that very section, with its increasing number of modern packing plants, the scrawny, wire-grass-fed cattle and the "razor-back" hog are being rapidly replaced by a finer grade of stock.

This seems to be getting away somewhat from chemistry, but there is chemistry in every point of it, and in these days when the problem of feeding the world lies so largely at our door and when chemists are daily asking themselves what they can do to help, the industrial possibilities of sorghum seem to call for serious attention. All in all, it is a promising field if the problems of marketing are satisfactorily solved and if chemists give to the matter that same effective work which in the past two years has astonished the nation. It would be an interesting outcome if sorghum should prove to be the Cinderella of American agriculture.

In the article on Storax, Dr. Jordan points out the full equivalency of the exudate of the "sweet gum" tree with the oriental storax, hitherto imported, the price of which, because of present restricted importations, has increased thirtyfold. If we add to this the further fact that the imported product is grossly adulterated with rosin, Burgundy pitch, castor oil and extracted storax, the relative cost of the storax itself is still further enhanced.

In the midst of this period of scarcity of this product let us remember that there is in the South a source of this material amply abundant to supply all of our needs. Again problems of collection and of marketing must be solved, but there has never been a more suitable time in our history for such exploitation.

Cannot our chemists, locally concerned, gain publicity and organized effort for such undertakings? Thereby they will bring us that much nearer the goal of national self-containedness.

THE COLOR TRADE JOURNAL

Clad in bright and artistic robes, illustrative of the industry it seeks to serve, there has come to our desk the initial number of the *Color Trade Journal*. Its editor, Dr. J. Merritt Matthews, needs no introduction to American chemists. His name is associated with every phase of the fight for a self-contained American dyestuff industry. In close touch with both the producers and consumers of dyestuffs, he

brings to its editorial management a wholesome point of view which should make his journal a strong influence in the thoughtful development of industrial policies essential to the future welfare of our domestic industry. The wide-awake and aggressive character of its manager, Mr. C. C. Bennett, gives assurance that this will be no humdrum periodical, but progressive, fearless, clean-cut and devoted to the interests of the industry as a whole.

The hearty welcome hereby extended to this new publication is based, not simply upon its own meritorious features, but also upon the happy feeling that its very existence is indicative of the rapid yet solid and substantial progress made by American chemists and chemical manufacturers in an industry whose absence, a short while ago, formed the basis for shallow-minded reproof of our chemists, but whose present magnitude constitutes conclusive proof of their energy, scientific skill and business daring.

THE NEW ADVERTISING MANAGER

Mr. M. A. Williamson has resigned the office of Advertising Manager for the American Chemical Society. Mr. Williamson has re-entered the service of the Norton Company, with headquarters in New York City, and carries with him the best wishes of all with whom he has been associated during the present year.

To fill the vacancy thus created, the Advertising Committee, after a careful survey of the field, has unanimously elected Mr. G. W. Nott, of New York City. Mr. Nott has been connected for several years with the advertising office of the Society's publications and is already familiar with the details of the work, the field to be covered, and the ideals which have governed this important part of the Society's activities. It is a pleasure to commend Mr. Nott to our advertisers, confident that his resourcefulness will make the advertising pages of the Society's journals of increasingly greater value to the American chemical industries, which now show, according to the latest available figures, a total capitalization of \$207,354,000.

It will be of interest to the members of the Society to learn with what practical unanimity our advertisers have recognized the justice of the recent action of the Committee in advancing the rates because of increased cost of publication and greater circulation of the journals.

EXPORTS PROHIBITED BY GREAT BRITAIN—TO JULY 14, 1917

Items not marked are prohibited to all destinations. Items marked * are prohibited to all ports and destinations abroad other than in British Possessions and Protectorates. Items marked † are prohibited to all destinations in foreign countries in Europe and on the Mediterranean and Black Seas, other than France and French Possessions, Russia, Italy and Italian Possessions, Spain and Portugal, and to all ports in any such foreign countries, and to all Russian Baltic ports.

C, Compounds; E, Extracts; P, Preparations; syn, synthetic; n. o. p., not otherwise prohibited; n. o. s. p., not otherwise specifically prohibited.

ORGANIC—COAL-TAR DERIVATIVES

COAL TAR, all products obtainable from, or derivable therefrom, suitable for use in the manufacture of dyes & explosives, whether obtained from coal tar or other sources, & mixtures & preparations containing such products or derivatives	*Acetanilide *Acetylsalicylic acid *Aspirin† & P †Allyl *Amidol & M *Amidopyrine †Aniline †Anthracene oil & M & P Antipyrine (phenazone) & P	*Benzozates *Benzene acid, syn Benzol & C & P Carbolic acid & C & P Dimethylaniline Dyes & dyestuffs, manufactured from coal-tar products, & articles containing such dyes or dyestuffs	*Guaiacol *Carbonate Hydroquinone & M Indigo, syn Metol & M Methylaniline *Methyl salicylate	Naphthalene & C & P Neo-salvarsan Nitro-toloul Novocain & P Phenacetin & P Picric acid & components Pyridine	Saccharin *Salicylic acid & P *Salipyrine *Sulol & P Salvarsan †Santonin & P Toloul & C & P Triphenyl phosphate Xylol & C & P
--	--	--	--	---	---

ORIGINAL PAPERS

ART OF COLORING GLASS¹

By H. ROSENTHAL

A number of writers have recorded the beautiful tints and colors that some glass assumes when exposed to sun and weather, particularly mentioning that among the fragments of glass found in the ruins of some of the eastern countries pieces of almost solid turquoise-blue were discovered and the glass windows of old homes and parts of glass bits at the seashore were tinted with these beautiful colors.²

Thomas Garfield³ quotes a series of experiments covering the coloring of glass by the action of the sunlight upon glass. Lillman's *American Journal*⁴ and the *Journal of the Society of Arts*⁵ mention glass turned gold color and also glass turned to purple.⁶ This reference was made by Dr. Faraday in the *Chemical Research*, 180, page 142.

Pelorge⁷ states that all glass is changed by the action of the sun, tests being made by covering part of the glass with paint and exposing for several years to the sun's action under various conditions; when the paint was removed, the result was varying depth of color on the same piece of glass. Of glass examined for color or examined edgewise, the tints which some of the glass assumed varied from greenish, yellowish, blue-green, brown, yellow to deep purple. The report also states very definitely that optical glass was exposed for a period of two years to the sun without any noticeable change. But the suggestion was made that if this could be exposed for a longer length of time, some reaction could be looked for.

An interesting point is brought out by one of the observers, viz., that photographers experience a noticeable change in their time of exposure when taking photographs under skylights. As the glass in the skylight becomes old, anything from one year or more, the time of exposure has to be increased, and experiments along this line show that the change of color in the skylight glass absorbs an appreciable amount of the actinic rays which can be easily substantiated by examining the spectrograms of the purple lenses.

PURPOSE OF THE PAPER

This paper describes experimental work done in the art of coloring glass by artificially produced short wave lengths of light using the ordinary quartz mercury arc, an X-ray tube, the Coolidge X-ray tube, and then a special X-ray tube for producing negative electrons.

In order to show the position of the rays "termed" short wave lengths of light, Fig. I is presented. The

chart indicates the wave lengths of radiations ranging from the visible part of the spectrum to X-rays and the gamma rays of radium.

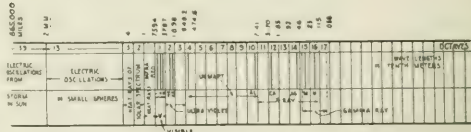


FIG. I—CHART SHOWING WAVE LENGTHS OF RADIATIONS

The numbers across the top give their respective wave lengths in Angstrom units. The Angstrom unit is equivalent to 10^{-10} meter. The numbers immediately below represent the number of octaves which these rays range over.

The region of about six octaves, beginning at 4 and ending at 10, represents the unmapped portion. This separates the extreme ultraviolet from the commencement of the very soft X-rays. The most easily absorbed X-rays, whose wave length has been determined, are the characteristic rays of aluminum with a wave length of 8.4 Å. u. Passing up through several octaves of X-rays, the limit indicated by the line "N" is reached; these represent the hardest, i. e., the most penetrating X-rays, which have so far been produced. The line "M" represents the medium penetrating ray. It will be noticed that some of the gamma rays, as produced by the disintegration of the radium atom, are of longer wave lengths than some of the shorter X-rays.

Data discussed in this paper were obtained at the writer's laboratory at Camden, N. J., several years previous to the granting of patent, and since then, through the courtesy of Dr. Coolidge and Dr. Whitney of the Research Laboratory of the General Electric Company and Dr. Luckiesh, of the Nela Research Laboratories; also some records were made by the Bureau of Standards, Washington, including some assistance given by Drs. Fisher and Hutton, of Philadelphia, the object of which is to show what has been done with the method of coloring glass and what are some other characteristics of the glass so colored.

HISTORY OF DEVELOPMENT

The first experiments, about eight years ago, were carried on with an ordinary X-ray tube and induction coil and the faint color of the glass was noticed after about two days' treatment. As the designs of the high tension apparatus were improved the period of treatment was very much lessened. In the meantime experiments were also made with other sources of rays, such as the incandescent burner and the quartz mercury arc, but it was not until the development of the special water-cooled, self-rectifying tube by Dr. Coolidge that it was possible to obtain the needed energy for producing results in a definite way.

The term color has been used to designate the tint or kind of hue white glass assumed after treatment,

¹ Presented at the regular meeting of the New York Section of the American Chemical Society, Chemists' Club, New York City, June 8, 1917.

² Fox, Phila., Crookes, England.

³ Philosophical Magazine, 4 series, 867, July to December issue.

⁴ September and November, 1867.

⁵ February, 1884.

⁶ This reference was made by Dr. Faraday in the *Chemical Research*, 1859, page 142.

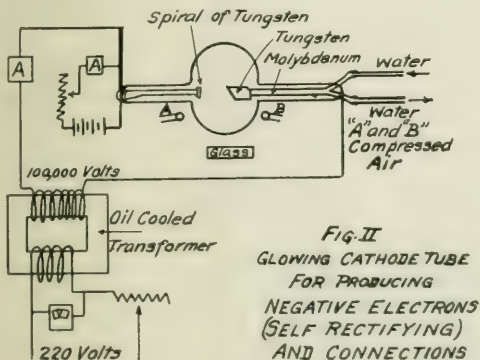
⁷ *Comptes-rendus*, January, 1867.

and depth of color is used to denote to what degree this hue or tint has been carried compared with white glass, gauging the color from the surface nearest to exposure to rays. In this paper the coloring of thin glass has been kept in mind which assumes that we obtain an even tint throughout the glass, but if thick glass is treated (over $\frac{1}{4}$ in.) the depth of color is pronounced, being deeper near the exposed side and gradually shading off.

The present investigation has been carried on with the most recently developed electrical apparatus and on standard glass, no attention at this time being paid to investigating the field of various glass compositions or to increasing the energy used in treatment of the glass.

DESCRIPTION OF APPARATUS

The vacuum tube (Fig. II) was about 4 inches in diameter with an anode terminal of solid tungsten metal supported on a rod of molybdenum and a cathode consisting of a tungsten spiral which can be electrically heated.



The vacuum of this bulb remains constant at all times, the penetration of the tube being governed by the heat of the cathode spiral, and unless the filament is heated the tube shows no conductivity in either direction, even with voltage as high as 100,000 volts.

The tube suppresses any current in the direction which does not make the hot filament cathode. It therefore is capable of rectifying its own current when supplied from an alternating source. In order to make this condition stable, the anode was water-cooled, and the glass was kept from overheating by being cooled by compressed air.

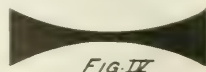
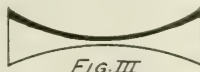
The amount of electrons sent out by the tube depends on the temperature of the filament. Increasing the voltage on the terminals increases the penetration of the rays. The tube can be operated continuously without exhibiting any appreciable change in characteristics.

The typical schedule for coloring optical lenses is as follows:

TREATMENT	RESULT
A. 100 M. A., 50 K. V., 1 min.	Light color
B. 100 M. A., 30 K. V., 1 min.	Medium color
C. 100 M. A., 30 K. V., 10 min.	Dark color

M. A. = Milliampere. K. V. = Kilo volts.

By controlling the penetration of the rays of the tube by varying the voltage, different degrees of color can be obtained. For example, in coloring an extreme double concave lens as Fig. III, it is possible to color it as marked by the heavy line, so that in looking through it, the effect of even tint will be received, thereby giving the effect which could not be produced in coloring glass. Inasmuch as it is easier to grind



lenses of this character from stock, material is usually taken from the ordinary flat glass to begin with and as it is ground away to the desired curve the thick portion will be dark and the thin light, the well-known result as shown in Fig. IV.

ACCURACY OF DATA

Current measurements were made with standard measuring instruments. The spectrophotometric curves were made from readings with spectrophotometer and the spectrograms with quartz prismatic spectroscopy on Cramer spectrum plates.

MEANS IN SCOPE OF PRESENT INVESTIGATION

This method opens up a new art in the coloring of glass and analogous substances. In the treatment of white glass for optical and scientific purposes peculiar photometric and spectroscopic, spectrophotometric results can be obtained. Fig. V illustrates the spectrophotometric curves of amber and amethyst glass made from glass chemically colored and compared with glass colored by this process.¹

"CROSS-FIRE THEORY"

In Roentgen-ray therapy where the rays are wanted for the treatment of the deeper parts of the body, the cross-fire theory is made use of. This method is used to minimize the ray action on the skin and superficial parts by selecting different ports of entry for the radiation, the theory being that if an organ is exposed from several directions instead of from one direction, only, then it receives several times that quantity of rays which it would receive if exposed in one direction only and the skin is only struck by the ray quantity emitted from the tube in one of the various positions.

This theory was proven in the following manner: A cube of glass with 2-in. square face was subjected to the cross-fire theory. A side was "rayed" by a beam $\frac{1}{8}$ in. in diameter. The glass side nearest the tube was colored darkest and shaded off towards the center, and as each of the eight sides were rayed we found in the center of the cube a small cubical spot, equal in color to any one of the colored surfaces.

Optical wedges can be made by the method just described. A colored glass on a black thin glass plate, by grinding, steps or coloring particles, with the coloring ray, can produce by passing a beam of light through the wedge, a spectrum of colors which will show a series of prismatic rays.

Optical wedges can be made by the method just described. A colored glass on a black thin glass plate, by grinding, steps or coloring particles, with the coloring ray, can produce by passing a beam of light through the wedge, a spectrum of colors which will show a series of prismatic rays.

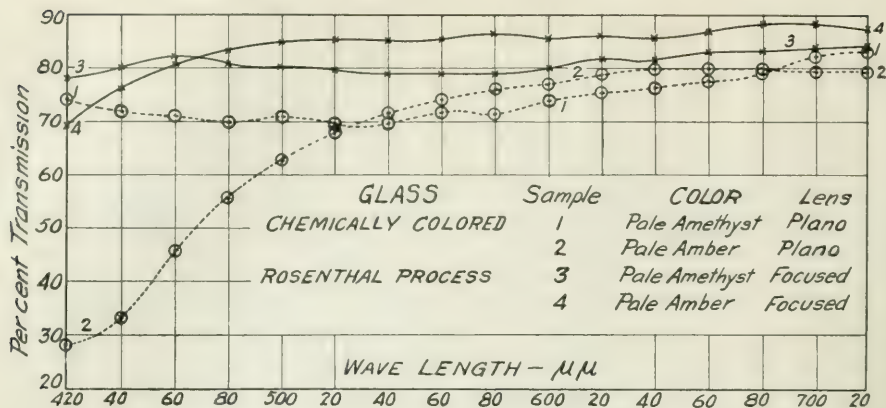


FIG. V—SPECTROPHOTOMETRIC CURVES OF AMBER AND AMETHYST GLASSES (B. S. Test No. 15518)

After repeated tests for index of refraction, strength, etc., no physical changes could be detected in the treated glasses, except that of the color which is not on the surface, but extends into and throughout the material, depending on the voltage and the thickness of the glass.

COLORING OPTICAL LENSES

The development of lenses, particularly colored lenses, is the result of man's desire to see with greater acuity and less effort; to produce this effect it is necessary to eliminate the irritating rays which cause discomfort and strain.

The white optical glass, after being colored by this process, has the same qualities and characteristics and is capable of performing the same functions as the original clear glass tinted or colored by the slow action of the sunlight extending over many years. The colors obtained were amethyst, amber, green and yellow tints.

In using this method in connection with optical lenses an almost ideal condition exists, *viz.*, in using the finished white optical lenses, which are made of the best glass obtainable, and then coloring it, we obtain a glass which has characteristics valuable to the oculist, it long being known that when eye-glass lenses are made of the sun-tinted glass, that such lenses would shade the eyes of the person wearing them from the actinic ray of the spectrum and in cases of hyper-sensitive retina, that different persons require lenses tinted to different degrees of density, in accordance with the degree of retinal irritation.

A glass may be of proper color to alter the light which we wish to allow to enter the eye and yet have a transmission coefficient much lower than the theoretically ideal glass.

In chemically coloring glass the tendency is always toward black, so that a glass might correspond to the ideal glass combined with a smoked glass.

There is, therefore, the problem of *transparency* besides the purely spectral problem, and you will note that the spectrophotometric curves shown of glass colored by this method have a high degree of trans-

parency and very little distortion in the visible spectrum.

SPECTROGRAMS

The spectrograms in Fig. VI show the relation of the amethyst-tinted lenses to the white optical lenses and show the desirable characteristics of the glass after treatment. The spectrograms marked purple Nos. 3 and 4, and the spectrograms marked No. 1 and 2 are very light amber-tinted lenses; for comparison, spectrograms are shown of the Iron Arc (bare) Clear glass, and the Quartz Mercury Arc.

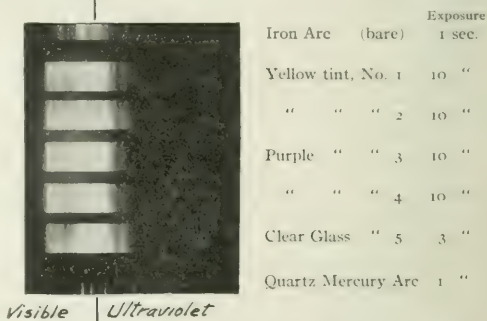


FIG. VI—QUARTZ PRISMATIC SPECTRA ON CRAMER SPECTRUM PLATES

The coloring of the glass follows the law that "the work done by any force varies with the time through which it acts." X-light follows the law that the work done by a given light varies inversely as the square of the distance from the source of light. This gives us the simple formula, $W = S/D^2$, in which W is the work done, D the unit distance, and S the time of exposure.

The next principle involved is that work done by X-light varies with the quantity of current (C) passing through the tube, other conditions remaining constant, whence $W = CS D^2$.

Another factor determining the work done is the penetration of the tube. This factor was checked by Prof. Wehnelt, the proof of which gives us the combined formulas, $W = SCP^2/D^2$, an expression

of the work done by X-light, using a tube of unit dimension, P being the penetration as measured on a Wehnelt penetrometer.

Using a slide rule covering the equation

$$X = \frac{D^2 T^2}{C P^2}$$

D = distance in inches between target and glass

T = thickness of glass

C = current measured in milliamperes

P = Wehnelt penetrometer readings

X = exposure in seconds

we have a formula based upon a hypothetical unit of light which one can vary to produce with exactness any desired result. Each make of glass, of course, has its own rate of speed of change by which the value X must be multiplied.

THEORY OF OPERATION

The coloring of purple glass is undoubtedly due to manganese, yet the color of this glass is not exactly the same as in the manganese specimens, which have been tested. This, of course, can possibly be accounted for in several ways, such as the difference in the chemical substance of the glasses, or due to the oxidation of the manganese, which may be different as obtained by radiant energy than by the regular glass manufacturing process. The other colors obtainable, very likely follow along the same lines, but it is also hard to believe that anything else but a direct physical change in the material, or a direct molecular rearrangement has taken place. Considering that by the application of heat, molecules can be rearranged, the action would appear, if taken synthetically, more naturally physical than chemical.

SUMMARY

I—White glass turns to different colors under this method.

II—Knowing the composition of the white glass, the color can be predetermined.

III—The depth of coloring of the glass is dependent on penetration of the rays, *hence controllable*.

IV—The action is molecular and not confined to the surface of the glass and the color is in and through the glass itself.

V—The action is reversible.

VI—In coloring glass by the above described method, results can be obtained which are not possible with glass colored by chemicals.

VII—Other analogous substances, such as porcelain, quartz, and some of the precious and semi-precious stones, particularly those colored by manganese, respond to this method of treatment.

The writer of this article makes no pretense to accurate scientific knowledge, but gives the results of his observations and methodical experiments with the well known phenomenon in the hope that they may add some note to the sum of human knowledge and may stimulate those who are better versed in scientific studies to ascertain the exact cause and operations of the interesting power of the short wave lengths of light.

THE CHEMICAL CONTROL OF AMMONIA OXIDATION

By PAUL J. FOX
Received June 21, 1917

In the oxidation of ammonia to produce nitrous or nitric acid, the ammonia, mixed with air, is passed over a catalyzer heated to a red heat. The ammonia content to the air-ammonia mixture is given either by running the air through aqueous ammonia or by mixing the ammonia gas with air. When the ammonia content is obtained by passing the air through aqueous ammonia, the mixture, of course, is saturated with water vapor at the given temperature. In the operation of this process, either on an experimental or manufacturing scale, one of the most pressing problems is the chemical control, for on it depends the accurate adjustment of the factors necessary to the efficiency of the plant. In fact in starting a new commercial unit, or getting data on a design of furnace, or merely in testing a new catalyzer, especially over any period of time, the principal practical issue is finding out exactly what the chemical performance is under the various conditions (temperature and character of catalyzer, speed and composition of ammonia-air mixture, etc.). The chemical control naturally falls into four parts: (1) the examination of the gas before passing to the catalyzer, and (2) after coming from the catalyzer, (3) the working up of the results, and (4) the determination of nitrous acid.

For the determination of the fairly high content¹ of ammonia in the entering gas, the ordinary gas analysis methods with mercury as confining liquid are applicable or the ammonia may be absorbed in standard acid and titrated. A thorough discussion of the various absorbing arrangements will be found in a paper by Edwards² on the absorption of ammonia in illuminating gas. The method by absorbing in standard acid has the advantage that a much larger sample can be used—in fact a continuous sample can be taken—and that no mercury is required. To test the Cumming absorber, the writer ran 1000 cc. of 10 per cent ammonia-gas through one like that figured by Edwards, another absorber being connected in series beyond it. Not a trace of ammonia passed into the second absorber, showing that one is sufficient to collect all the ammonia. It has occurred to the writer that with this type of absorber it is possible to determine the ammonia without making any titration. This is done by putting in a measured quantity of standard acid, coloring with an indicator and bubbling through the ammonia-air mixture until the color turns. If the gas has been collected in an aspirating bottle, the volume corresponding to the quantity of standard acid used is known, and the second of ammonia in the original mixture can be easily computed. The reason why this is possible is that in the Cumming absorber there is a fine streamlet, and with a little practice it is not difficult to hit the turning point as soon as the gas is completely of the same composition. At the same time, the ammonia is not leaving so in when the change will occur.

The absorption of ammonia in the Cumming absorber is a very rapid process, and with a little practice it is not difficult to hit the turning point as soon as the gas is completely of the same composition. At the same time, the ammonia is not leaving so in when the change will occur.

The writer fully agrees with the favorable opinion of Edwards on sodium alizarin sulfonate as an indicator for titration in the presence of ammonia. It is especially useful for making the ammonia determination without titrating. Though circulation is fairly good in the Cumming apparatus figured by Edwards, the writer suggests an altered form (Fig. 1) designed with

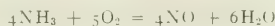


FIG. 1

a view to promote a more even circulation and avoid dead spaces, especially for use when the ammonia is determined by measuring the volume of gas (in an aspirating bottle) necessary to neutralize a measured quantity of standard acid.

In the figure, it will be noticed that the injector is placed slightly to the right of the mouth of the semi-circular lower part, which is made of somewhat larger tubing than the horizontal piece, having in view a rapid circulation, and reasonable capacity. The stopcock piece should be made of fine bore tubing with a minimum of dead space. The stopper may be of glass or rubber. It is obvious that a similar plan might be used for other gases, possibly even for carbon dioxide by staining caustic soda with phenolphthalein, passing the gas to decolorization, and using a measuring pump instead of an aspirating bottle, if more convenient.

The principal difficulty, however, is in the analysis of the exit gas, *i. e.*, the gas after leaving the catalyzer. The reaction may be considered as proceeding as follows:



but there is commonly some excess of oxygen, so that at least a part of the NO exists as NO_2 or N_2O_4 . Also, there may be uncombusted ammonia, as ammonium nitrite or nitrate present, and there is always, of course, water vapor and nitrogen. Most of the literature on this subject refers only to the examination of gases from arc processes, where there is no question of ammonia and where there is always a great excess of oxygen to convert NO into NO_2 . As N_2O_4 is an acid-forming oxide, forming a mixture of nitrous and nitric acids with water, the standard method consists in absorbing the oxides in standard alkali and titrating the excess of alkali, either with or without the addition of hydrogen peroxide to oxidize the nitrous to nitric acid. These methods are fully described and tested in a paper by Ehrlich and Russ.¹ The method by the absorption in standard alkali, first taking a measured volume of gas, is not applicable to the exit gas from ammonia oxidation since:

(1) When an attempt is made to obtain a sample, a large condensation of water takes place from the hot gas, making it impossible to get the true volume, to say nothing of the part of the nitrogen oxides dissolved in the water. Obviously the sample must be taken before condensation begins.

(2) There may not be sufficient oxygen present to oxidize all the nitric oxide (NO) to nitrogen dioxide

(NO_2), and nitric oxide is only slightly absorbed by water or alkali—water absorbs about 5 per cent of its volume at 15° when the partial pressure of the nitric oxide above is 760 mm.

(3) If hydrogen peroxide is added to the alkali, it is not certain that nitric acid is formed by the interaction of the hydrogen peroxide and the nitric oxide, for Schoenbein has shown that the acid liquid so formed causes potassium iodide paste to turn blue, whence he concludes that the compound formed is not nitric acid. A more serious objection is that, as also has been shown by Schoenbein, hydrogen peroxide abundantly oxidizes ammonia to ammonium nitrite.¹ This oxidizing effect of hydrogen peroxide on ammonia renders the reagent inapplicable—if the condition is not provided for—the determination of nitrogen oxides in the exit gas, since uncombusted ammonia would appear as oxidized nitrogen.

Ozone would be an ideal oxidizer for the case since it oxidizes without change of volume if it were not for the fact that it also oxidizes ammonia.² Ozone oxidizes nitrogen oxides, in the presence of moisture, to nitric acid. On the other hand, the use of hydrogen peroxide or similar oxidizes is advantageous, in fact necessary if complete absorption is to be obtained. This is because there is a decomposition of the nitrite ion in the sense of the following equation:³



The oxidizing agent is necessary to oxidize the nitrous acid to nitric acid, and thus prevent the decomposition mentioned. Incidentally to these questions, it must be remembered that the volume of the sample taken, or some similar datum, must be found in order to make the efficiency calculation. This must be ascertained by indirect means, as it is impossible to measure the volume directly on account of the abundant condensation of water, as previously mentioned.

It has occurred to the writer that the difficulties could be overcome and a satisfactory determination made by the following method: Aspirate the gas from the exit pipe, but before it reaches the absorption apparatus, mix it with a sufficient (measured) volume of oxygen or air to convert all the nitric oxide into nitrogen dioxide. It will be shown presently how it is possible to do this with no graduated apparatus. This insures that all the nitric oxide enters the absorption apparatus as nitrogen dioxide, without any of the ammonia being oxidized. Use two absorption tubes and in the first, place the standard alkali solution—say $\text{N}/10$ alkali—without anything else; in the second tube place a smaller quantity of standard alkali, together with hydrogen peroxide.⁴ By this means the ammonium nitrite stays in the first tube where there is no hydrogen peroxide to oxidize it.

It might be thought as an objection that as the solution in the first tube is alkaline, ammonia would be

¹ Schoenbein, Werth and Weber, *Ber.*, **7** (1874), 1745; see also other papers by Schoenbein in the *J. prakt. Chem.*

² Iluswax de Hossa, *Ber.*, **27** 1894, 1500.

³ Abegg and Pick, *Z. anorg. Chem.*, **61** (1906), 1-28.

⁴ The hydrogen peroxide in the absorbing liquid should have a concentration of 1 per cent.

¹ Ehrlich and Russ, *Monatsh.*, **32** (1911), 917.

set free, and carried over by the slow (aspirated) air current into the tube containing the hydrogen peroxide. Perman,¹ however, has aspirated air through aqueous ammonia solution of many different concentrations and has plotted $\frac{dc}{dt}$ against c (where c is the concentration of ammonia in the solution and t the time obtaining the result that at low concentrations of ammonia, $\frac{dc}{dt}$, i. e., the amount of ammonia removed in unit time, becomes very small. If his curve is produced so that $\frac{dc}{dt}$ becomes zero, the concentration is still much above what would be obtained in the first absorption tube. In other words, at the concentrations of ammonia in question no ammonia whatever is removed. The writer aspirated a current of air over night through an ammonia solution (about 8 per cent) and in the morning the solutions still smelled very strongly of ammonia. However, in case very large quantities of ammonia were passed, which would scarcely occur in practice, another tube could be inserted before reaching the hydrogen peroxide tube.

In the experimental test of the absorption, pure dry nitric oxide was made in a nitrometer and portions measured off in a gas burette, over mercury. From the burette it was conducted by glass tubing to one leg of a Y-glass piece, through the other leg of which entered the air. In each leg was a constriction to throttle the entering gases and prevent back diffusion, either of the air into the burette containing the nitric oxide, or of the nitric oxide into the air reservoir. The mixed gases then proceed to the absorption apparatus, of which the best form in the writer's judgment is a tall modified Emmerling tower (Fig. II) with a column of beads about five inches long.² A good many perti-

3 per cent hydrogen peroxide.¹ As only a small part goes over into the second absorber, it may be advantageously smaller, if "perhydrol" is used as a source of hydrogen peroxide. The aspiration is effected by an air-tight aspirating bottle with a rubber tube outlet at the bottom, running into a leveling bottle. At the end of the run, after leveling, the amount of water which had escaped is equal to the volume of air aspirated.²

So far as tests are concerned, it is of course not necessary to use an air or oxygen reservoir at all, since the total volume aspirated and the volume of the nitric oxide are known. In an actual test, however, the volume of air (or preferably oxygen) must be known in order to make the necessary allowance for it in calculating the volume of the sample taken. Instead of having a graduated vessel for the oxygen, one whose total contents are known—like a sampling pipette—is more convenient. One end is open and immersed in water in a battery jar (with a suitable guide above), and from the other end the oxygen may be drawn under an even pressure, the pipette filling up with water from below.³ In case the reservoir is not empty when the sample taking is completed, it is only necessary to continue the aspirating until the reservoir is empty of oxygen, and subtract its total volume as will be discussed below. Or, if desired, the volume of water admitted may be measured. In the tests the air was drawn from a reservoir to avoid possible oxides of nitrogen in the laboratory atmosphere. An alternative arrangement shown in the figure is equally convenient, and is better when air is used.

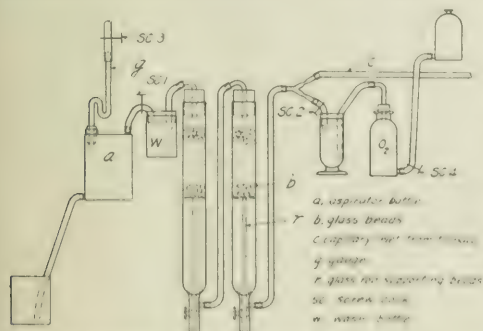


FIG. II.—APPARATUS FOR ABSORBING NITROGEN GASES

nent details as to the washing out and manipulation of this form of absorber may be found in the paper by Edwards. Two of these are used for the reasons set forth above. Into the first was placed 25 cc. of $N/10$ sodium hydroxide, and into the second, 10 cc. of $N/10$ sodium hydroxide and 25 cc. of 10 cc. of ordinary

Expt. No.	NO taken cc. 0.760 mm.	$N/10$ or $N/5$ soda cc. theory	$N/5$ or $N/10$ cc. found by titration	Recovery %	N_2 in Mixture
1.	23.5	10.49	10.61	101	7.6
2.	22.4	10.00	10.13	101	9.2
3.	15.3	6.83	6.95	102	11.1
4.	18.2	17.08	16.91	99	9.1
5.	30.9	13.79	13.98	101	12.2
6.	95.6	21.32	21.43	100.5	11.2
7.	95.9	21.39	21.56	100.8	11.5

As will be seen, the results, while very satisfactory, have a tendency to be a little high (with the exception of No. 4)—higher than would be accounted for by titration errors. In the case of No. 4, the gases were purposely passed faster than would ordinarily be done, but even here the results are good. Ehrlich and Russ⁴ working, as mentioned, on a direct combination of nitrogen and oxygen process, and without the complications necessary in ammonia work, as previously discussed, also obtained slightly high results, even when using (apparently) only one absorber. Indeed, if the extreme of accuracy were necessary, it would be possible to use pure nitric oxide from a nitrometer as the ultimate standard. It is advisable to obtain an "overall" correction for the whole apparatus,

¹ The alkali should be on top of the peroxide in the aspirator bottle.

² In making the tests on a compressed gas method of setting gas volume, oxide and air is preferable to nitrogen and air, since the latter gas is more difficult to handle. In the latter plan requires two legs, a gas aspirator bottle, and a gas reservoir. The trace of oxygen in the nitrogen is not a serious matter, since it is removed by the mercury even if it is not removed by the aspirator bottle.

³ A ready method of measuring the volume of gas is to use a graduated gas burette, closed with a stopcock, and connected to a reservoir of water. The gas is drawn from the reservoir into the burette, and the volume is read off. A watch bottle with water is connected to the reservoir, and the gas is drawn from the watch bottle into the reservoir.

⁴ *Chem. Ztg.*

by adding the standard alkali and peroxide, aspirating about a liter of air through, and removing the alkali, washing the apparatus, and titrating. In this way small errors in the measuring instruments, as well as the acidity of the peroxide, are taken up. This "overall" correction was used on Experiments 6 and 7 where much larger amounts of gas were handled than in Experiments 1-5, in which only the peroxide correction was applied.

The writer thought it worth while to see whether approximate results in the absence of ammonia and in spite of the objections mentioned might not be obtained by attempting to absorb nitric oxide mixed with air insufficient to convert the nitric oxide into nitrogen dioxide, in alkaline hydrogen peroxide. This would avoid the necessity of previously mixing the sample with oxygen, putting the duty of oxidizing the nitric oxide wholly on the hydrogen peroxide. It was found, however, that the nitric oxide bubbles freely through the alkaline peroxide, and turns into brown fumes on entering the air. Hydrogen peroxide instantly oxidizes nitrous acid, but only slowly and incompletely acts on nitric oxide, and possibly, as mentioned, not with the production of nitric acid.

In the making of an actual determination, the following practical details are worth mentioning: Set up the apparatus as in Fig. II. The sample is taken through a capillary tube placed as close to the catalyzer as possible without melting the glass.¹ The reason for using a capillary is that as soon as the exit gas cools, large quantities of water condense from it, and in a capillary this water is pushed along with the movement of gas. All this water must, of course, be included in the sample, but no water should be included that has condensed before the taking of the sample begins. Hence the taking of the sample must commence before the dew point is reached, or the results will be worthless.

The sample may be taken as slowly as desired to average the determination over some time—a plan highly desirable when working with catalyzers. About a liter of gas should be used, at least, to avoid letting small constant errors have too great an effect on the result. Great care must be taken to have tight connections throughout the apparatus—a condition not difficult to secure if first class, rather soft, rubber stoppers and good rubber tubing are available. Put 25 cc. $N/5$ caustic soda in the absorber nearest the sampling capillary and 20 cc. with 10 cc. of 3 per cent hydrogen peroxide in the other one. The wash bottle next the aspirating bottle saves the determination in case of a sudden violent passage of gas, and also indicates an insufficiency of oxygen, as the space above the small quantity of water it should contain has sufficient air to turn the passing gas brown if all the nitric oxide has not already been removed from it. Fill the bottle O_2 with oxygen, taking care that every bit of water is drained out,² elevate the leveling bottle about 2 feet and open SC 4, which puts the oxygen under a little pressure, SC 2 being, of course, closed. With SC 1 closed, put the outlet of the aspirating bot-

tle on a lower level, cautiously open SC 1 to let slow bubbles pass, and at the same time open SC 2 slightly to admit oxygen. The amount to admit depends on the strength of the exit gas as one volume of nitric oxide consumes one-half a volume of oxygen. But a much larger quantity of oxygen may be used, the rapidity of the bubbles serving as a guide, perhaps one bubble of oxygen to three of exit gas—a quantity of oxygen sufficient for all possible conditions. If desired, a wash bottle may be placed after the oxygen bottle. When the taking of the sample has been concluded, close SC 1 and SC 2, and the intake capillary, put the wash bottle near the aspirator over on its side, and level the contents of the aspirating bottle with its outlet bottle, finally opening SC 1 and SC 3 to get the level exact.¹ The volume of water in the outlet bottle is the quantity f . It is clear that it is of no importance whether the volume f is taken at the same temperature and pressure as that at which the entering ammonia-air mixture is analyzed or not, as the ammonia in the intake gas is expressed here as a ratio b . The quantity f must, however, be measured at the same temperature and pressure as the oxygen added. To find the volume of oxygen added, either continue passing it until the oxygen container (of known volume) is filled with water, or level the bottle and measure the water that has flowed in. In any case some oxygen must be passed to wash out the connections.

Titrate the liquid from each burette separately. Two or three washings are sufficient to remove the liquid from the beads if some adjustment has been made between the soda added and the nitrous gases present. If the liquid is acid, the determination is not necessarily lost. For an indicator, sodium alizarin sulfonate is the best, as it is not affected by moderate amounts of hydrogen peroxide or nitrous acid.² The gas is to be calculated to nitric oxide (NO) at the temperature and pressure at which the oxygen excess and f (or the volume in the aspirator outlet) is measured. This calculation can be quickly made with sufficient accuracy on a slide rule, considering that for this purpose nitric oxide is a perfect gas. Taking the gram molecular volume at 22412, we see that each cc. of $N/5$ alkali (previously corrected by the "overall" correction already mentioned) is equivalent to 4,482 cc. of nitric oxide at 0° and 760 mm. In the sequel the volume for room temperature and pressure is referred to as V_{no} .

Hydrogen peroxide is rather easily decomposed and the author thought that possibly enough oxygen might be carried over into the aspirator bottle to affect the results. To test this point, two portions of about a liter each of air were aspirated through the apparatus, and the hydrogen peroxide titrated with permanganate (ten cc. of peroxide, with 20 cc. of $N/10$ caustic soda). It was found that the alkaline

¹ SC 3. As the screw-cook too a water leveling gauge as the diameter of the aspirating bottle might be too large to get an accurate level in the ordinary way.

² An observation paralleling Schoenbein's was made here. If oxygen is deficient, and nitric oxide passes to the hydrogen peroxide absorber, a compound is formed that acts on the sodium alizarin sulfonate and causes irregularity. This is a sign of insufficient oxygen.

¹ The glass might well be platinumed or a silica tube used.

² The water may be poured out as there is no special point in having pure oxygen.

1 per cent peroxide yielded only in one case 6.0 cc. and in the other 6.6 cc. While this amount would scarcely affect the efficiency appreciably, it is advisable to subtract 6.0 cc. from the volume f . Possibly a suitable oxidizer not yielding gaseous oxygen could be found, but it hardly seemed worth while to search.

A point of advantage that has great weight in practice is that there is no limit to the length of time during which a sample may be taken. If it is desired to take a sample continuously, it is only necessary to get an aspirating bottle (or other vacuum device) large enough, and to arrange sufficient capacity in the absorbers. Those who have worked with catalyzers will appreciate this point. The arrangements suggested are such that it is possible to make a test without dismantling the apparatus, the liquids to be titrated, for example, being drawn off without disturbing the rest of the apparatus. Moreover, the sample may be taken at any speed, say one bubble every five minutes, if it should be desired to make a test over a considerable period of time.

An alternative and efficient absorbing medium for nitrous gases is sulfuric acid. As is the case with standard alkali, the gases must be previously mixed with oxygen as it is nitrogen dioxide and not nitric oxide which is absorbed. A trial with dry nitrogen peroxide and air with the writer's apparatus, using concentrated acid in the first tube and standard alkali and hydrogen peroxide in the second, showed that 98 per cent of the nitrous gases were absorbed in the first or sulfuric acid tube. Doubtless an arrangement could be devised whereby only one tube would be required for complete absorption, so far as dry nitrogen peroxide is concerned. For ammonia oxidation exit gas, however, two tubes would seem to be required as the acid in the first might become too dilute from the condensed water. For the determination both tubes would have to be rinsed out with concentrated acid, all the acid mixed and diluted to a known volume, and an aliquot part taken to be shaken out in a nitrometer. As this process is decidedly longer and less convenient than that with alkali and as the ammonia could not be determined in the sulfuric acid absorbent in a practical manner, no further experiments were made in this direction. Still, the method might be advantageous if it was desired to absorb large quantities of nitrogen peroxide, first cooling the gases thoroughly to remove the water, in a separate apparatus. Plain water was also tried as absorbent medium, adding some hydrogen peroxide to the second tube: a recovery of 92.4 per cent was obtained, from which it is clear that it is necessary to have the alkali.

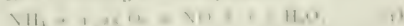
For the determination of ammonia in the exit gases, where the quantities are small, the most practical and available method is that in which the ammonia is oxidized by sodium hypobromite, and the resulting nitrogen measured in a gas burette. By this procedure, using the solution which has been titrated with standard acid to obtain the total nitrogen oxides, the ammonia can be estimated in 3 or 4 minutes. The

method, due to Knop, is described by Lunge,¹ but a simpler apparatus can be used.² Unless the temperature of the place where it is used is uniform water jackets should be applied. Use 12 cc. sodium hypobromite solution (25 cc. bromine and 150 g. sodium hydroxide in a liter) and 100 cc. of the solution taken from the first absorber, which has, of course, been titrated. If there is not so much solution, then use proportionately less sodium hypobromite, or, better, dilute so as to have nearly the same volume in each determination. The difference of readings is the nitrogen evolved, and doubling it the ammonia is obtained. There appears to be no advantage in using more than 12 cc. of sodium hypobromite solution. The results are much improved by making certain corrections. Around a plant where much ammonia is used, it is important to make a blank either on the distilled water or on the standard solutions used. The author found that this amounted to 0.40 cc. Further, the amount of nitrogen evolved is less than corresponds to the ammonia, doubtless mostly on account of the reaction not going to completion. The correction to be applied varies somewhat with the apparatus and conditions. For the writer's conditions, the list of corrections given in the *Chemiker-Kalender* was found to be of no use. To find the corrections, prepare a $N/10$ solution of ammonium sulfate, and determine the ammonia in it by the procedure described, using varying proportions up to 25 cc. of the ammonium sulfate solution. The blank must be subtracted. Calculate the cc. of nitrogen that 1 cc. of $N/10$ ammonium sulfate should yield at the temperature and pressure at which the determination is made, using the formula

$$V_t = 1.12 \frac{(1 + 0.00307 t) 760}{b - e}$$

V_t is the volume of nitrogen corresponding to 1 cc. of $N/10$ ammonium sulfate, at the temperature t and barometer b , where e is the tension of aqueous vapor corresponding to t , all the pressures being in millimeters of mercury. Working in this way, it will be found that a fairly constant factor can be found between the theoretical and observed volumes, which may then be applied to all results. This remark applies, of course, to small amounts of ammonia, up to 35 or 40 cc.

To calculate the efficiency consider any given volume, V_e , of entering gas mixture at t and p of first part which may be converted at t and p into V_t . The first part converts at t and p into V_t which is destined to react according to the equation



As the oxygen comes from air (20.9 per cent oxygen) the nitric oxide is absorbed by the alkali and the water condensed, 6 cc. solution at atmospheric saturation yield 4.75 volumes at gas N in the absorbing bottle. Call this perfectly condensed part V_{cond} .

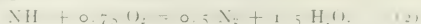
¹ *Zeitschrift für Analytische Chemie*, 1914, p. 115. Translated and Ref. 2, p. 115.

² *Zeitschrift für Analytische Chemie*, 1908, p. 115. Approximate results of a theoretical blank test are given.

³ It would obviously be useless to make any sort of test if large quantities of ammonia were escaping through the catalyzer unchanged.

V_c , and on passing through the catalyzer and absorbers¹ it shrinks from V_c to $0.678 V_c$.

The second part or stratum is that which reacts according to the reaction



That is, one volume of ammonia plus 3.59 volumes of air yield 3.34 volumes of nitrogen in the aspirating bottle. Call this second part, which yields nitrogen on combustion, V_n . The V_n on passing through catalyzer and absorbers shrinks to $0.728 V_n$. The third part is the excess of air, V_a , which passes through unchanged, and the fourth part is the excess of ammonia which passes through the catalyzer unchanged, but is absorbed in the absorption tubes. Call this lost ammonia V_l .

In operating a furnace, it is of course advisable to adjust it so that no ammonia escapes oxidation. Hence we first consider the case where there is no ammonia in the exit gas. If f is the volume collected in the aspirator bottle and f_c the same volume corrected, as will be mentioned below, so that f_c is the volume f would have if the correction proceeded according to (1) and (2) without admixture of oxygen, and if the nitric oxide were directly removed by the absorbers, we have

$$f_c = 0.678 V_l + 0.728 V_n + V_a \quad (3)$$

If b is the ratio of the ammonia to the given volume V_e of entrance gas,

$$V_{nh_3} = b (V_l + V_n + V_a) \quad (4)$$

where V_{nh_3} is the ammonia in V_e .

Since one volume of ammonia yields one volume of nitric oxide

$$V_{no} = 0.1433 V_c \quad (5)$$

where V_{no} is the volume of nitric oxide as calculated from the titration, and V_c contains 14.33 per cent of ammonia, which is the theoretical percentage for a perfect reaction. Also, considering the volume percentages of ammonia in V_c and V_n , we have

$$V_{nh_3} = 0.1433 V_c + 0.2178 V_n \quad (6)$$

Eliminating V_a between (3) and (2),

$$\frac{V_{nh_3}}{b} f_c = 0.3223 V_c + 0.2723 V_n \quad (7)$$

Eliminating V_n between (4) and (5),

$$V_{nh_3} = \frac{f_c + 0.1433 V_c}{1/b - 1.25} \quad (8)$$

Equations (5) and (6) are independently useful; (5) gives the contraction and (6) the total volume of ammonia used.

Since V_{no} is directly known from the titration, we can easily get V_c from (3). The efficiency is the volume of nitric oxide divided by the volume of ammonia.

$$\text{Efficiency} = \frac{V_{no}}{V_{nh_3}} = \frac{V_{no}(1/b - 1.25)}{f_c + V_n} \quad (9)$$

It will thus be seen that the calculation of an efficiency is a good deal simpler than might be supposed from the steps. The method does not necessitate the estima-

tion of the oxygen in f . In case the hypobromite or other test shows that ammonia has gone through the catalyzer unchanged, the equations must be modified as follows: If V_l is the lost ammonia in V_e , and considering that V_l is a separate part of V_e and does not form part of V_c , Equation (3) remains unchanged, all the lost ammonia being absorbed.

Since V_l is a part of V_e ,

$$V_{nh_3} = b (V_l + V_n + V_a + V_l) \quad (10)$$

Since V_{no} is determined by titration and does not include the nitric oxide neutralized by V_l ,

$$V_{no} + V_l = 0.1433 V_c \quad (11)$$

Equation (9) involves the assumption that the plant is not operating with such gross inefficiency that more ammonia is going through than is being oxidized. In this case the standard alkali in the absorbers would become more alkaline, and it would not be worth while to calculate the efficiency at all.

Equation (4) must be modified as follows:

$$V_{nh_3} = 0.1433 V_c + 0.2178 V_n + V_l \quad (12)$$

Eliminating V_a between (3) and (8),

$$\frac{V_{nh_3}}{b} f_c = 0.3223 V_c + 0.2723 V_n + V_l \quad (13)$$

Eliminating V_a between (10) and (11),

$$V_{nh_3} = \frac{0.1433 V_c - 0.25 V_l + f_c}{1/b - 1.25} \quad (14)$$

In the efficiency equation, V_l must be added to V_{no} as V_l neutralizes its equivalent of V_{no} , as determined by titration. Substituting V_c in known terms from (9),

$$\text{Efficiency} = \frac{V_{no} + V_l}{V_{nh_3}} = \frac{(V_{no} + V_l)(1/b - 1.25)}{V_{no} + 0.75 V_l + f_c} \quad (15)$$

The volume f is the final volume collected in the aspirator bottle at the temperature and pressure at which the experiment was made, or corrected for temperature and pressure if necessary. This volume f must be corrected ($= f_c$) because not only has oxygen been added, but a secondary reaction has taken place. The nitric oxide of Equation (1) has absorbed oxygen from the excess of air, V_a , and from the oxygen added. Since one volume of nitric oxide absorbs one-half volume of oxygen, and since V_{no} is the nitric oxide as determined by titration and does not contain a volume of nitric oxide converted to ammonium nitrite or nitrate by the volume (V_l) of ammonia escaping oxidation, we have the correction

$$f_c = f + 0.5 (V_{no} + V_l) - V_{ox}$$

where V_{ox} is the volume of oxygen added.

If the oxygen content of the gas in the aspirator bottle is determined, V_a may be found from it as a check, or a different method of calculating the efficiency might be adopted—but both these necessitate the determination of oxygen. In any case, it is useful to have the gas divided into components according to they way they act to the catalyzer and absorbers.

In the above discussion no mention has been made of aqueous vapor. It is obvious that its effects will, in the efficiency ratio, partly cancel out, but not entirely. In case a degree of accuracy is required such

¹The catalyzer is, of course, that of the plant being tested and the absorbers those of the testing outfit.

that the aqueous vapor must be taken into account, there is nothing to do but make the necessary corrections in each quantity as found—which is more simple than making a new set of equations.

It seems to be true, as first observed by Berthelot,¹ that nitrogen trioxide is first formed by the interaction of nitric oxide and oxygen even when the oxygen is in excess, but the nitrogen dioxide is so quickly formed that there is no danger of error from this source. Only traces of nitric acid are formed at the dilution of the gases used, though if pure oxygen and pure nitric oxide are mixed, larger quantities may result. These reactions in no way affect the titrations, and only the final volume as a small correction to a large volume.

In experimental work the total ammonia consumed can be found by titrating the liquor used for saturating the air (if the air is saturated by this means) before and after the experiment. But this is of course impossible in a manufacturing plant, since the intake and exit gas are sampled only, not taken as a whole.

For the nitrous acid, the most practical method for the case in hand is by the use of permanganate. In the procedure devised by Lunge,² the nitrous acid sample is placed in the burette and run into a measured excess of permanganate heated to 40–50°. The color change is not very prompt, and the method is inconvenient unless the approximate amount of nitrous acid is known. By working in the following way the results are obtained more quickly, the approximate quantity of nitrous acid need not be known, and—what is a matter of importance in some plants—no flame or heat is required. Prepare a dilute solution (about 1 volume of 3% hydrogen peroxide to 7 volumes of water) and titrate it with permanganate. Add a measured quantity, say 10 cc., of this solution to the nitrous acid sample, and titrate with permanganate. The nitrous acid is readily calculated from the difference. Even if the hydrogen peroxide had to be titrated for every determination, the method is more satisfactory than the direct use of permanganate. Of course the same assumptions are valid as to the presence of other oxidizable bodies, etc., as with the direct use of permanganate.

1605 EAST CAPITOL ST.
WASHINGTON, D. C.

THE EFFECTS OF EXPOSURE ON SOME FLUID BITUMENS

By CHARLES E. REEVE AND RICHARD H. LUNGE

Received April 16, 1917

In 1912, Hubbard and Reeve¹ published a paper¹ giving the results of exposure on some solid solid bitumens, and this was later followed by a paper by Reeve and Anderson in which the effects of exposure

¹ *Journal Ind. Eng. Chem.*, **57**, 87 (1915).

Lunge, *Monatsh. Chem. u. Min.*, 46, 141, 1911, 18; see also especially *Zeitsch. anorg. Chem.*, **1901**, p. 100.

² The Effect of Exposure on Bitumen. *Ann. Technol.*, **5** (1911).

15. A paper presented at the Eighth International Congress of Applied Chemistry, New York, September, 1915.

16. The Effect of Exposure on Tar Products. *J. Fuel Inst.*, October, 1916.

as limited to tar products were shown and some of the relations between the results of exposure and laboratory tests were discussed. In view of the interesting behavior shown by the various products considered in the above investigation, the authors felt that further results of value might be brought out by continuing a similar line of investigation to show the behavior of more fluid materials. The form of investigation is, moreover, more directly related to materials of this character, owing to the fact that they are largely used in surface treatment where they are directly exposed in a thin layer to the action of sun and air.

The exposures were made in a box of the same type as that used in previous work and shown in Fig. 1.

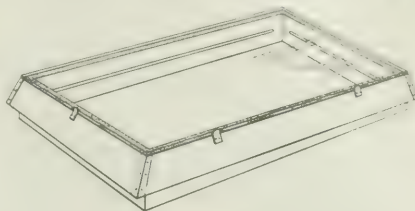


FIG. 1

For the information of those who are not familiar with the earlier publications on the subject, the following brief description of this box is given. It is made of 3/4-in. wood and has interior dimensions 25 × 14 1/2 × 2 in. A 1/4-in. plate glass cover rests on a strip of thick felt fastened to the edges of the box in order to make a tight joint and exclude all dust. For ventilation, slots are cut through each side of the box, and to prevent the entrance of rain these are protected by a thin board extending from the rim at an angle of about 45°. Cotton batting is packed under this board against the slots to exclude dust from the outside air.

The samples to be exposed were placed in 2-oz., seamless, flat-bottom, tin boxes, having a diameter of 6 cm. and a depth of 2 cm. In order to insure a uniform depth of sample, approximately 12 cc. of the material under test were used. Seven rows, each consisting of six boxes of the same material, were placed lengthwise of the box, which was set with its long side extending east and west outside a window having a southern exposure. The materials used and their characteristics are given in Table I. All tests made in connection with this work were carried out in the United States Office of Public Roads Bulletin 38.¹

The samples were exposed on January 2, 1917, at the end of every second month a sample was withdrawn and tested under the exposure test and through out a full year. The test at the end of each period included a general weighing, in case any loss or gain, a consistency test, and the determination of organic matter remaining in carbon residue, and fluid carbon. Where possible, permeability tests were made on the residue from exposure, otherwise, the consistency was determined by a fluid test at 40° C.

¹ Methods for the Determination of Bitumen and Petroleum. By Everett Hubbard and Richard H. Lunge.

TABLE I. ANALYSES OF PETROLEUM PRODUCTS USED IN TESTS

Sample Number	CRUDE PETROLEUM		OIL-ASPHALT CUT-BACK		PETROLEUM RESIDUUM	
	Mexican 6320	Trinidad 6335	6122	6121	Texas 6336	Trinidad 5857
Specific gravity 25/25° C.....	0.926	0.947	0.958	0.937	0.957	0.994
Flash point, °C.....	72	72	135	172	165	100
Burning point, °C.....	46	68	173	195	198	173
Specific viscosity.....	41.5 (25° C.)	88.1 (25° C.)	49.8 (25° C.)	27.1 (50° C.) 153.7 (25° C.)	43.0 (50° C.)	17.3 (100° C.)
Float test, 40° C.....	12.19	28.69	13.29	9.79	12.9°	1.22°
Per cent loss, 103° C, 8 hrs.....	15.19	4.46	22°	1.5°	6.32	12.03
Consistency of residue(a).....	67°	47°	99.94	99.92	18°	67° 30°
Bitumen soluble in CS ₂	99.97	99.88	99.94	99.92	99.92	99.82
Organic matter, insoluble.....	0.03	0.08	0.06	0.05	0.05	0.10
Inorganic matter, insoluble.....	0.00	0.03	0.00	0.00	0.03	0.08
Per cent bitumen insoluble in 86° B ₂ naphtha.....	12.79	8.88	8.19	11.85	0.65	9.51
Fixed carbon.....	7.23	4.84	4.12	6.81	1.47	5.63

(a) Float tests at 40° C.

WATER-GAS TAR PREPARATION

Sample Number 6321	
Specific gravity 25/25° C.....	1.126
Specific viscosity 50° C.....	29.8
Float test, 40° C.....	22.4 secs
Free carbon.....	2.43%
Loss at 163° C, 5 hours.....	19.27%
Penetration residue.....	10.6 mm

Distillation Test

Per cent by Weight	
Light Oils to 110° C.....	0.5(a)
110 to 170° C.....	1.6(b)
Heavy Oils:	
170 to 270° C.....	18.8(c)
270 to 315° C.....	13.1(a)
Pitch Residue.....	65.9

Dimethyl Sulfate Test

Per cent Insoluble	
Fraction.....	
270 to 315° C.....	7.5
315 to 350° C.....	10.0
350 to 375° C.....	7.5

(a) Clear. (b) Cloudy. (c) Slightly cloudy.

Table II gives the results which show the changes for each period at which samples were withdrawn from the exposure box.

It will be noted that at the end of two months the crude petroleum had lost 12.47 per cent and 14.57 per cent, respectively; the two cut-back products had each shown a slight increase in weight, while the Texas residual petroleum (6336) had shown a decided increase in weight, 2.16 per cent, and slight softening of the material as indicated by the float test at 40° C. It is interesting to note that the tar preparation (6321), which on distillation gave less than 2.1 per cent distillate to 170° C., lost 7.29 per cent during the two coldest months of the year.

The four materials above discussed were all used in adjacent experimental sections for the surface treatment of a limestone macadam road, so that a comparison of service with test results is possible. The treatments were applied simultaneously in the late fall when the conditions for a rapid setting up of the materials were about at their worst. The applications were covered with pea gravel. The behavior of the four products was in general accord with their relative behavior as shown in Table II. The crude

petroleums and the tar preparation soon developed a firm mat which withstood rain and snow under traffic without displacement or disintegration. The Texas residual petroleum (6336), however, rapidly worked into a deep mud in wet weather, and although it soon ironed out under fair weather conditions, it showed the same tendency to break up in rainy periods throughout the year. It will be noted that this particular product showed no material hardening in the exposure box at the end of a year as compared with the other three materials.

Referring again to Table II, it will be seen that all the materials show a consistent loss and hardening for 10 months. Penetration tests were possible on the two crude petroleum, the Trinidad petroleum residuum, and the water-gas tar preparation at the end of 4 months. The other materials remained fluid throughout the year, although the oil-asphalt cut-back (6122) behaved in a peculiar and interesting manner. After four months, this material separated into two distinct layers—a fairly greasy fluid above and a hard, brittle deposit on the bottom of the can. By heating gently and constantly stirring, a uniform mixture for testing was obtained at the end of four

TABLE II. CHANGES IN MATERIALS ON EXPOSURE IN BOX

CHANGES IN WEIGHT AND IN CONSISTENCY:

NOTE.—Where consistency is indicated in units of time, results are float tests at 40° C.; when no indication accompanies the figures, they represent penetrations at 25° C. (100 grams, 5 seconds). The melting point (Cube method) is included in tests on tar residues.

No.	ORIGINAL Specific Gravity	2 months: March 7	4 months: May 7	6 months: July 7	8 months: Sept. 7	10 months: Nov. 7	12 months: Jan. 7
		Float test 40° C.	Per cent Weight	Per cent Consistency	Per cent Weight	Per cent Consistency	Per cent Weight
6320	41.5 (25° C.)	—12.47	37.2°	—23.72	17.3	—27.50	30
6335	88.1 (25° C.)	—4.56	33°	—23.43	68	—26.60	31
6122	49.8 (25° C.)	+0.79	8.6°	—7.04	22°	—16.80	...
6121	27.1 (50° C.)	+0.76	16.2°	—2.65	26°	—9.57	50°
6336	43.0 (50° C.)	+2.16	7.8°	—3.30	24°	—9.42	1° 19'
5857	173 (100° C.)	+0.18	1° 12'	—6.09	83	—9.36	14
6321	29.8 (50° C.)	—7.29	1° 11'	—2.04	41	—27.34	4
			M. p. 54° C.	M. p. 77° C.	M. p. 78° C.	M. p. 82° C.	M. p. 78° C.

PERCENTAGE CHANGE IN INSOLUBLE ORGANIC MATTER(a)

No.	Original value	2 months	4 months	6 months	8 months	10 months	12 months
		Actual	Calculated	Actual	Calculated	Actual	Calculated
6320	12.65	+6.06	+1.57	+16.39	+2.99	+21.66	+4.80
6335	8.88	+7.57	+1.29	+12.60	+2.08	+31.27	+3.22
6122	8.19	—0.05	—0.06	+3.16	+0.58	+13.10	+1.65
6121	11.85	+1.02	—0.09	+3.80	+0.30	+8.68	+1.22
6336	0.65	+0.06	0.01	+5.60	+0.07	+13.43	+0.06
5857	9.81	+5.08	0.02	+18.01	+0.58	+27.88	+0.94
6321	2.43	+2.08	—0.18	+6.51	+0.51	+12.24	+0.92

PERCENTAGE CHANGE OF FIXED CARBON

No.	Original	2 months	4 months	6 months	8 months	10 months	12 months
		Actual	Calculated	Actual	Calculated	Actual	Calculated
6320	7.23	+1.76	+1.03	+4.05	+2.23	+5.99	+2.74
6335	4.84	+1.76	+0.82	+2.93	+1.48	+5.80	+1.76
6122	4.12	0.61	0.04	+1.37	+0.21	+2.98	+0.83
6121	6.81	+0.14	—0.05	+0.33	+0.18	+1.86	+0.72
6336	1.49	+0.47	—0.04	+0.78	+0.05	+2.32	+0.15
5857	5.63	+0.91	0.01	+2.43	+0.36	+4.59	+0.58

(a) No. 6321 data for "Insoluble in Carbon Disulfide," others for "Insoluble in 86° B₂ Petroleum Naphtha."

TABLE III—CHANGES ON 163° C. VOLATILIZATION

PER CENT LOSS AND CONSISTENCY OF RESIDUE						PER CENT GAIN IN INSOLUBLE ORGANIC MATTER						PER CENT CHANGES IN FIXED CARBON					
—5 HOURS—			—10 HOURS—			—5 HOURS—			—10 HOURS—			—5 HOURS—			—10 HOURS—		
No.	Loss %	Consistency %	Loss %	Consistency %	Loss %	Orig.	Actual	Calc.	Actual	Calc.	Actual	Orig.	Actual	Calc.	Actual	Calc.	Actual
6320	27.19	6'0"	29.39	190	31.81	12.65	+11.63	+4.64	+13.85	+5.18	+16.80	7.23	+4.39	+2.10	+5.10	+3.00	+5.69
6335	25.69	4'46"	28.31	242	31.05	8.88	+8.95	+3.07	+10.74	+3.50	+13.36	4.84	+3.73	+1.67	+4.30	+1.91	+4.81
6122	13.29	22"	19.50	1'8"	26.16	8.19	+0.99	+1.14	+3.31	+1.97	+6.69	2.90	4.12	+0.35	+0.64	+1.33	+0.99
6121	9.79	1'5"	16.30	5'18"	17.47	11.55	+3.85	+1.25	+7.23	+2.25	+8.68	6.81	+1.36	+0.74	+2.09	+1.93	+2.69
6336	6.32	18"	13.02	27"	15.42	0.65	+0.66	+0.04	+1.68	+0.10	+2.90	0.14	+0.57	+0.10	+1.11	+0.22	+1.33
5857	12.03	6'30"	13.50	188	15.36	9.51	+6.54	+1.30	+8.13	+1.48	+10.77	5.63	+2.02	+0.73	+2.78	+0.88	+3.01
6321	19.27	106	30.78	3	31.19	2.43	+5.39	+0.58	+6.68	+1.06	+7.49	1.10

(M. p. 75.8° C. M. p. 78.6° C.

(a) No. 6321 data for "Insoluble in Carbon Disulfide," others for "Insoluble in 86° B₆ Petroleum Naphtha."

months, but after this the components of the sample could not be sufficiently well mixed to yield consistency test results of any value. The sample, in fact, behaved in a manner somewhat similar to a naphtha insoluble determination, due, no doubt, to the fact that the asphalt used was cut or thinned with a distillate to which it was not closely allied. The results on the two cut-back products are particularly interesting from the fact that they show conclusively that such products, when fluxed with high-boiling distillates, as were those under test, cannot be expected to lose their volatile matter and develop a firm binding material under exposure.

The results also serve as a refutation of claims made for the great value of the "per cent of asphalt" test, which consists in determining the amount of residue of a given penetration obtained by evaporating the sample at a high temperature. A temperature as high as 260° C. (500° F.) is quite generally permitted in making this test, and petroleum products of the character represented by our Samples 6121, 6122 and 6336 will yield from 40 to 50 per cent of residue of 100 penetration. It is evident, however, that the high-boiling distillates driven off at a high testing temperature are not driven off under the exposure conditions of service, and the test is therefore not a correct measure of the value of the material.

In reviewing the results for 12 months' exposure, it will be seen that all the samples excepting No. 6336 showed a lower loss than at the previous period or even 8 months' period, and the two residues on which float tests were made showed a slight increase in fluidity. A thorough consideration of all details of the work yields no explanation that would make any error in details of the work responsible for these results. It has been shown in previous papers, referred to, and will be again demonstrated through data to be discussed later that changes other than those due to volatilization occur in bituminous materials exposed to atmospheric influences. Such changes may be responsible for the results obtained at the later periods in the present work, in that these later periods extended through cold weather when the volatilization with residuals that had been exposed through hot weather would materially diminish or cease, but reactions due to oxidation or other additive processes might continue.

In Table II the calculated percentages of insoluble organic matter represent the increase or decrease which would be brought about by the loss or gain reported in the same table. A detailed discussion of these results is perhaps unnecessary, but, as shown by

Hubbard and Reeve¹ in their work on harder bitumens, the increase in insoluble organic matter is far in excess of what it would be from mere volatilization of lighter constituents. This increase ranges from 7 times the calculated amount in the case of the oil-asphalt cut-back (6121) to 170 times the calculated amount in the Texas petroleum residuum (6336) and of particular interest in the latter case is the fact that this increase was attended with but relatively immaterial hardening of the sample.

Table II also gives the percentage change in fixed carbon for each period of exposure, compared with the calculated changes based on the loss in weight of the sample. As with the bitumen insoluble in naphtha, the fixed carbon shows a marked increase over what could be accounted for by loss of volatile constituents. Attention was called above to the fact that as compared with previous results all but one of the samples showed a slightly decreasing loss at 12 months, and it will be noted that most of the samples show a recession in the percentage of insoluble organic matter and fixed carbon which had been previously present. This phenomenon is too consistent to be attributed to errors in determinations, and would appear to be due to what are at present inexplicable changes in the bitumen.

In order to compare the effects of volatilization in laboratory testing with those obtained upon exposure, all the materials were subjected to the volatilization test¹ for 5-hour periods on 3 successive days, and tests were made on residues at the end of 5, 10, and 15 hours, respectively. The complete results are given in Table III and they clearly show that heating at 163° C. for even 5 hours produces changes in the material that cannot be accounted for by mere loss of volatile matter, although these changes are not as great as those produced through exposure to sun and air. In order to compare more readily the results of exposure with those of laboratory methods, separate tables have been prepared which embody the data of particular interest. In Table IV, for instance, results have been selected in which either the loss or consistency of the residue obtained by each method are nearly identical in order to show the difference in the other factor. It is shown that the loss by volatilization at 163° C. for 5 hours approximates the loss on exposure at the position given in the case of Nos. 6336, 6335, 6336, and 6336, but the increase in fixed loss, excepting No. 6336, was hardly attained exposure than after the volatilization test. This is particularly noticeable in the case of the two solid

TABLE IV.—SELECTED DATA FOR COMPARISONS OF RESULTS

LOSS AND CONSISTENCY OF RESIDUES				INCREASES IN ORGANIC MATTER INSOLUBLE				INCREASES IN FIXED CARBON			
Volatilization 163° C.				Volatilization 163° C.				Volatilization 163° C.			
Loss		Consistency		Loss		Consistency		Increase		Increase	
No.	Hrs.	Per cent		Mo.	Per cent	tency		Mo.	Calc.	Actual	
6320.....	5	27.19	6' 0"	5	27.62	41	5	4.64	11.63	11.63	4
	15	31.18	98	6	25.57	99	10	5.18	13.85	13.85	10
6335...	5	25.69	4' 46"	6	24.96	35	5	3.07	8.95	8.95	5
	10	28.31	242	10	26.60	13	10	3.50	10.74	10.74	10
6122...	5	13.29	22"	4	7.04	22"	5	1.14	0.99	0.99	5
6121...	5	9.79	1' 5"	10	9.57	50"	5	1.25	3.85	3.85	10
6336...	5	6.32	18"	6	6.20	48"	5	0.04	0.26	0.26	5
	10	13.02	27"	4	3.30	21"	15	0.12	2.00	2.00	10
5857.....	15	15.36	117	4	6.09	83	5	1.30	6.54	6.54	8
6321.....	5	19.27	106	4	20.94	41	5	0.58	5.39	5.39	4
	10	30.78	3	8	27.38	3	15	1.10	7.49	7.49	8

petroleums (Nos. 6320 and 6335), in which the residues from volatilization were too fluid for a penetration test, while after losing approximately the same amount on exposure they yielded residues having penetrations of 41 and 35, respectively. Samples 6320 and 6122 also offer interesting comparisons, since the consistencies in two instances are identical. In the case of the first material, however, it required a loss of 31.81 per cent by volatilization in an oven to produce a residue of the same consistency as that obtained through a loss of 25.57 per cent on exposure, while in the case of No. 6121 it required losses of 13.29 and 7.04 per cent to bring about the same result.

To show the relation between the increase in actual overcalculated organic matter insoluble in samples tested by laboratory methods and exposure, samples for comparison were selected at periods when the calculated increases based on the loss in weight were approximately equal. It is shown that in practically every instance the increase in organic matter as a result of exposure is several times greater than that produced through heating in a laboratory oven. The Texas residual petroleum (No. 6336) shows the most noticeable differences by the two methods where the calculated increase for 6 months' exposure is identical with that for 5 hours in the oven, whereas the actual increase by the former method is 12 times the actual increase obtained in the oven-heated sample. The two Trinidad products (Nos. 6335 and 5857) also show similar marked differences in the increases obtained by the two methods.

It will be noted that the oil-asphalt cut-back No. 6122 offers the only instance in which the actual increase was less than the calculated. This occurs in the residue from the 5-hour volatilization and the sample shows a similar peculiarity in the results of fixed carbon increases which were selected on a similar basis to that adopted for the other groups in Table IV. The data show to some extent the same relations between the results of oven and atmospheric exposure, although the differences between the fixed carbon increases are not as marked as those for organic matter insoluble.

It has sometimes been contended that the volatilization test at 163° C. was too severe, and that it subjected materials under test to changes that would not occur under ordinary conditions of exposure. The results above cited show that such an assumption is not altogether well taken, and that as a matter of fact the effects of atmospheric exposure are much

more pronounced than those obtained in the routine laboratory test.

The above data corroborate and amplify all previous data to the effect that bituminous materials upon exposure undergo changes that are due to something more than mere loss of volatile matter. Such changes occur in samples when subjected to the volatilization test in a laboratory oven, although the changes are greater when the exposure is made under atmospheric influences. These changes differ in both character and degree with different types of fluid bitumens, as would be expected from our knowledge of the varying chemical character of bituminous materials. Hubbard and Reeve in reviewing their work on semi-solid bitumens indicated that the increase in insoluble organic matter might be due to oxidation, and that the products might actually contain oxygen or be the result of nucleus condensation brought about by the reaction of oxygen with two or more hydrocarbons originally present in the bitumens. The conclusions in that case were based almost entirely on the results of atmospheric exposure, while in the present data the authors have included results obtained through the laboratory routine volatilization test. The fact that the organic matter insoluble also increases materially in a closed oven where the changes of oxidation are reduced to a minimum, would tend to indicate that other causes might be responsible for the changes which occur. While oxygen plays its part in the changes which occur, the authors are led to the conclusion that polymerization and intermolecular reactions induced by heat and possibly increased by the action of light are also very largely responsible for such changes, in addition to those which are accounted for by simple evaporation.

OFFICE OF PUBLIC ROADS AND RURAL ENGINEERING
WASHINGTON, D. C.

THE OXIDATION OF MINERAL OILS BY AIR I.—THE EFFECT OF SULFUR ON THE OXIDATION OF HYDROCARBONS WITH PARTICULAR REFERENCE TO ASPHALT

BY BENJAMIN T. BROOKS AND IRWIN W. HUMPHREY

Received May 15, 1917

It has long been known that on heating sulfur and paraffin, hydrogen sulfide is evolved.¹ Lidoff² made hydrogen sulfide by adding a petroleum "naphtha" to hot sulfur at 350° to 400° C. and in 1892 Dubbs obtained a patent in the United States for a process of

¹ Galletly, *Chem. News*, **24** (1871), 162.

² *Chem. Zvest.*, **1892**, 22.

case two pounds of residuum were placed in a glass flask and two or more such flasks heated in a large sand bath, the temperature of the sand bath and the temperature of the residuum being noted at frequent intervals.

That asphalts of exceptional hardness and high melting point can be made by the combined action of air and sulfur is shown by the fact that on air-blowing a sample of Mexican residuum, to which 8 per cent of sulfur had been added, for 31 hrs. at 220–230° C., a product was obtained which had a flowing point of 185° C. (366° F.) and a penetration of 7 mm. at 25° C. (100 g. weight and No. 2 needle, 10 seconds). Another product made by air-blowing a sample of the same residuum, to which 12 per cent of sulfur had been added, at 230–235° C. for 31 hrs. showed a flowing point of 200° C. (392° F.) and a penetration at 25° C. of 5 mm. (100 g. weight and No. 2 needle, 10 seconds). In practice, it is seldom desirable to produce products as hard as this, but the addition of much smaller amounts, 3 to 5 per cent of sulfur, had a marked effect in producing hard asphalts in much less time than is required by the usual air-blowing method. This is well indicated by Experiments 1b and 8b in Table I as compared with the results obtained with the same residuums under the same conditions but with the addition of 5 per cent sulfur. It will be noted that the time required to produce an asphalt of medium degree of hardness is reduced, by the addition of 5 per cent sulfur, to about one-sixth of the time necessary when no sulfur is added. It is to be expected, therefore, that residuums naturally containing relatively large amounts of sulfur will give hard asphalts by air-blowing in the least time.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH
UNIVERSITY OF PITTSBURGH

THE CHEMISTRY OF WOOD

III—MANNAN CONTENT OF THE GYMNOSPERMS

By A. W. SCHORGER

Received April 14, 1917

A marked difference between the conifers (*Gymnospermae*) and hardwoods (*Angiospermae*) occurs not only in the structure but also in the chemical composition of the wood. In a previous communication¹ it was pointed out that water-soluble galactans occurred in many of the conifers. The present paper has a special bearing on the relative amounts of mannan present in the various species.

So far as is known, carbohydrates yielding mannose on hydrolysis have been found in only one hardwood. Fromherz² obtained mannose from *Populus tremula* L. The lignocellulose purified by treatment with acid and alkali was heated with water in an autoclave at 150°. The aqueous solution, after boiling with sulfuric acid, was found to contain mannose. The writer, employing hydrolysis at atmospheric pressure, examined six species of hardwoods, among them *Populus tremuloides* Michx., but in no case was mannose detected.

The presence of mannans in various woods has been shown by several investigators. Tollens³ and associates found mannose in sulfite liquor, the raw material generally employed being *Picea excelsa* Lk. The presence of mannan in the wood of about a dozen conifers was shown by Bertrand,² who also made several quantitative determinations. Kimoto³ found 6.35 per cent mannan in *Cryptomeria japonica* Don. A study of several American species was made by Storer,⁴ but only two quantitative determinations were reported; the mannose hydrazone was identified microscopically.

Bertrand⁵ considers the source of the mannose from wood as a mannocellulose. This classification is not justified on account of the ease of hydrolysis of the parent carbohydrate, the latter falling properly into the class of hemicelluloses created by Schulze.

The presence of mannan in woods is of technical significance. According to Schwalbe⁶ waste sulfite liquors may be considered to contain sufficient fermentable sugar to give 60 liters of ethyl alcohol per "tonne" (2200 lbs.) of pulp, which is equivalent to 108 lbs. of alcohol per ton (2000 lbs.) of dry pulp. On the basis of a yield of 45 per cent of pulp, about 2.5 per cent of the dry wood is recovered as alcohol. The results obtained by Krause⁷ show that mannose constitutes about 60 per cent of the total fermentable sugars in sulfite liquor.

The various woods examined contain sufficient mannan alone to furnish 2 to 4 per cent alcohol so that considerable mannose is evidently destroyed during the cooking process. It is plain, however, that mannan must be considered the chief source of the ethyl alcohol.

By the hydrolysis of white spruce Kressman⁸ obtained 6.8 to 8.3 per cent of absolute alcohol. This species contains 7.12 per cent mannan from which it is theoretically possible to obtain 3.5 per cent alcohol. It is difficult, however, from available data to determine how much alcohol is derived from the mannose. Mannose⁹ is apparently as stable when heated with acids as dextrose but it is probable that considerable mannose is destroyed during the cooking since all the mannan would be hydrolyzed at the beginning of the reaction. Yeasts that ferment dextrose will usually ferment mannose equally well but exceptions occur.

EXPERIMENTAL

The method of determining mannan was the following: The wood, cut into sawdust, was so ground as to pass through a 40-mesh sieve. A portion was removed for determining moisture. Ten grams of the fine material with 150 cc. of hydrochloric acid, sp. gr. 1.025, were placed in an Erlenmeyer flask connected with a reflux condenser and boiled for three and one-half hours. The contents were then filtered into a 500 cc. flask, and the sawdust washed back into the Erlenmeyer with about 100 cc. of dis-

¹ Ber., **23** (1890), 2990; *Z. anorg. Chem.*, **8** (1892), 155; *Ann.*, **267** (1892), 349.

² *Compt. rend.*, **129** (1899), 1027.

³ *Bull. Coll. Agr. Tokyo*, **5** (1902), 284.

⁴ *Bussey Inst. Bull.*, **3** (1902), 32.

⁵ *Compt. rend.*, **129** (1899), 1025.

⁶ *Z. anorg. Chem.*, **23** (1910), 1540.

⁷ *Chem. Ind.*, **29** (1901), 217.

⁸ *This Journal*, **7** (1915), 920.

⁹ Fischer and Hirschberger, *Ber.*, **22** (1889), 365.

¹ Schorger and Smith, *This Journal*, **8** (1916), 494.

² *Z. physiol. Chem.*, **60** (1906), 237.

TABLE I—MANNAN CONTENT (PERCENTAGES) OF VARIOUS CONIFERS

No.	COMMON NAME	SPECIES	MANNAN	DESCRIPTION
1	Douglas Fir	(<i>Pseudotsuga taxifolia</i> Briton)	6.65	Cut in May; Washington
2	Corkbark Fir	(<i>Abies arizonica</i> Merr.)	6.57	May; 4 ft. up, 9 in. diameter. Arizona
3(a)	Western Larch	(<i>Larix occidentalis</i> Nutt.)	5.13	Montana
4	Arborvitae	(<i>Thuja occidentalis</i> L.)	1.44	Wisconsin
5	White Spruce	(<i>Picea canadensis</i> Mill.)	7.12	November; 12 ft. up; 13 in. diameter. Wisconsin
6	Longleaf Pine	(<i>Pinus palustris</i> Mill.)	4.75	May, Florida
7	Longleaf Pine	(<i>Pinus palustris</i> Mill.)	1.64	July; sapling 6 yrs. old; 1.5 ft. up; 2 in. diam.; Mississippi
8	Loblolly Pine	(<i>Pinus taeda</i> Linn.)	5.10	May, Florida
9(b)	Cuban Pine	(<i>Pinus heterophylla</i> Ell.)	5.81	Heartwood; tree 18 in. diam. (8 in. sapwood)
			A	B
			9.22	Sapwood; May, Florida
10	Sugar Pine	(<i>Pinus lambertiana</i> Dougl.)	4.67	Heartwood, California
11	Coulter Pine	(<i>Pinus coulteri</i> Lamb.)	5.22	June; 20 yrs. old; 5 ft. up; 13.5 in. diam. California
12	Coulter Pine	(<i>Pinus coulteri</i> Lamb.)	6.00	Tree cut in June; 30 ft. up; 19 in. diam.
			5.40	a. Heartwood; 8 in. diam.; 19 years old
			6.28	b. Sapwood; 62 years old. California
13	Monterey Pine	(<i>Pinus radiata</i> Don.)	7.68	February; 10 ft. up; 17.5 in. diameter; 35 years old. California
14	Pinon Pine	(<i>Pinus edulis</i> Engelm.)	6.00	May; 1 ft. up; 10 in. diam. Slow growth. New Mexico
15	California Swamp Pine	(<i>Pinus muricata</i> Don.)	3.07	June; 12 ft. up; 7.5 in. diameter; 12 yrs. old
16	Chihuahuana Pine	(<i>Pinus chihuahuana</i> Engelm.)	5.00	May; 3 ft. up; 5 in. diam.; 38 years old. New Mexico
17	Western White Pine	(<i>Pinus monticola</i> Dougl.)	6.93	June; 18 ft. up; 15 in. diam.; 230 years old. Montana
18	Western White Pine	(<i>Pinus monticola</i> Dougl.)	7.13	a. Heartwood; 13 in. diameter
			7.44	b. Sapwood, Montana
			4.22	June; 3 ft. up; 10.5 in. diameter, 2 in. being sapwood; 130 years old. Montana
19	Whitebark Pine	(<i>Pinus albiculis</i> Engl.)	4.64	May; 2 ft. up; 15 in. diam.; 110 years old. "Black jack" variety. Arizona
20	Western Yellow Pine	(<i>Pinus ponderosa scopulorum</i>)	5.40	Sapwood; June; 2.5 ft. up. California
21	Jeffrey Pine	(<i>Pinus jeffreyi</i>)	7.17	June; 14 ft. up; 9 in. diam., one-half being heartwood; 70 yrs. old. California
22	Digger Pine	(<i>Pinus sabiniana</i> Dougl.)	5.94	Heartwood; May; 10 ft. up; tree 8 in. diam
23	Limber Pine	(<i>Pinus flexilis</i> James)	5.41	May; 10 ft. up; 6 in. diam., 5 in. being heartwood. Colorado
24	Bristlecone Pine	(<i>Pinus aristata</i> Engelm.)	3.57	June; 3 ft. up; 8.5 in. diam.; 47 years old. California
25	Kaobone Pine	(<i>Pinus attenuata</i> Lemm.)	0.00	November, Wisconsin
26	Baswood	(<i>Thuja americana</i> L.)	0.00	December, Michigan
27	Sugar Maple	(<i>Acer saccharum</i> Marsh)	0.00	November, Wisconsin
28	Yellow Birch	(<i>Betula lutea</i> Michx.)	0.00	November, Missouri
29	Green Ash	(<i>Fraxinus lanceolata</i> Borkh.)	0.00	
30	White Ash	(<i>Fraxinus americana</i> L.)	0.00	
31	Aspen	(<i>Populus tremuloides</i> Michx.)	0.00	New Mexico

(a) Extracted with hot water to remove galactan previous to hydrolysis.

(b) Heartwood contained 10.4 per cent resin that was removed by extraction with ether previous to hydrolysis. The mannan content of the dry resin-free heartwood would be 6.54 per cent.

tilled water. The sawdust was then digested a short time under a Bunsen burner, and again filtered. This method of extraction was continued until the total filtrate amounted to 500 cc. The solution was then transferred to an 800 cc. beaker, neutralized with 10 per cent NaOH, rendered slightly acid with acetic acid, and evaporated on the steam bath over night to 150 cc. The solution was again filtered to remove humus matter, the filter being washed with a little cold water. A mixture of 10 cc. of phenylhydrazine and 20 cc. of water, rendered acid with glacial acetic acid, was added to the filtrate contained in a 200 cc. Erlenmeyer. The flask (with frequent shaking) was allowed to stand 2 hrs. The precipitate of mannose phenylhydrazone was collected in a weighed alundum or Gooch crucible, washed with cold water, then with acetone to remove resinous impurities, dried and weighed. The mannan content was calculated from the weight of the mannose phenylhydrazone by multiplying by the factor 0.6. The yields are based on dry wood, the moisture having been determined in an air oven at 105°.

The cream-colored mannose hydrazone was dissolved in hot 75 per cent alcohol and filtered, using a suction pump. The filtrate usually becomes opaque at once from the separation of micro-crystals of the hydrazone. Three crystallizations usually gave practically colorless crystals. The melting points of the various hydrazones varied from 188 to 190° by slow heating. The results obtained appear in Table I. The wood in all cases was taken from the trunk of the tree and unless otherwise stated the sample represents a radial section containing both heartwood and sapwood. The sample descriptions, where possible, are given in some detail since future work may show that the mannan content is dependent on such factors as the age of the tree, season and locality.

Duplicate determinations of the mannan content usually did not differ more than 0.3 to 0.4 per cent but occasionally differences as high as 1 per cent were observed. To determine if all the mannan had been hydrolyzed, the sawdust from limber pine heartwood and longleaf pine sapwood was air-dried after the first hydrolysis. This was again boiled with fresh acid and treated in the customary manner. Since the alundum crucibles increased in weight but 0.003 and 0.004 g., respectively, there was practically a quantitative removal of the mannan in one hydrolysis.

A longleaf pine tree 120 years old and 53 feet tall was felled in Mississippi in July. Small disks were cut from the trunk at the distances 2, 22, and 45 ft., respectively, from the ground, and their mannan content determined as follows:

TABLE II—MANNAN CONTENT OF A LONGLEAF PINE, *Pinus palustris*

No	DISK	HEARTWOOD		SAPWOOD	
	Diameter Inches	Mannan Per cent	Diameter Inches	Mannan Per cent	Diameter Inches
1	8.75	4.85	3.50	5.14	4.75
2	6.00	3.07	2.25	4.03	3.25
3	7.25			3.07 (13)	

(13) For entire disk heartwood and sapwood being indistinguishable.

The results obtained indicate that there is more mannan in the sapwood than in the heartwood, and that the mannan decreases progressively from the base of the tree upwards.

A radial section of a sugar pine log having a diameter of nearly 4 feet was divided into six parts and analyzed to determine if the mannan content varied appreciably from the center of the tree to the circumference. The results are given in Fig. 1. The mannan is uniformly distributed throughout the heartwood but decreased in the sapwood. The figure for the sapwood is the result of three determinations. This is the only exception observed in the general rule that the sapwood contains more mannan than the heartwood. This generalization is supported by the re-

sults from samples Nos. 9, 12 and 18, Table I, and disks Nos. 1 and 2, Table II. This suggests the possibility of obtaining considerably larger yields of ethyl alcohol from slabs and edgings than from mill-run sawdust.

According to Fischer,¹ when 0.1 g. of mannose hydrazone is dissolved in 1 cc. of concentrated cold hydrochloric acid, 5 cc. of water immediately added, and the solution examined in the polariscope using a 1 dm. tube, the *d*-compound gives a rotation of 1.2° to the left. The crude mannose phenylhydrazone obtained from *Pinus lambertiana* was recrystallized three times from dilute alcohol. Two different samples of the hydrazone purified in this way, using the proportions given by Fischer, had the rotations -0.657° and -0.796° . Lindsey and Tollens² found -0.761° for the mannose hydrazone obtained from sulfite liquor.

A portion of the practically colorless hydrazone was heated with phenylhydrazine acetate in aqueous solution for 1.5 hours on the steam bath. The yellow osazone obtained, after recrystallization from 60 per cent alcohol, melted at $203-4^\circ$.

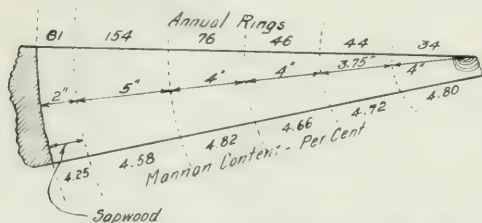


FIG. 1—MANNAN CONTENT OF RADIAL SECTION OF SUGAR PINE

A sugar solution obtained by the hydrolysis of white spruce was treated with phenylhydrazine acetate in the manner described above and allowed to stand over night. The hydrazone obtained was so very impure that a quantitative estimation of mannose was impossible. The hydrazone was dissolved in 75 per cent alcohol, the solution filtered, and allowed to crystallize. After these operations had been repeated four times the crystals melted at $186-8^\circ$.

It is proposed to extend this investigation to other species and determine if the amount of mannann in a given tree actually varies throughout the year. The statement of Czapek³ that mannans always belong to the reserve hemicelluloses requires confirmation. It is very questionable if the mannans, especially those occurring in the heartwood of trees, can be considered as reserve food materials.

SUMMARY

I—The results of the examination of 22 different species of Gymnosperms and 6 species of Angiosperms show mannann to be present in appreciable quantities in all the conifers but absent from the hardwoods.

II—It appears that the mannann content of the sapwood is generally larger than that of the heartwood; mannann decreases from the base upwards but remains

uniform throughout the heartwood in a radial direction.

III—Mannann is of industrial importance in the production of ethyl alcohol from sulfite liquor and by the hydrolysis of sawdust with catalyzers.

FOREST PRODUCTS LABORATORY
MADISON, WISCONSIN

THE PREPARATION OF ETHYLENE GLYCOL

By BENJAMIN T. BROOKS AND IRWIN HUMPHREY

Received May 15, 1917

The preparation of ethylene glycol has usually been effected through the hydrolysis, under different conditions, of ethylene bromide. The reason that ethylene bromide has nearly always been employed probably lies in the fact that this substance is easily made in the laboratory. However, Nef pointed out, long since, that alkyl bromides and iodides generally give larger proportions of olefines than the chlorides and that the latter derivatives invariably give the better yields in the so-called double decomposition reactions. Aqueous or alcoholic caustic alkali converts ethylene bromide almost quantitatively into vinyl bromide. Very good yields of ethylene glycol, about 70 per cent of the theoretical, can be obtained, starting with ethylene bromide, by passing through the diacetate, and even higher yields are said to be obtainable by employing the dibromide and aqueous silver carbonate.

In view of the relatively high cost of the materials (potash salts, bromine, etc.) required by the methods heretofore published, we have developed a method which permits the easy preparation of ethylene glycol in large quantities at low cost. For a starting point, ethylene chloride was selected in preference to the bromide, owing to the cheapness of chlorine and the ease with which ethylene, from alcohol or oil gas, may be converted into the dichloride.¹

The method which we have developed consists in heating a mixture of ethylene chloride, sodium formate and methyl alcohol to 165° C. in a suitable autoclave. An excess of methyl alcohol, six mols or more, is employed in order that the alcoholysis of the glycol formate may be very nearly quantitative.

As contrasted with the older methods, it will be noted that potassium salts have been replaced by sodium formate, and methyl alcohol is employed as a solvent. When this alcohol is employed in the reaction mixture, the isolation of the glycol ester is unnecessary since alcoholysis of the glycol formate occurs.

This is a special development of Henry's² studies on the equilibria in mixtures containing an organic acid and two alcohols, and was apparently first employed as a preparative method by Nef, who made acetol in this way. The reaction may be carried out in a simple steel, or preferably, copper-lined autoclave.

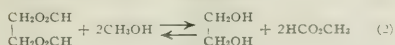
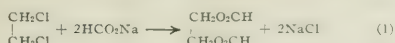
¹ Very pure ethylene chloride can be prepared if the chlorine ethylene reaction mixture is kept cold. The reaction develops considerable heat and, if not cooled, large proportions of trichloroethane are formed. In a small apparatus, proper cooling can be easily effected by mixing the gases in a glass or metal coil surrounded by cracked ice. The gases should not be dried. A private communication from Mr. K. P. McElroy states that very dry ethylene and chlorine may coexist for a long time without reacting.

² *Bull. Acad. roy. méd. belg.*, **1902**, 445.

¹ *Ber.*, **23**, 1890, 384.

² *Ber.*, **267**, 1892, 350.

³ "Biochemie der Pflanzen," Zweite Auflage, p. 657.



By employing considerable excess methyl alcohol the equilibrium is maintained by proportionately more glycol formate being converted to glycol, which amounts in the experiments here noted to about 85 per cent conversion.

EXPERIMENTAL

The experiments tabulated below indicate that the conditions for maximum yields are: heating the reaction mixture, consisting of one mol of ethylene chloride in five volumes of methyl alcohol and about three mols of sodium formate, to a temperature of 165 to 170° C. for about 7 hrs. At this temperature the pressure will vary from about 240 lbs. at the beginning to 290 lbs. per sq. in. after 7 hrs., and a pressure, when cold, of about 50 lbs., which latter pressure is undoubtedly due to the decomposition of a small amount of sodium formate. When autoclaves of several liters capacity are employed, it is highly desirable to stir the contents, which is most simply done by slowly rotating the autoclave.¹ Above 175° C. large proportions of diglycol are formed as is shown by Experiments 19 and 27.

TABLE I—YIELD OF GLYCOL, BY ACTION OF SODIUM FORMATE AND METHYL ALCOHOL ON ETHYLENE CHLORIDE

Exp.	No. of Mols Used Ethylene Sodium Methyl No. Chloride Formate Alcohol	Treatment Temp. Time °C. Hrs.	Pressure Max. Cold Lbs. Lbs.	Yield Per cent of Theoretical
3	1(a)	2.5 13.0	105	5
16	1	2.5 13.0	140	8
7	1	2.0 13.0	165	7
11	1	2.5 13.0	165	7
17	1	2.5 6.5	170	5
12	1	4.0 13.0	165	5
19	1	4.0 13.0	165	5
28	1	4.0 13.0	170	5
21	1	2.5 6.5	175	1.5
23*	1	2.5 6.5	165	5
24†	1(b)	2.7 13.0(c)	160	5
19†	1	2.7 13.0	175	5
27†	1	2.7 13.0	180	10

* 5 grams HgSO₄ added. † In rotating autoclave.

(a) 30 grams. (b) 50 grams. (c) 150 cc.

(d) 18 per cent "diglycol" also obtained.

(e) 35 per cent "diglycol" of b. p. 215 to 250° C. also obtained

The general procedure for isolating the glycols was as follows: After cooling, the slight "cold pressure" was released, the methyl alcohol solution poured from the crystalline salt and sodium formate mixture, the latter washed with a little cold methyl alcohol and the combined alcoholic solution distilled.

TABLE II—YIELD OF GLYCOL FROM ETHYLENE CHLORIDE BY THE ACETATE METHOD

Exp.	GRAMS MATERIALS USED Ethylene Sodium Acetate	Treatment Temp. Time °C. Hrs.	Pressure Lbs.	Yield Per cent of Theoretical
4	50 115	170 8	140	10
6	50 115	185 8	1	10
8	65 110	160	7	110

(a) Acetic acid. (b) Methyl alcohol (sp. gr. 0.81).

(c) Diglycol hydrolyzed by alcoholic HCl (see Henry, *Chem. Zentr.*

1 (1907, 114).

(d) This method yields the monoacetate at 145° C. (see Henry, *Ann.* 192, 244, Demole, *Ann.* 179, 117).

In some cases the methyl alcohol was distilled at ordinary pressure and the glycol then distilled *in vacuo*. In most cases, however, the glycol was distilled at atmospheric pressure.

This keeps the contents well mixed, prevents the formation of a salt cake in the bottom of the apparatus and very materially improves the yield as has already been shown by us in the case of the preparation of amyl acetate from chloropentene, anhydrous sodium acetate and acetic acid. (U. S. Patent Nos. 1,191,019)

The reaction of ethylene chloride with sodium acetate in glacial acetic acid takes place less readily, as is indicated by the lower yields in Experiments 4 and 6 in Table II.

A very small fraction boiling between 170° and 180° C. was always obtained, amounting usually to 8 to 10 per cent of the weight of the dichloride employed, which consisted of glycol diformate, boiling point 174° C.¹ Saponification of 10 g. of this ester yielded 7.5 g. of glycol, boiling point 190–196° C.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH
UNIVERSITY OF PITTSBURGH, PITTSBURGH, PA.

IODOMETRIC DETERMINATION OF CHLORINE IN CHLORIDES

By GREGORY TOROSSIAN

Received May 10, 1917

With the object in view of determining chlorine in chlorides quickly and accurately and without the use of silver nitrate, the well-known method for valuation of the available MnO₂ by iodine was applied. In the determination of the available MnO₂ by iodine the sample is treated with a quantity of hydrochloric acid in a small distilling flask, the liberated chlorine is carried through a glass tubing into a solution of potassium iodide and the liberated iodine is titrated with a N/10 sodium thiosulfate solution. In the proposed method for the determination of chlorine in chlorides the sample is mixed with finely powdered manganese dioxide, and treated with sulfuric acid (1 : 1 by vol.) in a distilling apparatus, as in the MnO₂ determination, and the chlorine, produced by the interaction of MnO₂ and the HCl set free from the chloride sample by the action of H₂SO₄, is conducted into a KI solution and the liberated iodine titrated as usual with N/10 Na₂S₂O₃. In this reaction between sulfuric acid and a chloride in the presence of MnO₂, the chlorine from the chloride is all distilled off, the spent liquor showing no chlorine when tested with AgNO₃. The reaction appears to be:



METHOD

THE REAGENTS REQUIRED—(1) Finely ground MnO₂ (passing 100-mesh sieve).

(2) Sulfuric acid (1 : 1 by vol. free from nitrates, hydrochloric acids, nitrates and nitrous fumes, etc.).

(3) Potassium iodide solution, 1% (approx. 100 cc.).

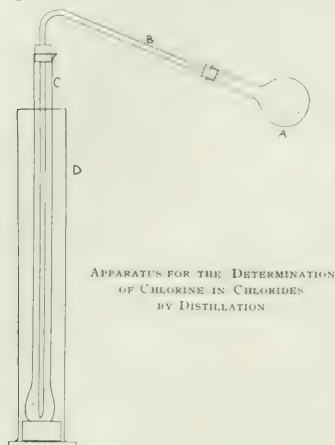
(4) N/10 sodium thiosulfate solution.

THE APPARATUS USED IN THE CASE OF THE DETERMINATION OF CHLORINE BY DISTILLATION WITH HYDROCHLORIC ACID AND IS SHOWN IN THE ACCOMPANYING ILLUSTRATION.

THE SAMPLING IN THIS METHOD IS VERY IMPORTANT. In the case of solids the sample must be finely powdered to insure intimate mixture with the sulfuric acid. If this is not done, there may occur a loss of chlorine during the operation by incomplete decomposition of the chloride. In the case of liquids the sample must be measured from a burette if necessary, by volume or weighed as the case demands, with ordinary adding and weighing. The amount of sample to be taken

for the analysis varies from 0.12 to 5 g., depending on the amount of chlorine present. For liquids, from 0.5 to 5 cc. or weights corresponding to these figures, are taken.

PROCEDURE—The weighed sample is thoroughly mixed on the weighing glass with about 2 g. of finely powdered manganese dioxide¹ and transferred into the



APPARATUS FOR THE DETERMINATION
OF CHLORINE IN CHLORIDES
BY DISTILLATION

round-bottomed flask *A*; 50 cc. of sulfuric acid (1 : 1 by vol.) are added and at once the flask is attached to the glass tubing *B*, which is inserted into the larger glass tube *C* containing 100 cc. of KI solution and surrounded with cold water in the cylinder *D*. The flask is now slowly heated with a gas burner and constantly agitated, not too strongly, but just enough to keep the contents in motion until boiling. The boiling is intermittently continued, with occasional agitation, for 3 to 5 minutes, when all chlorine is distilled over into the KI solution. The boiling is stopped, the flask quickly removed, and the glass tubing washed, inside and outside, into the main solution, which is transferred into a 600 cc. pear-shaped flask, then brought to a volume of about 200 cc. and titrated with a *N*/10 sodium thiosulfate solution previously standardized against pure iodine. One equivalent of iodine is equal to one equivalent of chlorine: 1 cc. *N*/10 $\text{Na}_2\text{S}_2\text{O}_3 = 0.003546$ g. Cl.

When a liquid is to be analyzed, the manganese dioxide is simply added to the sample in the flask.

If the chlorine in fluorides is to be determined the procedure is carried out in the same way as for the other samples. Some HF will be evolved, but it has no effect upon the final results and its action upon the glass is negligible.

If the sulfuric acid is free from nitric and hydrochloric acids, chlorides, nitrates and nitrous fumes, and the manganese dioxide contains no impurities capable of decomposing KI on volatilization, the boiling of the sulfuric acid and MnO_2 for over 8 or 10 minutes does not produce any appreciable coloration in the KI solution. The sulfuric acid may be heated to fuming to drive off HNO_3 , otherwise a blank test

can be run and appropriate correction made. The highest blank consumption of *N*/10 $\text{Na}_2\text{S}_2\text{O}_3$ did not run over 0.2 cc. in the author's experience and this was due to nitric acid found in the sulfuric acid used.

TABLE I
RESULTS BY SILVER CHLORIDE AND BY AUTHOR'S METHOD
On Basis of 1 Cc. $\text{Na}_2\text{S}_2\text{O}_3 = 0.0038204$ G. Cl

MATERIAL ANALYZED	No.	PER CENT CHLORINE		By I_2
		Calc.	By AgCl	
Sodium Chloride (NaCl)	1	60.66	60.66	60.74
	2	60.51
	3	60.91
	4	70.67
	5	60.73
	6	60.87
	7	60.81
Potassium Chloride (KCl)	1	47.56	47.52	47.49
	2	47.49
	3	47.49
	4	47.61
	5	47.61
	6	47.51
	7	47.54
$\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$	29.03	28.82	28.95
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	41.59	...	41.59
$\text{CuCl}_2 \cdot 2\text{KCl} \cdot 2\text{H}_2\text{O}$	44.45	...	44.67
Dry Cell Mixes.....	1	...	5.78	5.74
	2	...	5.40	5.49
Chloride Liquors (containing Mn, Zn, NiH and Ca)	1	...	17.75	17.65
	2	...	13.48	13.04
	3	...	10.92	11.06
Rare Earth Fluorides.....	1	...	0.10	0.13
	2	...	0.23	0.24
Manganese Ores.....	1	0.001
	2	0.005
	3	0.002

In Table I are tabulated the results of some determinations of chlorine in chlorides and products containing chlorides by the above method. If values in Table I for sodium chloride, which, by precipitation, gave 60.66 per cent Cl (the theoretical content), are used for the standardization of the sodium thiosulfate solution, the mean value for 1 cc. $\text{Na}_2\text{S}_2\text{O}_3$ gives 0.003815 g. Cl, and if this value is used to calculate Cl in the potassium chloride (Table I) the following figures are obtained:

Potassium Chloride No.: 1	2	3	4	5	6	7	Av.
Per cent Chlorine...	47.42	47.41	47.41	47.53	47.54	47.44	47.46

The figures given in this paper were obtained under the ordinary technical analytical laboratory conditions and no claims of extreme precautions and care are made by the author, but from the results given it is clear that the errors in the determination of chlorine in chlorides by the iodometric method described above are negligible for most purposes of ordinary laboratory analysis. The sodium thiosulfate solution can be standardized against sodium chloride which previously has been standardized by precipitation with AgNO_3 , and the mean of the three determinations taken as expressing the strength of the $\text{Na}_2\text{S}_2\text{O}_3$ solution, but the standardization against pure resublimed iodine answers the purpose very satisfactorily.

This method of iodometric determination of chlorine in chlorides is a very simple operation, inexpensive and accurate, and exceedingly quick; the entire procedure from weighing of the sample to the titration of the iodine does not consume more than 15 minutes. By this same method HCl in a mixture of hydrochloric and sulfuric acids can easily be determined without any precipitation.

This method also will serve as a quick qualitative test for ascertaining whether a given sample contains chlorine and the possible amount.

NATIONAL CARBON COMPANY, INC.
CLEVELAND, OHIO

¹ For larger samples the amount of MnO_2 can be increased.

A METHOD OF ASHING ORGANIC MATERIALS FOR THE DETERMINATION OF POTASSIUM

By P. L. BLUMENTHAL, A. M. PETER, D. J. HEALY AND E. J. GOTT

Received May 7, 1917

INTRODUCTORY

In a series of researches now in progress it was necessary to determine, quite accurately, small quantities of potassium in the presence of much greater amounts of organic materials, chiefly proteins, fatty acids and carbohydrates. Under such conditions, mechanical losses during ashing and the possibility of volatilizing potassium compounds would introduce serious errors into the work. The object of this investigation, therefore, was to ascertain the best method of ashing organic substances in which potassium was to be determined. This article is the first of a series of investigations. Other papers will follow as rapidly as the results warrant.

Of the various salts of potassium the chloride and the carbonate are the most volatile. The potassium of organic compounds, when ashed, is usually converted to the carbonate, except where sufficient chloride or sulfate ions to combine with all of the alkali are present. The nitrate, oxalate and other potassium salts of organic acids are converted to the oxide, hydroxide or carbonate, depending upon the conditions of ignition and the quantity of carbon dioxide present.

Rose¹ states that if the alkalis are present only as chloride it is possible, through lack of care, to volatilize the small amount of alkali salts present. On page 554 of the same book he states that the chlorides of the alkalis are much more easily volatilized when heated in the presence of air than when air is excluded.

Norton and Roth² show that potassium sulfate is nearly twice as stable as the carbonate and about seven times more stable than the chloride.

In addition to the possibility of loss of potassium salts by volatilization, there is every reason to believe that, in the removal of considerable quantities of organic material or ammonium salts by burning, some potassium is lost mechanically.

REAGENTS AND MATERIAL

The organic material selected for experimental work was a bacteriological culture medium containing small amounts of potassium salts. It varied slightly in composition from time to time, but the ratio of organic matter to potassium salts was fairly constant. This medium contained about 0.7 g. of organic matter (proteins, carbohydrates, etc.) in 25 cc. of solution. A portion of a high-grade, commercial preparation of potassium chloride was dissolved in water and, after filtering, was partially precipitated by running the solution into pure dilute ethyl alcohol, with constant stirring during the mixing. The finely crystalline salt so obtained was filtered, washed with dilute alcohol, dried for several hours at 100°, bottled while warm, and allowed to stand in a desiccator over calcium chloride. A portion of the salt was carefully weighed out and made up to the required volume at 20° C. This

solution was standardized by carefully evaporating measured portions with platinic chloride solution and, after the usual washings with acid alcohol, ammonium chloride solution and 80 per cent alcohol, the weight of potassium chloroplatinate was obtained and the potassium chloride content calculated.

Molar solutions of nitric acid, magnesium nitrate and ammonium nitrate were used in certain of the experiments; dilute sulfuric acid was prepared by mixing 184 cc. of distilled water with 100 cc. of concentrated sulfuric acid. The acid alcohol used in washing the potassium chloroplatinate was made by adding 100 cc. of concentrated hydrochloric acid to 1 liter of 95 per cent ethyl alcohol; the ammonium chloride solution was of 20 per cent strength and was saturated with potassium chloroplatinate in the usual manner.

METHOD OF ANALYSIS

Twenty-five cc. of medium were pipetted into a suitable silica evaporating dish, potassium chloride solution run in from a burette (except in the blanks) and the sulfuric acid and oxidizing agents added by means of dropping pipettes. The solution was evaporated on a rapidly boiling water bath, as low as possible. The black, gummy residue was carefully heated over a free flame or in a muffle furnace until white.¹

On cooling, 2 to 4 cc. of 1 : 1 hydrochloric acid were added, and the ash allowed to digest at room temperature over night, keeping the dishes under a bell jar. The solution was then filtered into small beakers, washing with hot water, and policing the dishes to remove the last traces of residue. Some calcium sulfate and silica are removed by the filtration. After the addition of the requisite excess of platinic chloride, the filtrate was evaporated to dryness on the water bath and, after cooling, was taken up with a few cc. of the acid alcohol. After settling, the clear yellow liquid was decanted through a glass filtering tube, having an asbestos mat, the residue was again washed by decantation with acid alcohol and then with the 80 per cent alcohol, to remove the last traces of platinic chloride and hydrochloric acid from the preceding wash. The bulk of the precipitate in the beaker was then treated with 4 to 6 cc. of the ammonium chloride wash, using a rubber policeman to break up the lumps and larger crystals, and stirring to hasten the solution of calcium and magnesium sulfates. After settling, the wash was decanted through the same tube which contained a little of the precipitate and the main precipitate was washed repeatedly by decantation with the ammonium chloride solution until clean.² The main portion of the chloroplatinate was then transferred to the filtering tube, the beaker policed, washed

¹ It was noted that where carbonaceous material occurred, much of graphitic nature, the results were erroneous. If the carbonaceous material was removed at once heating the extracted residue in a desiccator and the soluble material of the ash added to the same solution. A 25 to 4 rather tedious procedure, and one having no effect on the results, proved this method herein explained was discarded with a view to removing all the organic matter at one heating, even at the risk of losing a trace of potassium by volatilization.

² This material was examined by the method of the operator who was familiar with the appearance of a precipitate of potassium chloroplatinate given unnecessary.

¹ Handbuch der Analytischen Chemie, German Edition 1 (1871).

thoroughly with 80 per cent alcohol, and the tube dried for an hour at 98° C. After cooling and weighing, the precipitate was dissolved out by washing with hot water. The tube was then filled with 80 per cent alcohol and after drawing this through by suction it was again dried for an hour and, after cooling, reweighed. The difference in weight represented K_2PtCl_6 . Some silica usually remained on the asbestos mat but in no case was it found to vitiate the results. The direct method of estimating potassium without removing Fe, Ca or Mg, as herein described, has proved very satisfactory in this laboratory over a period of eight years.

EXPERIMENTAL

To determine whether sulfuric acid would retard possible loss of potassium, and whether heating in a muffle furnace offered any superiority over the usual method of burning off by moving the silica dish slowly over a Bunsen flame until the main evolution of gas had ceased, and then igniting till the residue was white, a series of ten experiments (Table I, Series A) was carried out, using 25 cc. of the medium for analysis.

Not knowing the exact potassium content of the medium, it was necessary to carry out some check analyses in which known amounts of potassium were added to the medium, in order to arrive at the amounts recoverable. A second series of experiments (Table I, Series B) was, therefore, made in which 5 cc. of KCl

TABLE I—RESULTS ON 25 CC. OF MEDIUM BY ASHING IN A MUFFLE FURNACE AND OVER A BUNSEN FLAME

No.	HEATING	SERIES A—NO ADDITION SULFURIC ACID			SERIES B—KCl ADDED		
		CC. H ₂ SO ₄	CC. KCl	Milligrams K	Taken	Found	Error
1	Bunsen	None		4.14	7.56	6.51	-1.05
2	Bunsen	None	4.26	4.25	7.56	6.24	-1.32
3	Bunsen	None	4.14		7.56	6.19	-1.37
4	Bunsen	None	4.28				
5	Bunsen	None	4.30	4.29			
6	Muffle	5 drops	4.71		7.59	7.74	+0.05
7	Muffle	4.85	4.63		7.59	7.82	+0.03
8	Muffle	5 drops	4.63		7.59	7.79	0.00
9	Muffle	5 drops	4.49		7.62	7.31	-0.31
10	Muffle	5 drops	4.14	4.31	7.62	7.21	-0.41

solution were added to each sample; the other details were identical with Series A, except that Nos. 4 and 5 were omitted. The potash content of the medium was taken from the averages in Series A, each average being assumed as a blank for the group in question.

From the results of these Series A and B, it is quite evident that in the absence of sulfuric acid, potassium is lost, presumably by volatilization, while there is a shade of evidence in favor of using a muffle furnace, because the results are a trifle higher. Theoretically, the muffle should reduce mechanical losses due to spattering and local superheating, because of uniform heating. It seemed possible, from Series B, that a larger quantity of sulfuric acid might improve the results even more. The sulfuric acid acts as an oxidizing agent in removing carbon and also as a "fixing" agent for the alkali salts present; therefore, a larger quantity of the acid ought to hasten the ashing process and reduce the possibility of loss of alkali salts by volatilization. Table II shows the effect of increasing the quantity of acid; the potassium content of this medium was slightly increased due to decrease in volume during sterilization.

TABLE II—SERIES C RESULTS WITH INCREASING QUANTITIES OF ACID, USING 25 CC. OF MEDIUM AND ASHING IN THE MUFFLE FURNACE

Dilute H ₂ SO ₄ Milligrams K found	10 drops	15 drops	20 drops	0.5 cc.	1 cc.	2 cc.	3 cc.	4 cc.
	5.15	5.02	5.40	5.16	5.18	5.11	5.19	5.37
	5.31	5.00	5.68	5.18	5.13	5.16	5.32	5.24
			5.16	5.13	5.20			

AVERAGE 5.18 5.01 5.41 5.16 5.19 5.14 5.26 5.30

The variations in Table II are quite small and one is hardly warranted in drawing conclusions from the analyses. However, the samples containing larger amounts of acid ashed more readily and left little carbonaceous residue with the silica, etc. The next series of experiments contained larger quantities of acid to throw further light upon the point. In Table III are given the results of another parallel series, carried out to determine whether the muffle or free-flame method of ashing gave the more accurate results.

TABLE III—SERIES D

Cc. H ₂ SO ₄	Cc. KCl	MUFFLE FURNACE Milligrams K			FREE FLAME Milligrams K		
		Taken	Found	Error	Taken	Found	Error
			4.84			4.52	
			4.91			4.55	
			4.84				
3	5	8.17	7.98	-0.19	7.86	6.80	-1.06
		8.17	7.55	-0.62	7.84	6.89	-0.95
		8.19	8.17	-0.02			
	10	11.40	11.43	+0.06	11.16	11.11	-0.05
		11.48	11.32	-0.16	11.18	9.58	-1.60
		11.50	10.79	-0.71			
3	25	21.42	20.69	-0.73	21.12	19.21	-1.91
		21.44	19.70	-1.74	21.10	18.79	-2.31
		21.42	21.16	-0.26			

The first five results in Table III are blanks on potassium content of the medium. These results are not acceptable in point of agreement, though some of the individual analyses are sufficiently close to theory; the analyses made by means of the muffle furnace are higher than those where the samples were ashed over a free flame. This means that there was less mechanical loss (spattering, foaming, etc.) and in all subsequent analyses the samples were burned in the muffle furnace. It was quite difficult to burn the last bit of carbon in this set because it was more or less graphitic in nature and was quite refractory. To avoid possible errors due to adsorption of potash in washing by the carbon remaining unburnt, etc., it was sought to find a method of ashing which would readily remove all of the carbon from the ash.

A series of experiments was tried in which the samples were evaporated and then charred over the free flame, after which the requisite amount of sulfuric acid and 10 to 15 cc. of water were added and the whole evaporated a second time and ashed. This treatment was devised in order to relieve the sulfuric acid of part of its function as an oxidizer: the charred mass was readily softened by water and acid and the subsequent ignition was a little easier to conduct because there was less foaming, etc. The analyses are quoted in Table IV, Series E.

Further investigations were made along the same line in which part of the carbonaceous material was removed by initial heating at relatively low temperatures, various materials being added to assist in the oxidation.

Table IV, Series F, shows the results obtained when the samples were first evaporated with 5 cc. of molar solutions of nitric acid, ammonium nitrate or magnesium nitrate, charred over a free flame and then treated with sulfuric acid diluted with water, evaporated

TABLE IV.—EFFECT OF ADDITION OF OXIDIZER

—SERIES E—NO OXIDIZER—				—SERIES F—OXIDIZER ADDED—			
KCl	H ₂ SO ₄	—Milligrams K—		KCl	H ₂ SO ₄	Oxidizer	—Milligrams K—
Cc.	Cc.	Taken	Found Error	Cc.	Cc.	Cc.	Taken Found Error
3	...	6.27	...	5	HNO ₃	...	6.67
3	...	6.00	...	5	HNO ₃	...	6.67
3	...	6.14	...	10	5	HNO ₃	12.98 12.94 —0.04
10	3	12.76 12.99	+0.23	10	5	HNO ₃	12.96 12.83 —0.13
10	3	12.75 12.73	—0.02	10	5	HNO ₃	12.99 12.55 —0.44
10	3	12.77 12.62	—0.15	...	5	NH ₄ NO ₃	...
10	3	12.77 11.92	—0.85	...	5	NH ₄ NO ₃	...
10	3	12.76 12.12	—0.64	...	5	NH ₄ NO ₃	12.76 11.83 —0.93
10	5	10	5	NH ₄ NO ₃	12.74 12.86 +0.12
10	5	5.76	...	10	5	NH ₄ NO ₃	12.77 11.89 —0.88
10	5	6.30
10	5	5.82
10	5	12.68 13.08	+0.40	...	5	Mg(NO ₃) ₂	...
10	5	12.67 13.03	+0.36	...	5	Mg(NO ₃) ₂	...
10	5	12.69 12.91	+0.22	10	5	Mg(NO ₃) ₂	13.02 12.99 —0.03
10	5	12.69 13.13	+0.44	10	5	Mg(NO ₃) ₂	13.00 12.60 —0.40
10	5	12.68 11.89	—0.79	10	5	Mg(NO ₃) ₂	13.03 12.76 —0.27

and ashed. The quantities of sulfuric acid were varied so as to determine under what conditions the removal of carbon could be most readily accomplished.

As in the other tables, the first results under the column headed "Mg. K found" represent the amount of potassium found in the organic medium: the variations from table to table are due to differences in the concentration of the medium, which varied in the different preparations. The differences in the values obtained for the same amount of medium in the same table are due to the impurities present in the reagents used in each method tried and to mechanical losses or errors inherent to the method.

In the above experiments, on attempting to char those determinations which had only nitric acid present, the material swelled rapidly to a very voluminous mass, resembling the ash obtained from burning mercuric isothiocyanate. The ammonium and magnesium nitrate experiments deflagrated: the latter was a slower and less violent deflagration and the ash was more porous, but the presence of the magnesium salts rendered the removal of the last traces of carbon difficult and the subsequent treatment of the ash for estimation of potassium was rendered very tedious for the same reason. The mechanical losses due to deflagration eliminate the last two methods of treatment, but the nitric acid method gave promise of better results, particularly if the formation of the puffy char could be controlled.

Accordingly, a series of determinations was outlined to study the action of nitric and sulfuric acids in re-

moving carbon, with a minimum loss of potassium.

In Table V, Series G, Experiments 1 to 7 were carried out as follows: The sample (with or without KCl) was treated with 5 cc. of molar nitric acid and 6 cc. of sulfuric acid, evaporated to pasty condition and then ashed in the muffle. Nos. 8 to 11 were treated with the same amounts of HNO₃ and evaporated as low as possible on the water bath, diluted with water and then carried down with 6 to 7.5 cc. of sulfuric acid. Nos. 12 to 18 were similar experiments on a new medium. Nos. 19 to 23 were evaporated with nitric acid and charred in a free flame, as were the determinations in Series F, after which sulfuric acid and water were added and the mixture evaporated to low volume and ashed.

Nos. 1 to 7 yielded results which are slightly closer to theory than any of the other methods and they are more regular than those of the other methods. Since this procedure was shorter, it was decided to investigate the method further.

These experiments, the results of which appear in Table VII, Series H, show greater regularity and closer duplication of individual series than any method as yet tested. It will be noted that practically all the results are low, the maximum error being 0.46 mg. where 21.81 mg. were taken, or about 2 per cent of the total potassium present. In working with such small quantities as have been employed in this investigation, such an error, while not desirable, is relatively negligible, as the long process involved in the analysis is bound to cause some mechanical losses. Series G shows that, while considerable quantities of sulfuric acid are necessary, a large excess is to be avoided, because of the increased danger of spattering during the removal of carbon by burning.

In closing it should be stated that the amounts of nitric and sulfuric acid used in this work will not necessarily be found suitable for all potassium determinations where organic matter is present. With 7 g. of various organic materials, and amounts of potash varying from 4 mg. to 21 mg., it has been found advisable to use at least 5 cc. of molar nitric acid and the same amount of 1:1 sulfuric, the amount of nitric acid can be varied, depending upon the quantity and nature of the organic matter present, as most of the excess acid will be removed through replacement by sulfuric acid and volatilization during evaporation. The amount of sulfuric acid should not be increased, except where very large quantities of organic matter are to be burned, to prevent the possibility of excessive losses through spattering.

CONCLUSIONS

1. In taking organic material, potassium is removed by spattering and volatilization in removing organic matter and ammonium salts.

2. Burning of carbon in a muffle furnace leads to more uniform results than does heating over a free flame.

3. Converting the potassium salt to sulfate and burning in a muffle furnace leads to more uniform results.

TABLE V.—EFFECT OF NITRIC ACID, 5 CC., USED IN EACH EXPERIMENT

SERIES G				SERIES H			
KCl	H ₂ SO ₄	—Milligrams K—		KCl	H ₂ SO ₄	—Milligrams K—	
No.	Cc.	Cc.	Taken Found Error	No.	Cc.	Cc.	Taken Found Error
1	6	...	6.80	1	6	...	8.68
2	6	...	6.34	2	6	...	8.78
3	5	6	9.93 9.91 —0.02	3	10	2	12.06 11.78 —0.28
4	5	6	9.91 9.95 +0.06	4	10	2	12.04 11.96 —0.08
5	10	6	13.08 13.21 +0.16	5	10	2	12.01 12.01 —0.00
6	10	6	13.06 13.05 —0.01	6	15	2	15.22 15.10 —0.12
7	10	6	13.09 13.16 +0.07	7	15	2	15.20 15.06 —0.14
8	6	...	6.49	8	15	2	15.22 15.84 +0.62
9	10	6	11.80 13.17 +0.37	9	15	2	15.20 15.06 —0.14
10	10	6	11.80 13.17 +0.37	10	15	2	15.20 15.06 —0.14
11	10	6	11.81 13.17 +0.36	11	15	2	15.20 15.06 —0.14
12	5.87	12	5.93
13	5.59	13	6.04
14	10	3	12.03 11.55 —0.48	14
15	10	3	12.03 11.81 —0.22	15
16	15	3	12.03 11.55 —0.48	16
17	15	3	12.03 11.55 —0.48	17
18	15	3	12.03 11.55 —0.48	18
19	6	...	7.07	19
20	6	...	6.86	20
21	10	6	13.78 13.41 —0.37	21
22	10	6	13.78 13.41 —0.37	22
23	10	6	13.78 13.41 —0.37	23

IV—Moistening the sample with sulfuric acid is not sufficient: enough sulfuric acid should be added to act as an oxidizer for carbon and to convert all inorganic elements present to sulfate.

V—Direct evaporation of the sample with nitric and sulfuric acids, preliminary to burning off organic matter, has proved the best method of securing uniform results and has materially reduced volatilization losses.

AGRICULTURAL EXPERIMENT STATION
LEXINGTON, KENTUCKY

SOURCES AND COMPOSITION OF SOME COMMERCIAL INVERT SUGAR SYRUPS WITH NOTES ON SORGHUM SYRUP

By STROUD JORDAN AND A. L. CHESLEY

Received February 8, 1917

At the present time numerous samples of commercial invert sugar syrups may be bought on the market under different trade names, and during the past year it has been estimated that more than 2,000,000 gallons of this material were used in the several industries which represented an expenditure in excess of \$1,000,000. The use of this material is on the increase and there is no limit to its application, for the great value of such a solution is that the sugars will not harden, as will sucrose, and that it will retain approximately 14 per cent moisture under most conditions. This fact has been utilized to prevent hardening of materials by substituting all or a portion of the sucrose used with invert syrup. A wide variation in these syrups will be found, going from inverted cane sugar syrups through inverted raw cane sugar syrups into the more or less complex molasses and invert sugar mixtures, which sometimes contain materials other than sucrose and invert sugar.

It is unnecessary to go into detail as to history, character and properties of invert sugar, for this is thoroughly covered in the literature,¹ but in general two grades may be bought on the market: these are known as "light" and "dark" or by some special brand.

THE LIGHT SYRUP is generally composed of a large amount of invert sugar and a small amount of unchanged sucrose, along with a trace of ash and from 0.05 to 0.2 per cent acidity, when calculated as tartaric. Organic acids are generally used in the preparation such as citric, tartaric, formic, and acid salts, as cream of tartar, but in some instances hydrochloric acid has been detected up to 0.15 per cent, partly combined and partly free.

THE DARK SYRUP is a complex mixture, being composed of invert raw sugar syrup, a mixture of invert raw sugar syrup and molasses, light invert sugar syrup and molasses, or invert sugar syrup and soured honeys along with wastes occurring around sugar

houses. It is so blended that it rarely carries over 72.5 per cent total sugars and a varying amount of this is invert, which may be seen from the analyses given later. It is impossible to determine the acid value of this material with any degree of accuracy since the color is too dark to allow titration.

METHODS OF ANALYSIS

For all determinations, the official methods, as given in *Bull.* 107 (revised), U. S. Dept. of Agr., Bur. of Chem., have been used. These methods have been replaced by later modifications appearing in the *Journal of Association of Official Agricultural Chemists*, where they may be found. In this connection it is well to point out the fact that sucrose cannot be estimated in these solutions by the Clerget method,¹ and that copper reduction methods have always been employed.

RESULTS

Analyses of products gathered from various sources during the past four years are given below in percentages and under each grouping will be found samples of similar origin.

No.	LIGHT SYRUP			No.	DARK SYRUP		
	Invert	Sucrose	Ash		Invert	Sucrose	Ash
A	1 77.80	3.33	0.02	A'	1 36.92	35.09	0.39
	2 78.60	2.87	0.12		2 48.52	22.62	1.47
	3 76.73	0.98	0.06		3 47.62	15.49	2.44
	4 76.70	2.19	0.05		4 47.04	22.80	1.98
	5 77.55	2.26	0.01		5 51.32	20.35	1.84
B	1 69.20	11.88	Traces	B'	1 29.23	46.63	0.22
	2 73.90	8.61	Traces		2 36.58	36.94	0.96
	3 72.62	6.37	Traces		3 31.57	43.46	1.03
	4 68.08	10.90	0.11		4 37.62	30.60	0.87
	5 76.80	2.56	0.11		5 53.28	23.77	0.41
C	1 74.72	2.27	Traces	C'	1 73.65	5.30	0.16
	2 74.96	2.58	Traces		2 67.77	8.44	0.06
	3 75.82	2.11	Traces		3 71.04	4.28	0.05
	4 75.76	2.30	Traces		4 71.82	4.01	0.07
	5 73.69	3.14	Traces		5 69.42	7.32	0.12
	6 75.29	0.49	Traces		6 46.88	22.30	3.07
	7 74.46	3.47	Traces		7 51.58	22.29	2.32
	8 74.96	2.49	Traces		8 48.85	22.26	3.51
	9 74.33	2.73	Traces		9 47.32	21.86	2.51
	10 74.96	1.94	Traces		10 35.19	35.84	2.98
M	1 44.05	33.57	Traces	M'	1 68.67	7.40	0.98
	2 72.37	5.42	Traces		2 64.28	6.35	0.43
	3 65.92	14.29	Traces		3 55.62	21.13	0.24
	4 69.20	11.88	Traces		4 18.00	52.51	0.99
	5 75.85	2.44	0.06		5 47.12	26.60	1.08
	6 71.40	8.27	0.40		6 54.46	23.24	0.23
	7 47.96	30.58	Traces		7 54.08	22.21	0.04
	8 66.00	11.50	Traces		8 60.38	14.95	0.05
	9 67.88	9.47	Traces		9 61.42	13.82	0.06
	10 71.42	6.51	Traces		10 43.54	28.79	2.41

Samples marked "A" show a very good inversion. The ash value of these samples would indicate that mineral matter of some nature had been introduced either to neutralize acidity or for some special purpose.

Samples marked "B" do not show a good inversion. The first three show that no mineral matter or foreign material is present because only traces of ash were found, but the last two evidently have material other than sucrose added. These inversions are not as nearly complete as the foregoing samples, but they were probably stopped at this point in order that there would be less tendency for dextrose and levulose to separate.

Samples marked "C" show very good inversion and correspond favorably with samples listed under "A," however, the amount of total sugar is not as great,

¹ Allen's "Commercial Organic Analysis," 4th Ed., pp. 375-6; British Patent, 16,540, 1889; Alfred Wohl; Browne's "Handbook of Sugar Analysis," p. 659; *Ibid.*, p. 273; Chemical Abstracts, 1 (1907), 645; *Deut. Zuckerind.*, 31, 1988; U. S. Dept. Agr., Bur. of Chem., *Bull.* 73, 75-6; *Ibid.*, 110, 63-4; U. S. Dept. Agr., *Farmers' Bull.* 477, 30; U. S. Patent, 1,181,086, 1916, N. W. Taussig.

¹ *Jour. A. O. A. C.*, II, 3 (1916), 138.; Allen's "Commercial Organic Analysis," 1, 375.

which is accounted for by the fact that 75 per cent sucrose solutions were inverted.

Samples marked "M" are of miscellaneous origin. Nos. 1 and 7 represent a syrup which will not crystallize under most conditions; however, its value is not as great as it would be had the syrup been properly inverted. No. 6 was inverted by the action of hydrochloric acid and a portion of the acid neutralized, which accounts for the high ash value: this sample was very unsatisfactory because it carried a burned taste, was dark in color and showed the presence of free hydrochloric acid. The other samples under this heading did not show enough difference to warrant special remarks.

Samples marked "A" represent a dark syrup which has evidently been made from molasses and light syrup, except for No. 1 which was probably made from raw sugar. This is accounted for by the odor, taste and high ash values.

Samples marked "B" are very similar to "A." Nos. 2, 3 and 4 were probably made from a low-grade sugar showing less than 90 per cent sucrose or from light syrup and molasses just as in "A." Samples 1 and 5 were probably made from raw sugars.

Samples marked "C," Nos. 1 to 5, inclusive, represent a dark syrup made from raw sugar showing at least 98 per cent sucrose. Nos. 6 to 10, inclusive, were made from 50 per cent syrup, and 50 per cent bright molasses, which showed an average ash of 5.5 to 7 per cent. These last five samples show that the ash value is a very good criterion for judging this material.

Samples marked "M" represent miscellaneous samples. Nos. 1, 2, 3, 6, 7, 8 and 9 were probably made from raw sugar. No. 4 was made from a low-grade raw sugar showing less than 90 per cent sucrose. No. 5 was made from 25 per cent of No. 4, 25 per cent refiner's syrup and 50 per cent light syrup. No. 10 was made from 50 per cent light syrup, 25 per cent New Orleans molasses, and 25 per cent Porto Rican molasses.

MOISTURE-HOLDING PROPERTIES

From practical experiments it has been determined that glycerine (95 per cent) will take up as much as 15 per cent of moisture, while the light invert sugar syrups will retain about 14 per cent, but one must not assume that these syrups will replace glycerine because of this fact. This becomes evident when glycerine and invert syrups are compared, for glycerine has a lubricating and softening effect and will "strike in" almost any porous surface at ordinary temperature. Invert syrups are sticky, adhere to the surface and require high temperatures or to be used as very dilute solutions before they will "strike in." These syrups may be used to replace glycerine where that material has been employed to effect conditions arising from the use of crystallizable sugar, for this hardening is due to crystallization more than to lack of moisture.

SPECIFICATIONS

While it is realized that the requirements of the various industries in which these syrups are used admit

of wide variations in composition, nevertheless it is felt that uniform classifications based upon specifications would be of value in contracting for such material. The following is therefore suggested after analysis of 150 samples, collected over a period of 5 years from more than 2,000,000 pounds of invert syrup, which has been furnished from 13 different sources. More than 500,000 pounds of this material have been made under the direct supervision of one of the authors, and in no cases have the following specifications been found high or impractical.

An objection might be raised over the percentage of total sugars required, but the limits set have not been found high. There should be no complaint about the sucrose invert-sugar ratio, since the value is directly affected by this constant. If a higher sucrose content is desired it is an easy operation to add a sucrose solution and if invert syrups are to be bought we recommend that they should meet one of the following requirements:

1—*Light syrup special* shall consist of at least 75 per cent total sugars, due to invert sugar and sucrose alone. The sucrose in such a syrup cannot well exceed 2.5 per cent, and the ash value should never exceed 0.02 per cent. Only organic acids should be used, which must never exceed 0.1 per cent, when calculated as tartaric.

2—*Light syrup*: similar to (1) except the sucrose should not exceed 20.00 per cent and the syrup should be bought on its total sugar units.

3—*Dark syrup special* shall be made from raw sugar, water and a suitable organic acid, which shall not exceed 0.3 per cent by weight of the syrup. At least 75 per cent of total sugars, due to sucrose and invert sugar alone, shall be present and the sucrose should not exceed 5 per cent. The ash value of this material cannot well exceed 0.5 per cent.

4—*Dark syrup* shall be made from any suitable blend of invert syrups and molasses. The total sugars should never fall below 72.5 per cent, of which at least $\frac{2}{3}$ shall be due to invert sugar and not more than $\frac{1}{3}$ shall be due to sucrose. The ash value of this material cannot well exceed 2.5 per cent. No acid value may be set, but in general it will conform to requirements under "3" above.

SORGHUM SYRUP

In every case where invert syrups are manufactured a certain amount of raw or granulated sugar is required which means that this much sugar is imported into the United States, only to be used again in the production of invert syrups. Therefore, it is desirable to look for natural economical sources which will furnish the amount necessary, and incidentally build up the sugar industry in the United States. After reviewing the literature on sorghum¹ one's attention is necessarily called to the fact that it had to be given up as a source for the production of cane sugar because of the presence of invert sugar, starch, dextrin and

¹ U. S. Dept. Agr. Bur. 80, 1888; 26, 1892, 99, 1896, 24, 1899; U. S. Dept. Agr. Transac. Bur. 477, 1911.

gums which prevented crystallization. Now it has been estimated that approximately 17,000,000 gallons of sorghum syrup were produced in the U. S. during the year 1900, and since that time the industry has grown larger in certain localities. It has also been estimated by one farmer who has grown sorghum for 50 years, that the average cost of production of 15,000 gallons of syrup yearly is about 19 cents per gallon.

Of course there are by-products in this manufacture which may be utilized, such as seed from the sorghum cane for the production of alcohol and some planters claim that sorghum seeds are worth as much for feeding purposes as an equivalent amount of Indian corn. The fodder or roughage may also be saved and used as a food for cattle; however, very little success has been obtained by feeding this to horses and mules on account of the exceedingly rough nature of the blades, which causes sore mouth. The value of the seeds is due to the high percentage of starch which gives them high food value. There is a custom in certain sections of North Carolina of feeding these cane seed-heads to hogs and it is claimed that a row of cane will furnish as much food from the seeds as a row of corn the same length. It will be seen, therefore, that sorghum is not only a source of syrup but also a source of cattle and hog food which makes it equivalent to corn, a fact which should not be overlooked, especially at this time when food and food products are so scarce. The advantage of cane over an equivalent amount of corn may be seen to be the amount of syrup obtained from the stalk since corn stalks are not utilized and when this fact is taken into consideration along with the fact that cane may be planted closer together it will be seen that cane is worth approximately twice as much as corn.

The syrup produced will furnish a source of all the so-called dark invert syrups and it is also possible to produce the light syrup by passing the dark through a "Char" filter. The use of this material will make it possible to obtain equivalent sugar units at approximately 75 per cent of the cost when compared with invert syrups made from cane sugar. The only drawback to this source is that the syrup is generally used up locally and no centralized market exists for its purchase; however, the demand for this material should warrant the establishment of such a market.

To test out sorghum along with other commercial invert syrups a representative 10-gallon sample was taken at random from 1200 gallons made at Barnesville, Georgia, during October, 1916, and an average analysis on this material is given herewith:

ANALYSIS OF SORGHUM SYRUP					Acidity as Tartaric
	Solids	Ash	Sucrose	Reducing Sugars	
Percentages	74.63	2.82	40.00	28.42	0.79
				Gums and Extractive	
				4.03	

This sample was made from a variety known as Texas ribbon cane by grinding in a three-roller mill, straining the juice through a piece of burlap and allowing this to run immediately onto an evaporator heated by a

wood fire. No control was attempted; as far as could be seen, the only means of determining the finishing point was by the break in the bubbles formed in the boiling syrup. This point, along with the heat of the fire, was controlled at will by a so-called syrup maker who had been making syrup for the past thirty years.

The amounts of reducing sugars and sucrose may be varied by following out suggestions given by A. Hugh Bryan in the Bulletin¹ just referred to; however, for general information it might be well to state that these methods depend on the fact that sucrose is inverted in the presence of certain acids and enzymes. The general procedure is to add very little lime, or none at all, in defecating the syrup but to allow the natural acidity to cause further inversion in the sucrose content when the syrup is cooked. This process may be augmented by warming up the juice in an auxiliary tank before evaporation, in which case inversion is increased. Some makers allow the cane to remain in the field for twenty-four hours or more after cutting, which procedure may be taken for its worth. The fact remains that the high ash value of finished sorghum syrup will not allow of inversion so that this process must be attended to at the source and it is felt that by proper selection of the variety planted along with suitable control of the juice before evaporation a product may be made which will be a satisfactory substitute for the invert sugars of commerce. This last statement is borne out by the fact that sorghum had to be given up as a source of cane sugar because it was possible to obtain but little crystallization when the syrup was allowed to stand.

It is interesting to note that the gums in sorghum syrup were composed largely of starch and dextrin which will prevent crystallization when taken with the percentage of reducing sugars present.

A sample was exposed for six weeks without crystallization and at the end of that time it showed approximately 15 per cent of water. Of course some of this was held mechanically by the skin which formed on the surface and which was broken from time to time but the moisture content will always compare favorably with light syrups. This same sample was still soft and pliable without showing signs of crystallization at the end of four months.

The best grade of sorghum syrup should be made from the natural juice of the several varieties of sorghum cane, by extraction or expression and subsequent evaporation. No alkali nor alkaline salts should be used to defecate the juice. The finished syrup should contain at least 70.00 per cent of total sugars, not more than 5.00 per cent starch and gummy matters, and not more than 3.00 per cent of ash (mineral matter). The acidity of such material cannot well exceed 0.8 per cent, due to acids naturally present in the cane juice and calculated as tartaric. The color and taste should be large factors in judging this material.

544 PARK AVENUE
BROOKLYN, NEW YORK

VINEGAR INVESTIGATION A STUDY OF THE CHANGES THAT CIDER UNDERGOES DURING FERMENTATION AND PROLONGED STORAGE AND ITS SUBSEQUENT CON- VERSION INTO VINEGAR IN ROTATING GENERATORS

By B. G. HARTMAN AND L. M. TOLMAN

Received May 7, 1917

INTRODUCTION

In the fall of 1913, the Bureau of Chemistry started an investigation of cider vinegar made by the use of a certain type of rotating generator. Analyses of cider vinegars made by this process show a decidedly low content of non-sugar solids and it was mainly for the purpose of determining the reason for this that the investigation was made.

The work was conducted at Medina, N. Y., and extended over a period of two years. During this time the process was under the personal supervision of one of the authors and no opportunity was neglected to make the investigation, in its various stages, entirely authentic. In the course of the work about 70 samples were collected and analyzed. In order that no question could be raised as to the authenticity of the samples, the various containers (fermenters, clearing tanks, generators, etc.) were washed with a part of the material in the nature of a test run, in identically the same manner as in the investigation proper. The various products of this test run were analyzed and found to agree very well in chemical composition with the corresponding products of the investigation proper.

The fruit used represented a good quality of the usual run of western New York apples for vinegar making, Baldwins and Greenings predominating. The starting materials comprised two lots of 20,000 gallons each of first pressing and one lot of 2,500 gallons of second pressing juice. These lots were obtained from practically the same stock so that little difference in their chemical composition was expected.

PROCESS

The fruit was grated and the finely ground pulp subjected to hydraulic pressure in the customary manner. The juice running from the presses had a temperature of about 50° F. and had a pleasant, clean taste. The yield was about 170 gallons per ton of apples. The solids at the various pressures did not vary much; if anything, there was a slight decrease in the solids as the pressure increased, but this was not consistent. The juice was pumped into fermenters of 20,000 gallons capacity and allowed to ferment spontaneously. The pomace remaining after the juice had been removed was firm and dry. This pomace was stored in heaps for about three days and then repressed without the addition of water under the same conditions as the first pressings. During the storing period the pomace showed signs of fermentation, evidenced by a rise in temperature in the center of the heap. The second pressing juice, which amounted to about one-ninth of the total available juice of the apple, was fermented spontaneously. Both the first and second pressing juices after completing fermentation were aged for about one year in the original fer-

menters. After this time, the fermented first and second pressings were mixed in a ratio of about 6 : 1, respectively: i. e., 8047 gallons of each of the first pressings, and 2,103 gallons of the second pressings. This mixture constituted the cider vinegar stock, being the starting material for the subsequent operations. The stock was aged for one month, and was divided into two parts. One part was cleared on beechwood shavings and the other part was filtered through paper pulp. The time occupied for clearing was about twelve days. The cleared and filtered stocks were then pumped into the generators, ten generators for each portion. The generators were of the rotating type. They consisted of a rectangular tank of about 480 gallons capacity, for holding the stock, and a cylindrical drum filled with beechwood shavings. The drum dipped into the cider to the depth of about one-third of its diameter and revolved very slowly through the stock in the tank about 1 1/2 turns in 24 hours. The heat of acetification caused sufficient circulation of air to furnish the oxygen required for the life of the acetic bacteria. In this mode of generating it is not necessary to prepare a feed, the stock being generated without the addition of vinegar. In Table I the average temperature of the generator room, the temperature in the generators, and the acidity for the cleared stock are given. Practically the same conditions prevailed for the filtered stock:

TABLE I—GENERATOR RECORD OF THE CLEARED STOCK

	End of	1st	2nd	3rd	4th week
TEMPERATURES.		58°	60°	64°	65° F.
In Generators.....	75°	84°	84°	68°	62° F.
ACIDITY AS ACETIC ACID PER 100 CC.		5.0	5.0	6.1	6.1

The time required for generating the cleared and filtered stocks was about 27 days. The vinegars were then pumped into tanks filled with beechwood shavings where they were allowed to clear for almost one month, when they were drawn off into storing tanks. After storing for about seven months, the vinegars were finally cleared on beechwood shavings.

From this description, it is evident that, for the manufacture of vinegars by the process described, the time required is about two years. Practically the entire process is conducted in closed vessels whereby evaporation is reduced to a minimum.

The loss through shrinkage for the two first pressing juices during fermentation and storage was about 3.5 per cent on the average. An attempt was made to determine the shrinkage during the whole range of manufacture, but no satisfactory result was obtained.

The pomace remaining after the second pressing juice was removed showed a slight amount of 0.4 per cent and an acidity (as realized) of 0.45 per cent. The sediments remaining after the fermented cider had been stored one year had a volume ratio and contained dead yeast cells, bacteria, and small amounts of mold and starch. In Table II analyses of the sediments of the two pressings are given.

TABLE II

COMPOSITION OF SEDIMENTS, GRAINS PER 100 CC.

	Grain	Starch	Alb.	Total	Non-sugar	Yeast
Lot 1.....	19.3	11.5	2.5	33.3	0.250	0.001
Lot 2.....	16.1	10.0	2.5	28.6	0.215	0.001
Average.....	17.7	10.8	2.5	30.8	0.233	0.001

Since the material from which the sediments were obtained was approximately 20,000 gallons in each case, it appears from Table II that about 4 mg. of phosphoric acid as P_2O_5 and 10 mg. of ash per 100 cc. juice were removed during fermentation and storing.

TABLE III—COMPOSITION OF VINEGARS FROM THE INDIVIDUAL GENERATORS

CLEARED STOCK				FILTERED STOCK			
SOLIDS G. per 100 cc.	ALCOHOL % by volume	ASH G. per 100 cc.	ACID as acetic G. per 100 cc.	SOLIDS G. per 100 cc.	ALCOHOL % by volume	ASH G. per 100 cc.	ACID as acetic G. per 100 cc.
1.19	0.08	0.32	6.48	1.21	0.18	0.32	6.60
1.26	0.08	0.31	6.45	1.36	0.08	0.31	6.60
1.21	0.28	0.32	6.60	1.44	0.70	0.32	6.48
1.23	0.30	0.31	6.69	1.51	0.25	0.32	6.43
1.32	0.26	0.32	6.69	1.37	0.08	0.30	6.72
1.32	0.63	0.32	6.30	1.37	0.33	0.31	6.42
1.22	0.41	0.32	6.60	1.38	0.35	0.31	6.43
1.28	0.19	0.32	6.69	1.43	...	0.32	6.72
1.27	0.04	0.32	6.69	1.38	0.08	0.33	6.57
Av. 1.24	0.25	0.32	6.57	1.39	0.17	0.32	6.54

In order to obtain an idea of the composition of the vinegars from the individual generators, a sample was taken from the spigot of each generator just before drawing off into the run-off tanks.

The average composition of the vinegars from the individual generators agrees fairly well with that of the composite vinegars from the run-off tanks. However, there is some variation among the vinegars from the generators of the same set.

From Table IV it will be seen that there is quite a difference in chemical composition between the "1st Pressing Juices" analyzed at Medina and at the

Bureau. This is especially true of the sucrose content and, in a less degree, of the non-sugar solids and fixed acids. The discrepancies are explained by the fact that the Bureau samples were sterilized for one hour at 180 to 190° F. and analyzed about four months after the Medina samples were analyzed. Analyses made at Medina and the Bureau of second pressings show the same discrepancies as noted above and are due to the same causes.

Table IV shows quite a difference in solids, non-sugar solids and fixed acids between the vinegar stock proper and the theoretical composition of the vinegar stock. This difference is due to changes during standing before analysis was made.

FIRST PRESSING JUICES—There is no material difference in chemical composition between the two juices. (See Table IV.)

SECOND PRESSING JUICE—Table V shows the difference in composition between the first and second pressing juices:

TABLE V—COMPOSITION OF 1ST AND 2ND PRESSINGS

PRESSING	1st	2nd
Alcohol, per cent by volume	0.07	2.25
Solids, grams per 100 cc.	14.98	8.74
Sugars as invert sugar before inversion, grams per 100 cc.	11.92	5.45
Sucrose, grams per 100 cc.	0.24	0.10
Non-sugar solids, grams per 100 cc.	3.19	3.19
Ash, grams per 100 cc.	0.33	0.37
Total P_2O_5 , mg. per 100 cc.	27.4	32.7
Fixed acid as malic, grams per 100 cc.	0.57	0.74
Volatile acid as acetic, grams per 100 cc.	0.02	0.26

It is reasonable to assume that the juice still remaining in the fresh pomace, after the removal of the first

TABLE IV—COMPOSITION OF JUICES, FINISHED VINEGARS AND INTERMEDIARY PRODUCTS: RESULTS IN GRAMS PER 100 CC. EXCEPT WHERE OTHERWISE NOTED

	Date Sampled	Sp. Gr. 15.6° C.	SUGARS as Invert Sugar										VALEIC ACIDS as Acetic	FIXED ACIDS as Malic (a)	ASH	ALKALINITY (b) of Water	TOTAL P ₂ O ₅ Mg. per 100 cc.	GLYCERIN	PANTOGENS	PACININS (N X 6.25)
			Alcohol, Per cent by volume	Solids by Weighing	Inversion before	after Inversion	Evaporation after	Sucrose by Copper	Non-sugar Solids	Volatile Reducing Substances as Invert Sugar	Acid as Malic as Acetic (a)	Volatiles as Acetic (a)								
JUICE, 1ST PRESSING:																				
from Press.....	10/22/13	1.0620	15.63	10.35	12.51	2.05	3.23	0.69	0.09	0.59	0.07	34.0	27.4	0.26	0.020	0.035
from Press.....	10/23/13	1.0595	15.23	9.90	11.81	1.81	3.52	0.70	0.07	0.62	0.07	34.0	27.4	0.26	0.020	0.035
composite, analyzed Medina.....	10/24/13	1.0585	0.05	14.83	9.39	11.81	2.30	3.14	0.67	0.02	0.65	0.02	34.0	27.4	0.26	0.020	0.035
composite, analyzed Bureau.....	10/24/13	1.0592	14.98	11.92	12.17	0.24	2.82	0.59	0.02	0.57	0.02	34.0	27.4	0.26	0.020	0.035
fermented.....	12/ 3/13	0.99870	7.58	1.78	0.06	1.72	0.80	0.43	0.32	33.2	26.5	0.25	0.040	0.046	0.046	
fermented, stored.....	11/23/14	0.9998207	4.0	1.58	0.03	1.55	None	0.83	0.47	0.31	33.3	26.5	0.26	0.028	0.046	0.046	
from Press.....	10/24/13	1.0581	14.67	9.01	12.38	3.20	2.46	0.63	0.01	0.63	0.01	34.0	27.4	0.26	0.020	0.035
from Press.....	10/28/13	1.0584	0.01	14.67	8.90	12.08	3.02	2.73	0.64	0.02	0.63	0.02	34.0	27.4	0.26	0.020	0.035
composite, analyzed Medina.....	10/28/13	1.0574	8.61	11.62	2.86	0.74	0.02	0.72	0.02	34.0	27.4	0.26	0.020	0.035
composite, analyzed Bureau.....	10/28/13	1.0579	0.29	14.83	11.53	12.14	0.58	2.72	0.64	0.02	0.62	33.2	26.5	0.25	0.040	0.046	0.046	
fermented.....	12/ 3/13	0.99849	7.59	1.66	0.05	1.61	0.82	0.48	0.29	33.2	26.5	0.26	0.040	0.046	0.046	
fermented, stored.....	11/23/14	0.99820	7.38	1.54	0.03	1.51	None	0.82	0.48	0.29	33.3	26.5	0.27	0.26	0.020	0.038	
JUICE, 2ND PRESSING:																				
from Press.....	10/27/13	1.0341	2.10	8.86	5.17	5.28	0.10	3.59	1.07	0.25	0.79	0.37	34.0	27.4	0.26	0.020	0.035
composite, analyzed Medina.....	10/27/13	1.0325	2.54	8.85	5.28	5.44	0.15	3.42	1.14	0.26	0.85	0.39	34.0	27.4	0.26	0.020	0.035
composite, analyzed Bureau.....	10/27/13	1.0334	2.25	8.74	5.45	5.56	0.10	3.19	1.03	0.26	0.74	0.37	37.0	32.7	0.24	0.350	0.350	
fermented.....	12/ 3/13	1.0058	2.58	7.27	0.20	0.22	0.00	2.52	1.47	1.01	0.35	0.36	35.0	31.6	0.24	0.350	0.350	
fermented, stored.....	11/23/14	1.0053	5.45	2.13	0.09	2.04	None	1.47	1.02	0.34	0.39	38.0	31.7	0.25	0.193	0.074	
Vinegar Stock: 1st and 2nd Pressings, mixed.....	12/ 7/14	0.99849	7.00	1.51	0.03	1.48	None	0.78	0.49	0.24	0.33	35.0	25.8	0.25	0.041	0.044	
Vinegar Stock:	1/ 5/15	0.99850	7.01	1.51	0.03	1.48	None	0.77	0.47	0.25	0.33	34.6	26.0	0.25	0.046	0.044	
cleared.....			5.75	1.30	0.03	1.27	None	1.31	1.02	0.18	0.30	31.6	21.4	0.24	0.048	0.023	
filtered.....	1/ 5/15	0.99860	7.01	1.51	0.03	1.48	None	0.77	0.48	0.24	0.33	34.6	26.0	0.25	0.046	0.044	
Vinegar:																				
cleared stock.....	1/31/15	1.0156	0.20	1.26	0.07	1.19	0.27(*)	6.52(†)	6.45	0.08	0.33	33.6	23.8	0.24	0.073	0.035	
filtered stock.....	1/30/15	1.0150	0.18	1.34	0.07	1.27	0.27(*)	6.45(†)	6.37	0.07	0.32	31.6	22.0	0.25	0.073	0.035	
Cleared Vinegar:																				
cleared stock.....	3/ 1/15	1.0152	0.20	1.30	0.06	1.24	0.30(*)	6.52(†)	6.45	0.08	0.33	33.6	23.3	0.24	0.071	0.035	
filtered stock.....	3/ 1/15	1.0159	0.17	1.43	0.08	1.35	0.28(*)	6.47(†)	6.41	0.07	0.32	33.2	23.6	0.25	0.076	0.035	
Vinegar, stored:																				
filtered stock.....	10/ 2/15	1.0159	0.04	1.32	0.45	0.12	1.20	0.33(b)	6.47(†)	6.44	0.03	0.30	34.4	23.7	0.24	0.083	0.033	
cleared stock.....	10/ 4/15	1.0155	0.06	1.20	0.45	0.11	1.09	0.34(b)	6.63(†)	6.58	0.06	0.31	34.6	22.1	0.25	0.076	0.033	

SUMMARY

Juice, analyzed Bureau: composite, 1st Pressing.....	10/24/13	1.0592	0.07	14.98	11.92	12.17	...	0.24	2.82	...	0.59	0.02	0.57	0.33	34.0	27.4
composite, analyzed Medina.....	10/27/13	1.0334	2.25	8.74	5.45	5.56	...	0.10	3.19	...	1.03	0.26	0.74	0.37	37.0	32.0
Juice, fermented, stored:																				
1st Pressing.....	11/23/14	0.99820	7.40	1.58	0.03	...	1.55	None	0.83	0.47	0.31	33.3	26.5	0.26	0.028	0.046	0.046	0.046
2nd Pressing.....	11/23/14	1.0053	5.45	2.13	0.09	...	2.04	None	1.47	1.02	0.34	0.39	38.0	31.7	0.25	0.193	0.074	0.074
Vinegar stock, proper.....	12/ 7/14	0.99849	7.00	1.51	0.03	...	1.48	None	0.78	0.49	0.24	0.32	33.0	25.8	0.25	0.041	0.044	0.044
Vinegar, filtered stock.....	1/30/15	1.0150	0.18	1.34	0.07	...	1.27	0.27	6.45(*)	6.37	0.07	0.32	31.6	22.0	0.25	0.073	0.035	0.035
Cleared Vinegar.....	3/ 1/15	1.0159	0.17	1.43	0.08	...	1.35	0.28	6.47(*)	6.41	0.07	0.32	33.2	23.6	0.25	0.076	0.035	0.035
Vinegar, stored: filtered stock.....	10/ 3/15	1.0159	0.04	1.32	0.45	...	0.12	...	1.20	0.33	6.47(*)	6.44	0.03	0.30	34.4	23.7	0.24	0.083	0.033	0.033

(*) Determined in distillate.

(†) Determined by difference.

(a) On all juices and stocks determined indirectly, in all vinegars determined directly.

(b) Cc. N/10 acid per 100 cc.

pressing, has practically the same composition as the first pressing juice proper and that the increase in the non-volatile constituents is due to a concentration of material through evaporation of water and alcohol during the storing of the pomace before pressing. This concentration was figured to be about 15 per cent. There is a marked loss of alcohol and acetic acid during storing of pomace—about 23 per cent of the total alcohol and acetic acid.

The analyses of the two juices and their fermented products are so much alike that it will suffice to confine the discussion to either. This is also true of the two final vinegars. In order to afford a more intelligent presentation of the material to be used, the data essential to the discussion are assembled in the summary of Table IV.

DISCUSSION OF RESULTS

In the following discussion of the analytical results and the changes which take place during the process, the influence which the second pressing juice has upon the composition of the vinegars has been disregarded. This was done for the sake of convenience.

ALCOHOL—The fermentation was very complete. The small amount of copper reducing substances (0.03 g. per 100 cc.) reported as invert sugar is probably due to pentosans. Theoretically the fermented and stored juice should contain 6.2 g. of alcohol per 100 cc. Of this amount, 6.2 g. are accounted for, there being no apparent loss of alcohol.

GLYCERIN remains fairly constant during the entire process.

NON-SUGAR SOLIDS—The total reduction of non-sugar solids during the process (from juice to finished vinegar) is about 58 per cent. Of this amount about four-fifths occurs during fermentation and storing of the cider and one-fifth during acetification and storing of vinegar. Of the total loss, about one-third is accounted for through the conversion of malic acid into lactic acid during fermentation, and oxidation of malic acid during acetification. The remaining two-thirds may be attributed to precipitation of pectins and gums chiefly.

VOLATILE REDUCING SUBSTANCES do not occur in the juice or in the fermented juice. They appear for the first time in the vinegar so that it may be said that they are the product of acetification. The volatile reducing substances increase during the ageing of the vinegar.

VOLATILE ACID AS ACETIC—Based on the alcohol and acetic acid content of the vinegar stock, the vinegar produced should theoretically have contained 7.7 g. of acetic acid for 100 cc., whereas only 6.4 g. of actual acetic acid are accounted for, or, during acetification, there is an apparent loss of 17 per cent acetic acid. During clarification and storing of the vinegar there is a loss of about 1 per cent acetic acid, so that the total loss of acetic acid during the entire process amounts to approximately 18 per cent of the total available acetic acid. This is a very good yield. In practice the loss of acetic acid during acetification is played at 25 per cent, it being figured that 1 per cent alcohol by volume will yield 6.8 g. of acetic acid. The short-

age in acetic acid is in part accounted for by the formation of esters (0.8 g. ethyl acetate = 1.1 g. acetic acid) so that the real loss of acetic acid during the entire process is a trifle less than 3 per cent. This calculation does not take the concentration during acetification into account as it was impossible to determine this shrinkage.

FIXED ACIDS—The loss of fixed acids will be discussed later.

ASH—The analysis does not show a loss of ash during fermentation and storing. That there is a slight loss during this period was discussed in connection with Table II. During the storing of the vinegar there is an appreciable loss, about 6 per cent.

TOTAL P₂O₅—Although there is only a slight decrease in P₂O₅ during alcoholic fermentation and storing (probably due to assimilation as food during the growth of the yeast), there is an appreciable loss of this ingredient during the acetification, about 12 per cent.

PENTOSANS, or their equivalent, increase about 100 per cent during the acetification and storing of the vinegar. The increase in the reducing substances reported as sugars is very likely due to these so-called pentosans.

TABLE VI—CHEMICAL COMPOSITION OF THE FINAL VINEGARS
Results in grams per 100 cc. except where otherwise noted

STOCK:	FILTERED	CLEAR
Specific gravity at 15.6° C./15.6° C.	1.0193	1.01531
Alcohol, per cent by volume	0.03 0.05	0.05 0.06
Glycerin	0.23 0.24	0.24 0.25
Solids	1.31 1.32	1.19 1.22
Sugars as invert Sugar:		
before inversion	0.45 0.45	0.45 0.45
after evaporation	0.12 0.12	0.11 0.11
Non-sugar solids	1.19	1.10
Volatile reducing substances	0.33	0.34
Polarization direct at 27° C., undiluted, 200 mm. tube	—1.0° V.	—0.9° V.
Total acid as acetic	6.47 6.46	6.62 6.64
Volatile acid as acetic	6.44	6.58
Fixed acids as malic	0.03 0.03	0.05 0.06
Volatile esters as ethyl acetate	0.80 0.79	0.85 0.91
Pentosans	0.083	0.076
Formic acid	0.0004	0.0004
Proteins (N × 6.25)	0.033 0.033	0.035 0.032
Lead precipitate	medium	medium
Alcohol precipitate	0.19 0.20	0.21 0.20
Polarization of alcohol precipitate	0	0
Color, Brewer's scale, 1 g. in cell	4.0	4.0
Per cent color removed (fuller's earth)	25	25
Ash	0.30 0.30	0.30 0.31
Alkalinity, cc. N/10 acid per 100 cc:		
soluble ash	34.4	34.6
insoluble ash	6.0	5.8
Total P ₂ O ₅ , mg. per 100 cc.	25.0 24.7	21.8 22.5
Soluble P ₂ O ₅ , mg. per 100 cc.	10.2 11.1	10.2 10.4
Insoluble P ₂ O ₅ , mg. per 100 cc.	12.8 12.8	11.6 11.9
Sulfur trioxide (SO ₃)	0.004	0.004
Chlorine (Cl)	0.001	0.001
Potassium oxide (K ₂ O)	0.156	0.162
Sodium oxide (Na ₂ O)	0.008	0.003
Magnesium oxide (MgO)	0.013	0.015
Calcium oxide (CaO)	0.014	0.010
Silica (SiO ₂)	0.0010	0.0008
Malic acid	0.032	0.035
Succinic acid	0.007	0.010
Lactic acid	0.28	0.18
Tannin and coloring matter	0.074	0.071
Acetates as acetic acid	0.043 0.043	0.035 0.034

Table VI presents the chemical compositions of the final vinegars. The organic acid constituents are interesting because they give an idea of the fermentative processes which take place during alcoholic fermentation and acetification. The decrease of fixed acids during fermentation and storing is due to the loss due to the breaking down of malic acid into lactic acid and carbonic acid. The lactic acid found in the final vinegar made from the filtered stock is 0.18 g. per 100 cc. Assuming that this lactic acid was formed from malic acid only, it follows that about 0.34 g. malic acid was destroyed before lactic acid. Unfortunately,

the malic acid was not determined in the juice. However, from the alkalinity of the water-soluble ash and the fixed acidity of a juice, it is possible to calculate the total malic acid approximately. To do this, it must be assumed that the fixed acidity in an apple juice is due principally to malic acid. Calculated in this manner, the two lots of juices originally contained approximately 0.46 and 0.45 g. combined, and 0.34 and 0.40 g. free malic acid, respectively, or about 0.83 g. total malic acid, average for the two juices. Accordingly, the fermented and stored cider contained approximately 0.49 g. of total malic acid. The final vinegar contained about 0.040 g. of total malic acid.

CONCLUSIONS

From the figures given above it is apparent that:

- (1) During fermentation a large part of the malic acid of the apple juice is destroyed to form lactic acid.
- (2) During acetification the remaining malic acid is almost entirely oxidized.
- (3) The fixed acid in the vinegar is chiefly lactic acid.

Other points of interest concerning the organic acid constituents are the presence of acetates in the vinegar and indications of minute amounts of formic acid, as shown by Fincke's method.

Concerning the ash constituents, it is noted that 75 per cent of the ash consists of potassium carbonate.

METHODS OF ANALYSIS

Wherever possible, the methods approved by the Association of Official Agricultural Chemists were employed.

MALIC ACID was determined by the method of C. von der Heide and H. Steiner.¹

SUCCINIC ACID was determined by the method of C. von der Heide and H. Steiner.²

LACTIC ACID was determined by the method of W. Moeslinger.³ On account of the presence of appreciable amounts of acetates in the vinegars, the method was modified to remove the acetates. This was accomplished by the addition of 2 cc. of concentrated hydrochloric acid after distilling off the volatile acids and evaporating to a small bulk, adding water and again evaporating, repeating this operation three times before proceeding with the determination of the lactic acid.

ACETATES—The acetates were determined in the residue from the volatile acid determination. To the residue in the distilling flask, 5 cc. of a 20 per cent phosphoric acid solution were added and the distillation continued until 15 cc. of distillate required not more than 3 drops of *N*/10 alkali for neutralization. The acidity of the distillate was determined by titration and calculated as acetic acid.

Recognition is due to Mr. E. H. Berry, of the Chicago Laboratory, for assistance rendered in the analyses of a number of the samples.

DEPARTMENT OF AGRICULTURE
BUREAU OF CHEMISTRY
CHICAGO, ILLINOIS

¹ *Z. Nahr. Genu. sm.*, **17** (1909), 307.

² *Ibid.*, **17** (1909), 291.

³ *Ibid.*, **4** (1901), 1123, Barium Chloride Method.

THE ACID CONTENT OF FRUITS

By W. D. BIGELOW AND P. B. DUNBAR

Received April 21, 1917

HISTORICAL

The statements found in the literature regarding the characteristic acids of the various fruits are most diverse. This is probably due in many cases to the inaccuracy of the methods used for their identification and determination, although it is quite possible that variations in the kind of acid present may sometimes occur in the same variety of fruit when grown under differing conditions. The method which has generally been used for the determination of both citric and malic acids in fruit juices depends on the precipitation of the acids in the form of calcium or barium salts and the separation of these by means of their differing solubilities in water and alcohol. The separations obtained in this way are usually far from sharp and may readily lead to errors.

The burden of evidence in the literature seems to indicate that tartaric acid is not an ingredient of fruit juices except, of course, of grape juice. W. Kaupitz¹ and R. Kayser² claim to have found tartaric acid in raspberries, but their statements are contradicted by numerous authors.³⁻⁷ Kunz⁸ reports citric acid as the acid of raspberries. Kunz and Adam⁵ state that strawberries, raspberries, elderberries, currants, cranberries and peaches contain citric acid but no malic nor tartaric. They find that citric acid is the predominating acid of huckleberries, gooseberries and apricots but state that malic acid is also present. Tartaric acid was not found by them in these fruits. Krzizan and Pahl⁹ and Krzizan⁶ found citric acid only in raspberries. Kayser² reports citric as the principal acid of raspberries, but found malic and tartaric acids also. Jørgensen³ found citric as the predominating acid of raspberries and huckleberries with a small amount of malic, and in raspberries traces also of succinic but no tartaric; elderberries were found to contain only citric. Hempel and Friedrich¹⁰ report the examination of four samples of raspberry juice. The first contained much citric acid and a not inconsiderable amount of malic. The second contained about equal amounts of both acids, while the other two contained much malic acid with traces only of citric. Keim¹¹ found both malic and citric acids in cherries. W. Nacken¹² found citric and malic acids in huckleberries. Mach and Portele¹³ in cranberries. According to Stolle¹⁴ cranberries (*Vaccinium oxycoccus*) contained only glyoxylic acid, while Aparin¹⁵ reports only citric acid.

From the work of the authors just quoted, Windisch and Schmidt,¹⁶ from whose paper these references are taken, draw the following conclusions: Citric and malic acids are the characteristic acids of fresh fruit juices, excluding grape juice. Succinic acid is found in small quantities in fresh fruit, especially in the unripe condition, but tartaric acid does not occur in other fruits than grapes. In berries, in general, citric acid predominates and most berries contain, in addition, malic acid in very small quantities. Of the

* Numbers refer to bibliography on page 767.

stone fruits, in cherries and plums malic predominates, if it is not present exclusively. The question of the acids of peaches and apricots must be left open, the widespread assumption that these fruits contain malic acid as the predominating acid being shaken by the researches of Kunz and Adam. In seed fruit, such as the apple and the pear, malic acid predominates or is almost exclusively present except for tannic acid. The total acidity of berries should, therefore, be expressed as anhydrous citric acid and of cherries and seed fruits as malic acid.

In addition to the statements summarized above by Windisch and Schmidt, a number of other articles on the fruit acids have appeared which are of interest principally because of the diversity of the statements made. Truchon¹ and Martin-Claude¹⁷ report tartaric acid in strawberries, black currants, quinces, apricots, unripe cherries and in traces also in green gage plums. No tartaric acid was found in white currants, pears and apples. They report citric acid in apricots and in faint traces in unripe cherries although it was not found in ripe cherries. Chauvin, Joulin and Canu¹⁸ state that the acidity of black currants, cherries, quinces, strawberries, raspberries and apricots is due to tartaric acid, while that of red and white currants,

Reineclaude, Mirabelle and Orleans plums, pears and apples is due to citric. Muttelet,¹⁹ on the contrary, reports the predominating acid of cherries as malic with no citric and only undeterminable traces of tartaric. He states that strawberries, raspberries and red and black currants contain citric acid, with traces only of tartaric and no malic. Warcollier²⁰ found no tartaric acid in either apples or pears. Paris²¹ reports the presence of citric acid and a small amount of malic acid in strawberries. He finds no oxalic, tartaric, salicylic or benzoic acids.

Jørgensen³ reports malic as the principal acid of cherries. He found no tartaric acid and only found traces of succinic and citric. Roux and Bonis²² state that malic acid predominates in cherries but report also citric and tartaric acids.

Scurti and Plato²³ report the acidity of oranges as due to citric and malic acids. The same acids were found by Borntrager and Paris²⁴ in pomegranates.

In addition to the foregoing, the presence in many fruits of salicylic, benzoic and formic acids has been reported, but with the exception of benzoic acid in cranberries, these have never been reported except in exceedingly small amounts and they have no place in the present consideration. For more convenient refer-

TABLE I. THE ACIDS OF FRUITS: RESULTS REPORTED BY PREVIOUS WRITERS

FRUIT	AUTHOR	DATE	REFERENCE	ACIDS REPORTED
Apple	Truchon & Martin-Claude	1901	<i>Ann. chim. anal.</i> , 6 , 88	No tartaric
Apple	Chauvin, Joulin & Canu	1908	<i>Mon. sci.</i> , 69 , 449	Citric
Apple	Warcollier	1901	<i>Ann. fals.</i> , 4 , 389	No tartaric
Apricot	Truchon & Martin-Claude	1901	<i>Ann. chim. anal.</i> , 6 , 85	Tartaric and citric
Apricot	Kunz & Adam	1906	<i>Z. Nahr. Genussm.</i> , 12 , 670	Citric predominates; some malic, no tartaric
Apricot	Chauvin, Joulin & Canu	1908	<i>Mon. sci.</i> , 69 , 449	Tartaric
Cherry	Keim	1891	<i>Z. anal. Chem.</i> , 30 , 401	Malic and citric
Cherry	Truchon & Martin-Claude	1901	<i>Ann. chim. anal.</i> , 6 , 85	Tartaric and traces of citric in unripe cherries
Cherry	Kunz & Adam	1906	<i>Z. Nahr. Genussm.</i> , 12 , 670	No citric in ripe cherries
Cherry	Jørgensen	1907	<i>Z. Nahr. Genussm.</i> , 13 , 241	Malic
Cherry	Chauvin, Joulin & Canu	1908	<i>Mon. sci.</i> , 69 , 449	Malic; no tartaric; traces only succinic and citric
Cherry	Muttelet	1909	<i>Ann. fals.</i> , 2 , 383	Tartaric
Cherry	Roux & Bonis	1909	<i>Ann. fals.</i> , 2 , 150	Malic; no citric; mere traces tartaric
Cranberry				Malic predominates; citric and tartaric present
(Small American)	Scheele	Crell's <i>Ann.</i> , 10	Citric
(Vaccinium)				
(Moosbeere)				
(Moosbeere)	Stolle	1900	<i>Z. Ver. Zuckerind. N. F.</i> , 37 , 609	Gluconic
(Moosbeere)		1904	<i>Z. Nahr. Genussm.</i> , 8 , 83	Citric
(Mountain Cranberry)	Mach & Portele	1890	<i>Landw. Vers.-Sta.</i> , 38 , 69	Citric and malic
(<i>V. vitis-idaea</i>)				
(Freiselbeere)	Kunz & Adam	1906	<i>Z. Nahr. Genussm.</i> , 12 , 670	Citric, no malic nor tartaric
Current				
(Black)	Truchon & Martin-Claude	1901	<i>Ann. chim. anal.</i> , 6 , 85	Tartaric
(White)	Truchon & Martin-Claude	1901	<i>Ann. chim. anal.</i> , 6 , 85	No tartaric
	Kunz & Adam	1906	<i>Z. Nahr. Genussm.</i> , 12 , 670	Citric, no malic nor tartaric
(Black)	Chauvin, Joulin & Canu	1908	<i>Mon. sci.</i> , 69 , 449	Tartaric
(Red and White)	Chauvin, Joulin & Canu	1908	<i>Mon. sci.</i> , 69 , 449	Citric
(Red and Black)	Muttelet	1909	<i>Ann. fals.</i> , 2 , 383	Citric, traces only tartaric; no malic
Elderberry	Kunz & Adam	1906	<i>Z. Nahr. Genussm.</i> , 12 , 670	Citric, no citric
Gooseberry	Kunz & Adam	1906	<i>Z. Nahr. Genussm.</i> , 12 , 670	Citric predominates; some malic; no tartaric
Huckleberry	Sackey	1895	<i>Forschungen über Lebensmittel</i> , 2 , 480	Citric and malic
Huckleberry	Kunz & Adam	1906	<i>Z. Nahr. Genussm.</i> , 12 , 670	Citric predominates; small amount malic, no tartaric
Huckleberry	Jørgensen	1907	<i>Z. Nahr. Genussm.</i> , 13 , 241	Citric, small amount malic
Orange	Scurti & Plato	1909	<i>Nähr. anal. u. vers. sta.</i> , 8 , 41, 450	Citric and malic
Peach	Kunz & Adam	1906	<i>Z. Nahr. Genussm.</i> , 12 , 670	Citric, no malic nor tartaric
Pear	Truchon & Martin-Claude	1901	<i>Ann. chim. anal.</i> , 6 , 85	No tartaric
Pear	Chauvin, Joulin & Canu	1908	<i>Mon. sci.</i> , 69 , 449	Citric
Pear	Warcollier	1901	<i>Ann. fals.</i> , 4 , 388	No tartaric
Pineapple	Kayser	1909	<i>Z. offic. Chem.</i> , 10 , 18	Citric, also malic and tartaric
Plum				
(Green Gage)	Truchon & Martin-Claude	1901	<i>Ann. chim. anal.</i> , 6 , 88	Traces tartaric
(Green Gage)	Chauvin, Joulin & Canu	1908	<i>Mon. sci.</i> , 69 , 449	Citric
Pomegranate	Borntrager & Paris	1898	<i>Z. Nahr. Genussm.</i> , 158	Various predominates, some citric, some malic
Quince	Truchon & Martin-Claude	1901	<i>Ann. chim. anal.</i> , 6 , 84	Tartaric
Raspberry	W. Kayser	1909	<i>Pharm. Ztg.</i> , 41 , 240	Tartaric
Raspberry	B. Kayser	1906	<i>Z. Nahr. Genussm.</i> , 12 , 670	Citric, no malic nor tartaric
Raspberry	Kunz & Adam	1906	<i>Z. Nahr. Genussm.</i> , 12 , 670	Citric, no malic nor tartaric
Raspberry	Kreizen & Pfaff	1906	<i>Z. Nahr. Genussm.</i> , 11 , 90	Citric, no malic nor tartaric
Raspberry	R. Kretz	1906	<i>Z. Nahr. Genussm.</i> , 12 , 31	Citric, no malic nor tartaric
Raspberry	B. Kayser	1906	<i>Pharm. Ztg.</i> , 40 , 118	Citric, no malic nor tartaric
Raspberry	Hempel & Friedrich	1906	<i>Z. Nahr. Genussm.</i> , 12 , 3	Citric, no malic nor tartaric
Raspberry				
Raspberry	G. Jørgensen	1907	<i>Z. Nahr. Genussm.</i> , 13 , 241	Citric and malic
Raspberry	Chauvin, Joulin & Canu	1908	<i>Mon. sci.</i> , 69 , 449	Citric
Raspberry	Muttelet	1909	<i>Ann. fals.</i> , 2 , 180	Citric
Strawberry	Truchon & Martin-Claude	1901	<i>Ann. chim. anal.</i> , 6 , 85	Citric
Strawberry	Paris	1902	<i>J. Lom. nat.</i> , 26 , 35	Citric
Strawberry	Kunz & Adam	1906	<i>Z. Nahr. Genussm.</i> , 12 , 670	Citric, no malic nor tartaric
Strawberry	Chauvin, Joulin & Canu	1908	<i>Mon. sci.</i> , 69 , 449	Citric
Strawberry	Muttelet	1909	<i>Ann. fals.</i> , 2 , 383	Citric

ence, the statements found in the literature regarding the presence of malic, citric and tartaric acids in fruits are presented in tabular form in Table I. Table II contains a summary of what appear to be the most

TABLE II—SUMMARY OF MOST RELIABLE STATEMENTS BY PREVIOUS WRITERS ON THE ACIDS OF FRUITS

FRUIT	PREDOMINATING	REMARKS
Cherries	Malic acid	Other acids, if present, only in traces
Cranberries	Citric acid	Benzoic acid present to the extent of 0.04 to 0.05 per cent; other acids, if present, only in traces
Currents	Citric acid	Other acids, if present, only in traces
Huckleberries	Citric acid	Some malic acid
Raspberries	Citric acid	Other acids, if present, only in traces
Strawberries	Citric acid	Other acids, if present, only in traces

reliable statements by previous writers regarding the acid contents of the more common fruits.

EXPERIMENTAL WORK

Methods for the quantitative determination of malic acid were suggested by Yoder²⁵ in 1911 and later by Dunbar and Bacon.²⁶ These methods depend on the increase in the optical rotation of solutions of malic acid when treated under definite conditions with uranyl acetate. Citric acid when present does not interfere with the determination but special treatment is required in the presence of tartaric acid for the reason that the optical rotation of the latter acid is also increased by treatment with uranyl acetate. The most favorable limits for the determination of malic acid by the optical method are between 0.2 per cent and 2.5 per cent of malic acid. The error within these limits seldom amounts to more than 5 per cent of the malic acid present when solutions are clear enough to be polarized without difficulty.

In the case of dark-colored solutions, however, much difficulty is sometimes encountered in making the polarizations and it is then necessary to resort to the use of bromine as a bleaching agent. When bromine is used the error may be somewhat higher than that stated above. The polariscopic method is entirely applicable to the determination of malic acid in fruit juices which are not highly colored and it is also applicable, but with less accuracy, to colored juices in which the use of bromine as a bleaching agent is necessary. In the latter case the error is always in the same direction, the amount of malic acid found being less than that actually present.

The determination of the malic acid content of several varieties of apples and other fruits generally regarded as containing malic acid only, showed in many cases a remarkably close agreement between the malic acid determined by the polariscopic method and that calculated from the total acidity found by titration with standard alkali. This seemed to indicate that, contrary to the usual idea, malic acid exists in these fruits almost entirely in the uncombined condition. In view of these results it seemed worth while to determine the amount of malic acid present in all the common fruits.

A determination of the citric acid content of these fruits was also considered desirable. A method for this determination has been described by Pratt.²⁷ It depends on the precipitation of the acid as barium citrate, its conversion to acetone by oxidation with potassium permanganate in acid solution, and the distillation and collection of the acetone in Denigès'

reagent from which it may be precipitated in weighable form by boiling. This method at first gave promise of considerable accuracy and it was consequently used for the determination of citric acid in most of the fruits examined.

A more extended study of the method led to the conclusion, however, that it cannot be relied upon. The most favorable limits for the determination are given as from 0.05 to 0.15 g. of citric acid. A series of 15 determinations was made using water solutions of pure citric acid containing from 0.06 to 0.15 g. of the acid and distilling directly without previous precipitation as barium citrate. The percentage recovered in this series varied from 72.2 per cent to 101.9 per cent, averaging 84.3 per cent. Two other solutions, containing, respectively, 0.4 and 0.2 g. of citric acid, were treated exactly as described in the method including precipitation as barium citrate. The percentages of citric acid recovered were, respectively, 44 per cent and 166 per cent. It was found also that the presence of both malic and tartaric acids interfered very seriously with the determination as will be evident from the figures given in Table III. Even

TABLE III—SHOWING INFLUENCE OF MALIC AND TARTARIC ACIDS ON THE DETERMINATION OF CITRIC ACID BY THE PRATT METHOD

GRAMS CITRIC	ACID PRESENT	CITRIC ACID GRAMS FOUND	PER CENT RECOVERY	TREATMENT (see below)
0.25	0.375	0.282	113	A
0.30	0.60	0.484	161	A
0.20	0.60	0.294	147	A
0.30	0.30	0.307	102	A
0.075	0.50	0.090	120	B

A—Acids precipitated as barium salts.

B—Solution distilled direct without precipitation.

wider variations were obtained in duplicate determinations of citric acid made on fruits. These figures seem to confirm the statement of Jørgensen³ that the quantitative determination of citric acid by means of its oxidation with potassium permanganate in acid solution is impracticable. It may be said, however, that a paper has recently been published by J. J. Willaman describing a "Modification of the Pratt Method for the Determination of Citric Acid."²⁸ According to the author, this modified method if followed rigidly will give much more satisfactory results than the original. The writers have not as yet had an opportunity to test the modified method.

In view of the unsatisfactory nature of the results obtained with known solutions no reliance has been placed on the values for citric acid obtained by the Pratt method in the fruits examined, but qualitative conclusions have been drawn as to the presence or absence of citric acid. Where no precipitate or only a very slight one was obtained, it was concluded that no citric acid was present, while a large precipitate was taken to indicate the presence of the acid.

Since the completion of the work reported in this paper, a modification of Stahre's²⁹ pentabromacetone method for citric acid has been published by Kunz.³⁰ This method is applicable in the presence of malic and tartaric acids and has been applied to the determination of citric acid in fruit juices and similar products by Dunbar and Lepper³¹ with very satisfactory results.

Most of the fruits examined were obtained through the cooperation of the Bureau of Plant Industry of

the U. S. Department of Agriculture which also classified the fruits. Thanks are especially due to Messrs. A. V. Stubenrauch and C. P. Close of that Bureau for their assistance in this work. In some cases, where only one or two samples of a particular fruit were examined, they were purchased in the local market without classification.

The method followed in preparing the fruits for analysis was approximately the same in all cases. The flesh only of stone and seed fruits was squeezed by hand through a cloth bag to obtain the juice. In the case of berries, the whole fruit was treated in this way. Cherries were squeezed without pitting, but the stone was not crushed. Analyses were made immediately on the freshly expressed juice.

The total acidity of the juice was determined usually on 5 g. samples by titration with *N/10* sodium hydroxide, using phenolphthalein or a solution of azolitmin on a spot plate as the indicator according to the color of the juice under examination. Malic acid was determined by the method given below. This is the method originally described by Dunbar and Bacon²⁶ modified by the use of alcohol for the precipitation of pectins, as described by Pratt.³²

Place a weighed amount of the fruit juice, generally 100 g., in a 500 cc. beaker. With vigorous stirring add about two or three times the volume of 95 per cent alcohol. This throws out the pectins usually in such form that after standing a few minutes they may be gathered into a coherent mass. Decant the liquid through a filter and wash the precipitate twice with 95 per cent alcohol. Evaporate the combined filtrates in a current of air on the water bath to about 75 cc. After cooling, make up the solution to 100 cc. in a measuring flask, using 10 to 15 cc. of 95 per cent alcohol and distilled water. The temperature when the volume is finally made up to the mark should be close to that at which the polariscope readings are to be taken.

Treat about 25 cc. of the solution so obtained with powdered

uranyl acetate, adding enough of the salt so that a small amount remains undissolved after 2 hours. Two and one-half grams of uranyl acetate will usually be sufficient, except in the presence of large amounts of malic acid. In case all the uranium salt dissolves more should be added. Allow the mixture to stand for three hours, shaking frequently. Filter through a folded filter until clear and polarize if possible in a 200 mm. tube. If the solution is too dark to read in a 200 mm. tube, a 100 or 50 mm. tube may be used. It is desirable, however, to use the longest tube possible in order to reduce the error of the determination.

Treat the remainder of the original solution with powdered normal lead acetate until no further precipitation results. Cool in an ice bath and filter through a folded filter until clear. Warm the filtrate to room temperature and add a small crystal of lead acetate to determine whether the precipitation is complete. If no further precipitate results, remove the excess of lead completely with anhydrous sodium sulfate, filter until clear, and polarize. Solutions which are sufficiently clear and contain less than 10 per cent of sugar may be polarized directly without treatment with lead acetate.

Polarize at room temperature with white light, taking care that all solutions are polarized at the same temperature. Make at least six readings in each case and take an average of these. In this work a standard, Lippich type, triple field saccharimeter was used, the light being furnished by an electric bulb placed behind a ground-glass plate. Calculate all readings to the basis of a 200 mm. tube. Multiply the algebraic difference between the two readings by 0.036. The product will equal the weight

of malic acid $\left\{ \begin{array}{l} \text{CH}_2\text{COOH} \\ | \\ \text{CHOHCOOH} \end{array} \right\}$ in grams per 100 cc. of the solution as polarized.

In the case of clear, light-colored fruit juices which are easily polarized, the preliminary treatment with alcohol may be omitted. Polarize one portion of the sample directly without any treatment whatever. Treat another portion with uranyl acetate and then polarize. Calculate the weight of malic acid present from the difference between the readings as described above.

TABLE IV—ACID CONTENT OF APPLES (RESULTS IN PERCENTAGES)

Lab. No.	DESCRIPTION	Source of Fruit	Total Acid (a)	Malic Acid (b)	Analyst
P 21870	Baldwins	(1)	0.57	0.60	Dunbar
P 22518	Maiden Blush green	(1)	1.68	1.68	Dunbar
P 22519	Early Ripe green	(1)	1.09	1.02	Dunbar
P 22520	Gravenstein green	(1)	1.27	1.21	Dunbar
P 22521	Kimball (picked 7-8-11)	(1)	0.80	0.65	Dunbar
P 22543	Kimball (picked 2-25-11)	(1)	0.72	0.75	Dunbar
P 22517	Sweet Bough green	(1)	0.21	0.11	Dunbar
P 22542	Sweet Bough (picking ripe)	(1)	0.13	0.08	Dunbar
P 22702	Unclassified (sour)	(1)	0.62	0.52	Dunbar
P 22779	Tompkins King	(2)	0.41	0.45	Pratt
P 22780	Tolman	(2)	0.16	0.22	Pratt
P 22781	Ronette de Regmard	(2)	0.61	0.58	Pratt
P 22782	Principe de Tunis	(2)	0.28	0.36	Johnson
P 24083	Principe de Tunis	(3)	0.31	0.45*	Johnson
P 24084	Excelstar	(3)	1.11	1.22*	Johnson
P 22709	Unclassified (Crabs)	(3)	0.27	0.61	Dunbar
P 24080	Unclassified (sour)	(3)	0.78	0.73	Treuthardt
P 24085	Piromore (Crabs)	(3)	1.11	1.34*	Johnson
P 24090	Norfolk Beauty Crab	(3)	1.81	1.49*	Johnson
P 22709	Sweet Crab	(3)	0.56	0.57	Dunbar
P 22709	made	(3)	0.54	0.52	Dunbar
P 22709	made	(3)	0.49	0.43	Dunbar
P 24050	Bureau	(3)	0.49	0.50	Johnson

(1) Maryland Experiment Station, College Park, Md. (2) Experiment Station, Cornell U. S. V. Experiment Farm, Arlington, Va.

(a) By titration as malic acid. (b) By uranyl acetate method.

TABLE VI—ACID CONTENT OF CHERRIES (RESULTS IN PERCENTAGES)
Analysts: F. P. Fitzgerald and P. B. Dunbar

Lab. No.	VARIETY	Total Acid (a)	Malic Acid (b)	Citric Acid (c)	Acid other than Malic (d)
P 24054	North Star	2.18	0.41	Present	0.10
P 24054	Cherries	2.07	none	Present	2.07
P 24055	White Transparent	1.98	none	Present	2.07
P 24056	Prince Albert	3.37	0.11	Present	2.69
P 24057	Louise Market	2.38	0.06	Present	2.32

(a) By titration as citric acid. (b) By uranyl acetate method.

(c) Qualitative test. (d) Expressed as citric acid.

TABLE V—ACID CONTENT OF CHERRIES (RESULTS IN PERCENTAGES)

Lab. No.	VARIETY	Total Acid (a)	Malic Acid (b)	Citric Acid (c)	Analyst
P 22504	California Napoleon (Royal Anne)	1.01	0.78	ad.	Dunbar
P 22505	Black Republican	0.97	0.76	ad.	Dunbar
P 22508	Black Republican	0.87	0.62	ad.	Clark
P 22509	Unclassified	2.01	1.09	ad.	Johnson
P 22981	Unclassified	1.32	1.21	ad.	Johnson
P 22982	Unclassified	1.44	1.30	ad.	Johnson
P 24033	Unclassified (Red-sweet)	1.00	1.08	Absent	Uncl.
P 24035	California Wax	0.56	0.46	Absent	Uncl.
P 24036	Unclassified (Red-sour)	1.54	1.37	Absent	Uncl.
P 24037	Red Heart (?)	0.85	0.87	Absent	Uncl.
P 24038	Unclassified (Cal. Red)	0.80	0.88	Absent	Uncl.
P 24039	Carleton	0.86	0.84	Absent	Uncl.
P 24040	Montmorency N. Y.	1.31	1.38	Absent	Uncl.
P 24041	Schmidt (N. Y.)	0.63	0.61	Absent	Uncl.
P 24042	Windsor	0.82	0.85	Absent	Uncl.
P 24043	Montmorency	0.76	0.76	Absent	Uncl.
P 24045	Ace	0.56	0.73	Absent	Uncl.
P 24046	Max Duke	1.10	0.99	Absent	Uncl.
P 24046	Early Richmond	1.16	1.08	Absent	Uncl.
P 24048	Unclassified (Mazzard wild)	1.03	1.00	Absent	Uncl.

(a) By titration as malic acid. (b) By uranyl acetate method.

(c) Qualitative test. (d) Expressed as citric acid.

TABLE VII—ACID CONTENT OF CHERRIES (RESULTS IN PERCENTAGES)

Lab. No.	VARIETY	Total Acid (a)	Malic Acid (b)	Citric Acid (c)	Acid other than Malic (d)
P 24044	Unclassified	0.69	0.69	Present	0.00
P 24048	Unclassified	1.72	0.69	Present	0.00
P 24052	Unclassified	0.69	0.69	Present	0.00
P 24050	Hempstead	1.24	1.24	Present	1.44
P 24051	Lady Phipps	0.83	0.83	Present	0.44
P 24053	Unclassified	0.69	0.69	Present	0.00
P 24059	Unclassified	0.69	0.69	Present	0.00

(a) By titration as citric acid. (b) By uranyl acetate method.

(c) Qualitative test. (d) Expressed as citric acid.

TABLE VIII—ACID CONTENT OF PEARS (RESULTS IN PERCENTAGES)

Lab. No.	VARIETY	SOURCE	Total Acid by Titration (as Malic)	Malic Acid by Uranyl Acetate Method	Citric Acid Qualitative Test	Acids other than Malic (expressed as Citric)	ANALYST
F 22733	Kieffer	Anacostia, D. C.	0.50	0.14	Present	0.34	D. S. Pratt
F 22734	Kieffer	Sandy Springs, Va.	0.48	0.09	Present	0.37	D. S. Pratt
F 22751	Kieffer	New Jersey	0.55	0.10	Present	0.43	J. M. Johnson
F 22754	Kieffer	N. Y. State Expt. Sta.	0.80	0.14	Present	0.34	J. M. Johnson
F 22776	Kieffer	N. Y. State Expt. Sta.	0.37	0.03	Present	0.07	J. M. Johnson
F 22768	Le Conte	N. Y. State Expt. Sta.	0.48	0.04	Present	0.42	J. M. Johnson
F 22773	Idaho	N. Y. State Expt. Sta.	0.21	0.00	Present	0.20	J. M. Johnson
F 22738	Bartlett	New York	0.30	0.03	Present	0.26	D. S. Pratt
F 22741	Bartlett	California	0.35	0.02	Present	0.32	D. S. Pratt
F 22748	Bartlett	California	0.34	0.11	Present	0.22	D. S. Pratt
F 22750	Bartlett	New York	0.26	0.00	Present	0.25	D. S. Pratt
F 22737	Bartlett	District of Columbia	0.36	0.46	Absent	D. S. Pratt
F 22731	Angouleme	Vienna, Va.	0.19	0.27	Absent	D. S. Pratt
F 22732	Angouleme	New York	0.15	0.26	Absent	D. S. Pratt
F 22755	Angouleme	New York	0.21	0.33	Absent	J. M. Johnson
F 22735	Seckel	New York	0.18	0.24	Absent	D. S. Pratt
F 22736	Seckel	Alexandria, Va.	0.20	0.21	Absent	D. S. Pratt
F 22749	Seckel	New York	0.19	0.30	Absent	J. M. Johnson
F 22772	Seckel	N. Y. State Expt. Sta.	0.06	0.09	Absent	J. M. Johnson
F 22761	Seckel	California	0.23	0.26	Absent	J. M. Johnson
F 22761	Winter Nelis	Monterey, Cal.	0.17	0.25	Absent	J. M. Johnson
F 23001	Winter Nelis	N. Y. State Expt. Sta.	0.11	0.21	Absent	J. M. Johnson
F 22774	Winter Nelis	N. Y. State Expt. Sta.	0.25	0.29	Absent	J. M. Johnson
F 22762	Clairegrou	California	0.10	0.09	Absent	J. M. Johnson
F 22785	Clairegrou	Monterey, Cal.	0.08	0.10	Absent	J. M. Johnson
F 22767	Clairegrou	N. Y. State Expt. Sta.	0.10	0.14	Absent	J. M. Johnson
F 22763	Anjou	Santa Clara, Cal.	0.21	0.19	Absent	J. M. Johnson
F 22775	Anjou	N. Y. State Expt. Sta.	0.27	0.34	Absent	J. M. Johnson
F 22777	Easter	N. Y. State Expt. Sta.	0.19	0.19	Absent	J. M. Johnson
F 22786	Easter	Monterey, Cal.	0.22	0.34	Absent	J. M. Johnson
F 23000	Easter	Boston, Mass.	0.14	0.22	Absent	J. M. Johnson
F 22744	Beurre Hardy	Boston, Mass.	0.16	0.14	Absent	D. S. Pratt
F 22908	Pound	0.17	0.19	Absent	J. M. Johnson
F 23002	Pound	0.14	0.21	Absent	J. M. Johnson
F 22740	Like Gray Doyenne	Near Dist. of Col.	0.17	0.18	Absent	D. S. Pratt
F 22742	Like Gray Doyenne	California	0.23	0.35	Absent	D. S. Pratt
F 22745	Like White Doyenne	New York	0.19	0.16	Absent	D. S. Pratt
F 22739	Probably Sheldon	California	0.19	0.21	Absent	D. S. Pratt
F 22743	Sheldon	Near Dist. of Col.	0.17	0.19	Absent	D. S. Pratt
F 22751	Florinda	Santa Clara, Cal.	0.14	0.11	Absent	D. S. Pratt
F 22752	Comice	Santa Clara, Cal.	0.16	0.24	Absent	D. S. Pratt
F 22764	Bosc	Santa Clara, Cal.	0.23	0.18	Absent	J. M. Johnson
F 22766	Jones	N. Y. State Expt. Sta.	0.25	0.33	Absent	J. M. Johnson
F 22769	Lamarline	N. Y. State Expt. Sta.	0.11	0.03	Absent	J. M. Johnson
F 22770	Fitzwater	N. Y. State Expt. Sta.	0.26	0.26	Absent	J. M. Johnson
F 22771	Reeder	N. Y. State Expt. Sta.	0.21	0.27	Absent	J. M. Johnson
F 22999	Glout-Morceau	0.10	0.19	Absent	J. M. Johnson

TABLE IX—ACID CONTENT OF PLUMS (RESULTS IN PERCENTAGES)

Lab. No.	VARIETY	SOURCE	Total Acid (a)	Malic Acid (b)	Analyst
F 4074	Burbank	Local market	0.69	0.65	F. F. Fitzgerald
F 24086	Abundance	{ Expt. Farm, { { Arlington, Va. }	1.33	1.24	J. M. Johnson
F 24087	Abundance	{ Expt. Farm, { { Arlington, Va. }	1.12	1.04	J. M. Johnson
UNCLASSIFIED:					
F 22573	(Large red)	Local market	0.55	0.36	D. S. Pratt
F 22587	(Japanese red)	Local market	1.70	1.60	D. S. Pratt
	(Purple)	Local market	2.15	2.39**	D. S. Pratt
	(Red)	Local market	1.70	1.60**	D. S. Pratt
	(Large white)	Local market	1.41	1.51	D. S. Pratt
	(Small red)	Local market	0.79	0.88	D. S. Pratt

* Test for tartaric acid, negative. ** Test for tartaric and citric acids, negative.

(a) By titration (as malic). (b) By uranyl acetate method.

TABLE X—ACID CONTENT OF MISCELLANEOUS FRUITS (RESULTS IN PERCENTAGES)

Lab. No.	FRUIT	Total Malic Acid (a)	Citric Acid (b)	Acids other than Malic (c)	Analyst
F 22791	Banana	0.26(a)	0.24	Pratt
F 24098	Cantaloupe	0.18(b)	none	Johnson
F 24099	Cranberries	2.80(a)	0.56	Present	1.14 Pratt
F 24103	Peaches	2.65(a)	0.71	Present	1.85 Pratt
		0.51(a)	0.49	{ Probably } { absent }	Johnson
F 22792	Persimmon	0.09(a)	0.09	Johnson
F 22756	Pomegranate	4.52(b)	none	Present	4.52 Pratt
	Quince, unripe	0.90(a)	1.00	Absent	Pratt
F 24028	Raspberries, red	1.51(b)	0.03	Present	1.48 Johnson
F 24097	Watermelon	0.05(a)	0.20	Absent	Johnson

(a) As malic acid. (b) As citric acid.
(c) By uranyl acetate method. (d) Qualitative test.

The Prout method for citric acid previously described was also applied in most cases, but, as already stated, only qualitative conclusions were drawn therefrom. No attempts were made to determine volatile acids, salicylic, formic or benzoic acids, as these are well known to be present only in minute quantities, except in the case of cranberries, which may contain benzoic acids in amounts up to 0.05 per cent.³³

The results obtained are presented in Tables IV to X, inclusive. These represent the work of the following analysts: R. F. Bacon, D. S. Pratt, C. W. Clark, J. M. Johnson, F. F. Fitzgerald, E. L. P. Treuthardt and P. B. Dunbar. As will be seen from a study of the tables, a very close agreement was found in many cases between total acid as malic determined by titration and total malic acid found by the optical method. In some cases, when such agreement was discovered, no examination for citric acid was made.

This agreement is especially noticeable in apples and cherries. It seems evident that in these fruits, at least in most cases, the acidity is due to malic acid

alone, and that this acid is present only in the free condition. The old method of reporting combined malic acid in fruit as calculated from the alkalinity of the ash appears, therefore, to be based upon an incorrect assumption. It is interesting to note also that the acidity of unripe apples, as well as of ripe apples, is due entirely to malic acid and that no combined malic acid is present. This will be seen in Table IV. The Maiden Blush, Early Ripe, Gravenstein and Kinnard apples, all of which were picked green, show a very close agreement between total acidity expressed as malic and total malic acid. This is not true of the Sweet Bough apple, but the low acidity of this apple makes it probable that the percentage error in both determinations is rather high.

The results obtained in the examination of pears, which are shown in Table VIII, are most interesting. It will be seen that with few exceptions the varieties which are named first in the table, Kieffer, Le Conte, Idaho and Bartlett, contain little or no malic acid, while citric acid is shown to be present. One sample of

Bartlett pears, F. 22737, appeared to contain only malic acid, while one sample of Kieffers, F. 22776, contained a predominating amount of malic. No explanation is offered of these exceptions. All the other varieties of pears examined contained no citric acid, the acidity being due apparently in most cases to malic acid alone. Here again, the close agreement between total acidity as malic and total malic acid is very apparent in many varieties.

The acidity of plums, like apples and cherries, appears to be due entirely to malic acid which is probably present for the most part in the free state. Currants always contain citric acid and may or may not contain malic acid. Gooseberries contain large amounts of malic acid and also give strong reactions for citric acid.

In the case of the samples reported in Table X, only one or at most two of each variety were examined. It is consequently impossible to draw general conclusions from these results. In the samples of persimmons and bananas examined, malic acid probably occurred alone. The pomegranate contained no malic acid but apparently only citric, and this is also true of the cantaloupe. Malic acid predominated in the watermelon, quince and peach, while citric was probably absent. The cranberries contained both acids while the red raspberries contained citric, with malic, if present at all, only in traces. The acid of the apricot has not been positively identified, but the evidence seems to be that tartaric or perhaps dextromalic acid is present in this fruit for the reason that a positive

increase in polarization was obtained on treating it with uranyl acetate. The acid of the huckleberry has not been positively identified, traces only of malic acid having been found, with no citric. Some samples of blackberries appeared to contain only citric acid, some contained malic acid in traces with no citric, while others gave no reactions for either malic or citric.

The conclusions reached regarding the acids of the fruits examined have been collected in Table XI.

TABLE XI.—SUMMARY OF THE ACIDS FOUND IN THE FRUITS EXAMINED
As will be noted in the text, apricots, blackberries and huckleberries were also studied but definite results on their acid contents were not obtained.

FRUIT	ACIDS FOUND
Apple	Malic only
Banana	Probably malic only
Cantaloupe	Malic none—probably all citric
Cherry	Malic only
Cranberry	Citric probably predominates—malic also present
Currant	Citric probably predominates—malic sometimes present
Gooseberry	Malic and citric
Peach	Probably malic only
Pear	Malic only in some varieties; citric probably predominates in others with small amounts of malic
Persimmon	Probably malic only
Plum	Malic only
Pomegranate	Probably all citric—no malic nor tartaric
Quince	Malic only—no citric
Raspberry (red)	Probably citric only—malic, if present, in traces only
Watermelon	Malic, no citric

These generalizations are not put forward as final. It is possible that later work may modify them in some particulars. Undoubtedly traces of acids other than those here considered occur in many fruits and it is possible that these may sometimes be found in important quantities. The results obtained on pears emphasize the danger of drawing general conclusions as to the acid content of fruits from the analysis of a limited number of varieties or even of a limited number of samples. It is believed, however, that the general conclusions drawn from those cases in which a considerable number of samples were examined are correct.

DEPARTMENT OF AGRICULTURE
BUREAU OF CHEMISTRY
WASHINGTON, D. C.

THE DETERMINATION OF NITRATE IN SEWAGE BY MEANS OF ORTHO-TOLIDINE

By EARL R. POLES and H. L. SUGG

Received April 3, 1917

The determination of nitrate in sewage and sewage effluents has been the subject of extensive investigations, out of which no wholly satisfactory methods have as yet been evolved. The chemical method of Schinbe-Tiemann is tedious to perform and the use of acid ferrous chloride is probably the most accurate method available. But it has required a tedious procedure. The gasometric acid method, as developed by Giff, which gives most beautiful results with positive action for its use, is not available for use with sewage or sewage effluents on the titrating action of chlorine. Various reduction methods depending upon the action of various hydrogens in either acid or alkaline solution have been claimed to give more prompt and accurate results than the gasometric method. Indications may be complete, i. e., to ammonia or nearly to nitrite, either of which

Transactions—Chemical Section of the American Chemical Society, 1917, 16, 1000, 1001.

J. Ind. Eng. Chem., 16, 1000, 1001.

BIBLIOGRAPHY

- 1—W. Kaupitz, *Monat. Zentralhalle*, **41** (1900), 347.
- 2—R. Kayser, *Z. analyt. Chem.*, **12** (1900), 185 and 191.
- 3—Jorgensen, *Z. Nahr. Genussm.*, **13** (1907), 241.
- 4—Windisch and Buchm. *Ibid.*, **8** (1904), 347.
- 5—Kunze and Adam, *Z. österr. Apoth.-Ver.*, **44** (1900), 187; *Z. Nahr. Genussm.*, **12** (1906), 670.
- 6—Krzizan, *Z. analyt. Chem.*, **12** (1906), 323 and 342.
- 7—Halmi, *Z. Nahr. Genussm.*, **15** (1908), 153.
- 8—Kunze, *Z. österr. Apoth.-Ver.*, **43** (1905), 749; *Z. Nahr. Genussm.*, **12** (1906), 300.
- 9—Krzizan and Plahl, *Z. Nahr. Genussm.*, **11** (1906), 205.
- 10—Hempel and Friedrich, *Ibid.*, **13** (1906), 725.
- 11—Keim, *Z. anal. Chem.*, **30** (1891), 401.
- 12—W. Niackon, *Monat. über Leben-mittel*, **2** (1898), 380.
- 13—Mach and Porcia, *Landw. Ver. Sta.*, **38** (1900), 69.
- 14—Stollé, *Z. Ver. Zucker- und S. F.*, **37** (1900), 609.
- 15—Aparin, *J. Russ. Phys. Chem. Gesellschaft*, **12** (1903), 146; *Z. Nahr. Genussm.*, **8** (1904), 384.
- 16—Windisch and Schmidt, *Z. Nahr. Genussm.*, **17** (1909), 584.
- 17—Truchon and Martin-Claude, *Ann. chim. anal.*, **6** (1904), 85.
- 18—Lehmann, *Journal und Chem. Mon.*, **69** (1908), 419.
- 19—Muttetlet, *Ann. fab.*, **3** (1909), 385.
- 20—Wassellier, *Ibid.*, **4** (1911), 488.
- 21—Bates, *Chem. Zts.*, **36** (1907), 248.
- 22—Pouss and Boute, *Ann. fab.*, **2** (1909), 180.
- 23—Smith and Plater, *Ind. Eng. Chem. Anal.*, **41**, Part C, **3** (1909), 100.
- 24—Hornberger and Pohl, *Z. Nahr. Genussm.*, **1898**, 148.
- 25—Yoder, *Trans. Canadian*, **3** (1911), 36.
- 26—Dunham and Brown, *J. S. Dept. Agr., Bur. of Chem., Canada*, **76** (1913), 896.
- 27—Pohl, *J. S. Dept. Agr., Bur. of Chem., Canada*, **88** (1916), 100.
- 28—Wassellier, *J. Am. Chem. Soc.*, **38** (1916), 1908.
- 29—Wassellier, *Nachricht. Chem.*, **2** (1894), 141; *Z. anal. Chem.*, **36** (1891), 198.
- 30—Kunze, *Arch. Chem. Med.*, **7** (1901), 88; *Z. Nahr. Genussm.*, **12** (1906), 670.
- 31—Dunham and Pohl, *Ind. Eng. Chem. Anal.*, **41**, Part C, **3** (1909), 100.
- 32—Pohl, *J. S. Dept. Agr., Bur. of Chem., Canada*, **88** (1916), 100.
- 33—Mason, *J. Am. Chem. Soc.*, **37** (1915), 676; *Canadian J. Nahr. Genussm.*, **19** (1915), 31; *Anal. Chem.*, **1**, S. Dept. Agr., Bur. of Chem., Canada, **90** (1916), 61.

is capable of accurate determination by a simple procedure.

Tieman-Gartner early pointed out the possible errors of both acid and alkaline reductions. Reduction in acid solution, using a two-metal pair such as copper and zinc, has found general adoption in England, while in the United States alkaline reduction with aluminum according to Hazen and Clark¹ has been adopted as the standard procedure.² In addition to being time-consuming, this procedure has never been wholly satisfactory and does not yield uniformly accurate results even in the hands of experienced workers. Certain methods depending upon the nitration of organic compounds, analogous to the phenol-sulfonic acid method, have been proposed from time to time. Among these may be mentioned the brucine method of Noll³ and the narcotine method of McRae.⁴ Both of these methods involve rather intense color changes which are more or less affected by the actual manipulation, especially as regards the concentration of acid and temperature of reaction, and do not lend themselves to close color comparison. These have not been generally adopted.

Ortho-tolidine was first employed in the qualitative detection of minute quantities of free chlorine and hypochlorite by one of the writers in connection with a court case in which the presence or absence of residual available chlorine was a matter in dispute. Ellms and Hauser⁵ made the first detailed study of the quantitative aspects of this test and offered certain suggestions relative to the reaction involved. The test has since come into quite general use in connection with the treatment of water supplies by hypochlorite or free chlorine.

Since the color change in ortho-tolidine is probably due to oxidation and may be induced directly by free chlorine, it occurred to us that this reaction might be made use of indirectly in the estimation of nitrate. The direct application of an acid solution of ortho-tolidine to a water containing nitrate does not produce an appreciable color even in the presence of chlorides. If, however, the water be evaporated to dryness, the acid toloidine solution added, and concentrated sulfuric acid subsequently added, there is, first, liberation of chlorine from the chlorides by reaction with the nitric acid, and, secondly, the characteristic oxidation of ortho-tolidine by the liberated chlorine. A similar color change will take place even in the absence of chlorides, but it has been found that in this case the reaction is not consistent and the resulting color is much more dependent upon conditions of technique. While there has been no careful study of the reactions involved in these color changes, the results of our investigation lead us to believe that we are dealing in the one case with the direct oxidation by chlorine and in the other with nitration possibly accompanied by a certain amount of simultaneous oxidation. Since this color test is found to be favored

by the presence of chlorides, it has been studied in further detail as a possible method of nitrate determination in sewage.

The following technique has been developed and is recommended:

REAGENTS

(1)—*Sodium hydrate and sodium chloride solution.* Dissolve 5 g. sodium hydrate and 1.5 g. sodium chloride; make up to 100 cc.

(2)—*Ortho-tolidine solution.* Dissolve 0.4 g. *o*-tolidine¹ in 100 cc. *N* hydrochloric acid.

(3)—*Sulfuric acid*, specific gravity 1.84, nitrate-free.

(4)—*Standard nitrate solution.* Dissolve 0.72 g. pure potassium nitrate; make up to one liter. Take 10 cc. and dilute to 100 cc. Of this solution 1 cc. is equivalent to 0.01 mg. of nitrogen as nitrate.

(5)—*Potassium dichromate solution, N/40.*

PROCEDURE

To 25 cc. of the sample in a 50 cc. Erlenmeyer flask, add 0.5 cc. of the NaOH-NaCl solution. Boil for about one-half minute, cool, and make up to volume, or make up to weight.² Put 1 cc. of the supernatant liquid in a 3 in. evaporating dish and evaporate to dryness on a water bath. If sample is suspected to contain more than 10 p. p. m. of nitrate use a proportionately smaller amount of supernatant liquid; if less than 1 p. p. m. use 10 cc. Add 0.2 cc. of the toloidine solution and mix the liquid with the residue by means of a stirring rod; it is important not to add more than 0.2 cc. of this solution, otherwise the mixture will be too dilute when the sulfuric acid is added. After it is well mixed, add 0.5 cc. of concentrated sulfuric acid, allowing it to flow gently down the sides of the dish. Do not mix. After 5 minutes wet the sides of the dish with the liquid. After half a minute dilute with about 5 cc. of distilled water. Pour the contents into a flat-bottom test-tube or a pill bottle, make up to 10 cc. and mix. Compare with the standards immediately or within 5 minutes.

Standards may be made up at the same time and in the same manner from the standard nitrate solution or permanent standards may be prepared from the dichromate solution. The following values have been found to match satisfactorily in our work, but as the technique and individual eyes vary, it is preferable to prepare these standards by actual comparison with colors produced from known nitrate values.

NITROGEN AS NITRATE	N/40 Potassium Dichromate	NITROGEN AS NITRATE	N/40 Potassium Dichromate
Thousandth Mg. (a)	Cc.	Thousandth Mg. (a)	Cc.
0.0.....	0.2	5.5.....	3.4
0.5.....	0.8	6.0.....	3.6
1.0.....	1.2	6.5.....	3.8
1.5.....	1.6	7.0.....	4.0
2.0.....	1.9	7.5.....	4.2
2.5.....	2.2	8.0.....	4.4
3.0.....	2.4	8.5.....	4.6
3.5.....	2.6	9.0.....	4.8
4.0.....	2.8	9.5.....	5.0
4.5.....	3.0	10.0.....	5.2
5.0.....	3.2	10.5.....	5.4

(a) P. p. m. when 1 cc. is taken for analysis.

¹ Ortho-tolidine is *p*-diamido-*m*-dimethyl-diphenyl, m. p. 128. Difficulty has been experienced in ordering by confusion with ortho-tolidine, a liquid.

² In practice we find that the half-minute boiling can be made to compensate exactly for the added reagent.

¹ *Chem. News*, 64 (1891), 162.

² A. P. H. A., "Standard Methods of Water Analysis," 1917, p. 24.

³ *Z. angew. Chem.*, 1901, p. 1317.

⁴ *Am. J. Pub. Hyg.*, 19 (1909), 307 (N. S., Vol. 5).

⁵ *This Journal*, 5 (1913), 915.

Certain experimental data upon which this technique is based will be presented to indicate in a general way the possible sources of error and the reasons for the various steps recommended.

It is necessary to carry out the final reaction in reasonably concentrated solution. The volume of this solution determines the temperature of the reaction with the sulfuric acid, and the concentrations of the various reacting substances undoubtedly affect the reaction between nitric and hydrochloric acids. A series of determinations upon a water containing 5 p. p. m. of nitrogen as nitrate was carried out by evaporating to dryness and then adding definite quantities of distilled water before proceeding with the addition of reagents. The following results were obtained:

Water added	0.0	0.5	1.0	2.0
Nitrate recovered	5.0	4.0	1.9	0.2

It is obvious, therefore, that the evaporation must be carried to dryness and the volume of reagents reduced to a minimum.

Any other oxidizing agent in the water would obviously influence the reaction and increase the apparent nitrate content. Of the possible compounds of this type, iron and manganese are the only ones likely to be met with in ordinary practice. It is therefore necessary to eliminate these two metals which is accomplished in the first step of the procedure by a brief boiling in the presence of an excess of sodium hydroxide. The absence of free chlorine or hypochlorite must, of course, be assured. The importance of a fairly complete removal of iron is shown in the following experiments. To the original sample of water containing 5 p. p. m. of nitrogen as nitrate, ferrous sulfate was added in varying quantities. The determination was then proceeded with, without removing the iron by precipitation. The following results were obtained in duplicate:

P. p. m. iron added	NITRATE READINGS	
0	5.10	4.75
25	6.00	5.75
50	6.75	6.50
100	8.50	8.00

It was undertaken at first to use ammonium hydroxide for the precipitation of iron and manganese. It was found, however, that a neutral or slightly alkaline solution of nitrate may rapidly lose nitrate if it is left on the water bath after becoming dry.¹ This effect is more noticeable in the presence of ammonium salts. If the solution be distinctly alkaline, however, and free of ammonium compounds, no such loss is experienced. The following experimental results illustrate this point. A water containing 5 p. p. m. of nitrogen was evaporated and left on the water bath for various periods after complete drying. A parallel set of dishes was treated in a similar manner except that the solution was made alkaline according to the recommended procedure.

Time on water bath after drying	NITRATE RECOVERED (DUPLICATES)			
	Alkaline		Neutral	
0 min.	5.0	5.0	5.0	5.0
18 min.	5.0	5.0	4.0	3.5
33 min.	5.0	5.0	2.5	2.5
48 min.	5.0	5.0	2.5	2.5

¹ See also Coll. I.

The addition of a slight excess of sodium hydroxide is also distinctly advantageous in that it precipitates most of the organic matter and leaves a fairly clear solution for the determination.

The employment of an alkaline solution is also necessary to eliminate the slight effect of a high nitrite content. That nitrite does not interfere under the recommended procedures is evidenced in the following experimental results:

Sample contained p. p. m.		NITRATE RECOVERED (DUPLICATES)			
Nitrate	Nitrite	Alkaline		Neutral	
5.0	0.0	5.0	5.0	5.00	5.00
5.0	5.0	5.0	5.0	5.00	4.75
5.0	10.0	5.0	5.0	5.00	4.75
5.0	15.0	5.0	5.0	5.00	5.00
5.0	20.0	5.0	5.0	5.25	5.25
0.0	20.0	0.0	0.0	0.50	0.60

The presence of chloride has been shown to be distinctly advantageous in producing a uniform and consistent reaction. The color produced is slightly more intense without chloride and is reduced by the addition of chloride up to approximately 50 p. p. m. Between this value and approximately 2,000 p. p. m. the concentration of chloride does not affect the result. Above this latter figure there is a rapid falling off as shown in the following experimental results. The tests actually made included a considerable series of chloride values between 100 and 2,000 p. p. m., but as the final result was consistent throughout this range, the table has been abbreviated by eliminating these figures. The water in this case contained 2.5 p. p. m. of nitrogen as nitrate. The value given is the average result of four closely agreeing observations in each case:

Chlorine as chloride (p. p. m.)	0	20	50	100	2000	5000	10000	20000
Nitrate recovered	2.8	2.7	2.5	2.5	2.5	2.1	1.5	1.4

The reaction is a rapid one and will be fully completed within 5 minutes. After this time has elapsed the mixture should be diluted and compared promptly with the standards because the color tends gradually to disappear. The following results indicate the importance of making the readings within 10 minutes at the outside:

Original sample contained p. p. m.	Reading after				Standard
	5	10	20	30	
2.5	2.8	2.80	2.25	2.25	2.00
5.0	5.0	4.75	4.50	4.25	4.00
7.5	7.5	7.50	7.25	7.00	7.00
10.0	10.0	10.00	9.50	9.00	8.00
1.0	1.0	1.00	0.85	0.75	0.50

The comparisons thus far recorded are based upon readings against standards prepared as described and under laboratory conditions, using tap water. To determine the value of this procedure under the condition of practice a mixture of equal parts of sewage and tap water was prepared, the mixture having been stored for a sufficient time to remove the possibility of there being any residual nitrite. Varying amounts of nitrate were then added to the mixture and nitrate determinations made by the orthotoluidine method and by the standard solutions method. The results in this comparative study are shown in the following table:

Sample contained	TOLUENE METHOD		REDUCTION METHOD			Av.
	1	2	1	2	3	
0.0 p. p. m.	0.0	0.0	0.27	0.25	0.3	0.27
2.0 p. p. m.	2.0	2.0	2.2	2.3	3.2	2.6
4.0 p. p. m.	4.0	4.0	4.5	4.6	4.3	4.5
6.0 p. p. m.	6.0	6.0	6.5	7.5	6.0	6.7
8.0 p. p. m.	8.0	8.0	9.0	10.0		9.5
10.0 p. p. m.	10.0	10.0	10.5	13.0		11.7

This table emphasizes the fact, to which attention has already been drawn by Hazen and Clark,¹ that the results of the alkaline reduction method are subject to considerable errors which are traceable for the most part to the elimination of ammonia from the nitrogenous substances of sewage. The procedure which is here outlined is rapid and remarkably simple in its technique and seems to obviate in a most satisfactory way most of the objectionable features of other methods. In the range from 1 to 10 p. p. m. of nitrogen as nitrate it is sensitive and reliable to 0.5 part; in the range 0 to 1.0 parts, to 0.05 part. It has been in continuous use at the Hygienic Laboratory during the past year and has given throughout consistent and concordant results which, in numerous cases where comparisons have been made, compare with the more laborious standard method of procedure as well as may be expected under the circumstances. It is believed that the major part of the discrepancies noted represent errors in the latter procedure.

TREASURY DEPARTMENT
U. S. PUBLIC HEALTH SERVICE
WASHINGTON, D. C.

A COMPARISON OF AMERICAN AND ORIENTAL STORAX

By STROUD JORDAN

Received April 7, 1917

The liquid or semi-liquid balsam obtained from "*Liquidambar styraciflua*," known in the United States as "sweet gum," has been recognized for a long while and samples were shown at the Paris Exposition in 1878. This material resembles liquid storax of the Levant and shows only a slight variation in composition.² It generally occurs in grayish or reddish

Large quantities of liquid storax have been imported from Asia Minor where it is gathered from the "*Liquidambar*" tree (*Liquidambar Orientale*), but scarcely any imports are received at the present time on account of European conditions. This material is used in pharmaceutical preparations, as a source of cinnamic alcohol and concentrated essence of storax, which are used in perfumery as fixatives, and as a general source of cinnamic acid and its compounds. It is unnecessary to go further into detail since this material is described elsewhere.¹

Since the imports of liquid storax have been practically discontinued it has become necessary to look for American sources and this article is simply a comparison of the American and Oriental storax of commerce, dealing with the crude materials as received. The analyses of storax given below were made on samples which were sold on the New York market from 1912 to 1917, showing the gross adulteration of this material. The sample of "sweet gum" analyzed, was gathered in Durham County, North Carolina, during March, 1917, and the genuineness of this article can be guaranteed. An average analysis of "sweet gum" is given, which will vary from time to time, according to locality and condition.

METHOD OF ANALYSIS

The general methods of analysis used are given in "Resins, Balsams and Gum Resins," by K. Dietrick, page 233, 1901.

In addition to the above analysis, the method as outlined in *Chemical Abstracts*, 2 (1908), 2845, for Peruvian balsam, has been followed out in some cases, as a comparison.

RESULTS

The following values have been obtained from the samples of crude storax and "sweet gum" examined:

ANALYSES OF COMMERCIAL STORAX AND OF "SWEET GUM"

MATERIAL Storax No.	Volatile Matter	Ether		Alcohol		Resin Cinnamene Esters	Resin Acids	CINNAMIC ACID		Acid No.	Sapon No.	Ester No.
		Ash	Insoluble	Insoluble	Insoluble			Free	Total			
1			8.18		39.30	24.24	8.22	5.41		54.5	145.0	90.5
2			2.16		25.89	1.00	53.35	1.87		80.5	133.0	52.5
3			4.88		31.75	14.87	15.83	3.60				
4	20.35	1.66	7.01		34.03	12.32	12.01	7.11		52.6	145.4	92.8
5			7.13		39.19	21.27	3.01	5.19				
6		0.28	3.68	3.68	54.90	18.79	2.63	7.69		59.5	166.2	106.7
7			3.24	3.25	51.39	9.42	13.22	8.14		60.9	153.8	92.9
8	20.64	1.48	7.98	7.98	35.12	2.58	22.30	3.73		42.2	148.9	106.7
9	23.49	4.48	5.17	8.02	37.34	9.75	16.74	5.57		50.3	115.7	65.4
10										99.3	127.3	28.3
11							54.76		3.19	100.4	135.4	35.0
12							55.10		1.65	91.2	134.8	43.6
"Sweet Gum"	22.87	0.32	5.24(a)	6.64(a)	22.86	34.76	2.11	12.65	28.02	68.7	131.6	62.9

(a) These insolubles were taken on different portions of the sample. The difference is due to the varying proportion of mechanical impurities and the alcohol insoluble on the same portion would show a smaller percentage than the ether insoluble

gray, opaque masses, which harden with age and upon exposure to the air, finally becoming very brittle. The fresh balsam is a clear, yellow-brown, semi-liquid of the consistency of honey and the purified "sweet gum" also exhibits the same characteristics although it is not so fluid as the fresh material. The hardened gum is gathered in certain localities and without further preparation is used as a chewing gum.

¹ Loc. cit.

² U. S. D. 1197, 19th Ed., Gildemeister and Hoffmann, "Volatile Oils," 1, 136; Watts' "Dictionary of Chemistry," 1 (1874), 496.

¹ E. J. Parry, "Food & Drugs" p. 492; U. S. D. 1197, 19th Ed.; Gildemeister and Hoffmann, "Volatile Oils," 1, 136; K. Dietrick, "Resins, Balsams and Gum Resins," p. 225; Watts' "Dictionary of Chemistry," 1 (1874), 497.

no offerings. Under normal conditions liquid storax will average about \$0.20 per lb., but even then it is the worst adulterated material ever examined in our laboratory, being adulterated with Burgundy pitch, colophony, castor oil and extracted storax. At \$0.20 per pound American storax cannot compete, unless some cheap method of production can be worked out; the Forest Service is now busy on this problem. It is believed, however, that this material can be obtained for \$0.50 to \$1.00 per pound and that after a market is found the supply may warrant a material reduction.

CONCLUSION

It would seem that "sweet gum" may be used in the place of liquid storax with good results; that it carries more cinnamic acid than commercial storax; that the odor and fixative properties of "sweet gum" are superior to the commercial variety of storax imported into the United States; that the southern portion of the United States should furnish all the storax required; that the old hardened balsam may be used in the manufacture of chewing gum.

CHEMICAL DEPARTMENT, AMERICAN TOBACCO COMPANY
60 FRANKLIN AVENUE, BROOKLYN, N. Y.

LABORATORY AND PLANT

NITRIC ACID SOPHISTICATION, A SERIOUS PRODUCTION MENACE¹

By JAMES R. WITHROW

Commercial nitric acid is shown in this paper to be capable of sophistication by sodium nitrate or other sodium salts—an adulteration which may have a serious effect on production, or upon yields in many chemical operations, and which may easily escape detection when the strength of acid is ascertained by determining specific gravity, or, in the case of sodium nitrate, by determining NO_3 content as well. It follows that other commercial acids may be subject to similar possibilities.

Dissatisfaction with the nitric acid return from the recovery system in a chemical plant in Ohio led to investigation of various factors entering into the situation. About that time the operating chemical engineer called attention to the fact, which he had just discovered, that the workmen had been frequently noticing a small amount of a white material rattling out of the carboys when they were up-ended to pour out the last of this nitric acid. The discovery was made in a shipment of "Aqua Fortis 40° Pale." A "handful" of the crystals saved for inspection looked suspiciously like poorly developed rhombohedrons of sodium nitrate, though it was felt that they surely must be sodium sulfate or acid sulfate from a "boil-over" during nitric acid manufacture.

A qualitative examination revealed only a trace of sulfates while the nitrate test was strong even after much washing. Subsequent partial analysis showed SO_4 1.05 per cent and Na 37.39 per cent. It seemed probable, therefore, that this particular shipment of acid, at least, was saturated with sodium nitrate. Part of our unduly high nitric consumption and poor recovery could be caused by this fact if sodium nitrate were soluble to any extent in the acid. This seemed improbable when one remembers how easily concentrated acids precipitate soluble salts upon addition to the aqueous solutions of many such salts. The specific gravity alone had been utilized in checking shipments of acid as they arrived and it is evident that the nitrometer also would be likely to give unreliable results in such a case. Titration would, of course, detect adulteration with any salt but a

little used because of the common presence of free sulfuric acid. We at once resorted to evaporation for residual salt determination and proceeded to investigate carefully the whole matter to see if our operation economy difficulties were chargeable to any extent to this sodium nitrate content in the nitric acid. It was obvious that if sodium nitrate were soluble to any extent in nitric acid it would be profitable to get the desired specific gravity or even NO_3 content in nitric acid manufacture by adding sodium nitrate, thus saving the expense of sulfuric acid, yield troubles, upkeep and depreciation. At 9 cents per pound at point of shipment, the selling price of the acid in question, the returns on the investment should be reasonable. In fact, as an industrial chemical achievement other discoveries and developments in nitric acid production in recent years would be puny in manipulation saving, alongside of this method of "butting up" nitric acid, and also as far as the ledger is concerned.

The solubility of sodium nitrate in nitric acid of various strengths could not be located in the literature for the acid concentration we were using, though it does exist for weaker acids.¹ This work gives data which show that 34 per cent HNO_3 (25.5° B $^\circ$) will dissolve 7 per cent NaNO_3 which raises the mixture to about 30° B $^\circ$.

It seemed likely that if sophistication had been practiced either solid sodium nitrate was dissolved in weak nitric acid, or in strong nitric acid which was then diluted to 40° B $^\circ$, after the whole had been warmed in each case and allowed to cool in contact with excess sodium nitrate to avoid supersaturation; or, a saturated solution of sodium nitrate was added to weak nitric acid and the excess (precipitated) sodium nitrate, if any, used in preparing the next batch of sodium nitrate solution; or, strong nitric acid was added to saturated or strong sodium nitrate solution and the mixture diluted to 40° B $^\circ$. In each method solutions water or other water solutions could be added to reduce the specific gravity to the required strength if the mixture resulting had more of it. The use of solid nitrate would require heating in the mixture, a manufacturing nuisance.

Our interest was to get the correct strong acid results of the last plan, and this was accomplished.

¹Read before the American Institute of Chemical Engineers, Cleveland Meeting, June 1-6.

Received June 10, 1917. Accepted for publication June 10, 1917. Published by the American Chemical Society, June 10, 1917.

in part by changing the source of acid. No exhaustive laboratory investigation was conducted but merely sufficient work to insure our position in case of controversy, for it was stoutly maintained by acid-makers that no material amounts of NaNO_3 or other salts could be held in solution. Though many data were accumulated, details need not be given, as they were necessarily complex and the end results sufficiently emphasize the facts.

THE POSSIBILITIES USING SOLID SODIUM NITRATE

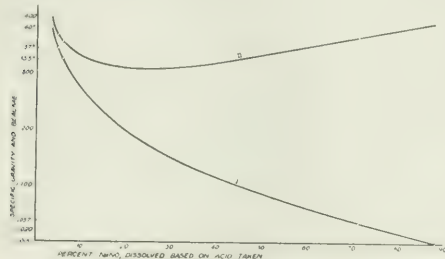
Nitric acid of various strengths was found to dissolve considerable sodium nitrate and this was facilitated by heating the mixture.

Table I shows data obtained when a nitric acid (42° Bé.) was diluted with water to various strengths and the specific gravity taken, and these solutions then warmed to slight fumes with solid sodium nitrate and allowed to cool to the indicated temperature in contact with excess nitrate crystals in each case.

TABLE I

NITRIC ACID			FINAL SOLUTION		
Sp. Gr.	Gravity Bé.	Per cent NaNO_3 Dissolved on Basis of Acid Taken	Sp. Gr.	Gravity Bé.	Temp. °C.
1.381	40	3.24	1.401	41.5	15°
1.381	40	3.96	1.392	40.8	22°
1.343	37	4.70	1.368	39.0	15°
1.324	35.5	5.74	1.356	38.0	15°
1.037	...	70.94	1.366	38.9	15°

It follows from the general trend of Curve I, which gives the specific gravity of acid which will dissolve the amounts of NaNO_3 indicated, that as the specific



gravity of the curve falls off the solubility of sodium nitrate in the nitric acid rapidly increases. Curve II shows the displacement or increase in specific gravity by solution of NaNO_3 in the acids of different specific gravities, showing the great displacement at low acid concentrations.

To see how much water could be added to a saturated solution of sodium nitrate in nitric acid which was originally 40° Bé. without lowering the final gravity below 40° Bé., some 42° Bé. acid (sp. gr. = 1.408) was diluted to sp. gr. 1.381 (40° Bé.), requiring about 9 per cent water. Excess sodium nitrate was then added and in 30 minutes the sp. gr. was 1.40 (41.4° Bé.). Water was then added until sp. gr. had returned to 1.381 (40° Bé.). The temperature rose slightly during the operation. The nitrate dissolved at 15° C. was 3.24 per cent of the weight of the 40° Bé. acid used. This permitted 6.0 per cent water to be added without lowering the gravity below 40° Bé., or 9.24 per cent total addition by weight. Curve III shows the rise in density and gain in weight due

to the solution of NaNO_3 in 40° Bé. acid and the fall in density and total gain in weight upon adding water.

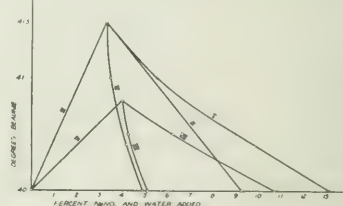
When saturated NaNO_3 solution containing 46.8 g. NaNO_3 per 100 g. replaced the water in the above work, and the HNO_3 was saturated with 3.24 g. NaNO_3 per 100 g. of the original 40° Bé. acid, and all work was conducted at 15° C., not permitting the temperature at any time to go below 15° C., it was found that each addition of nitrate solution caused a separation of solid NaNO_3 . Eventually NaNO_3 had been added to the extent of 4.8 per cent of the 40° Bé. acid taken, and to bring the sp. gr. back to 40° Bé. there had been 8.3 per cent of water or a total addition of 13.1 per cent of the weight of the 40° Bé. HNO_3 used to dissolve NaNO_3 .

The dilution of the NaNO_3 - HNO_3 mixture was carried out in steps which may be summarized as follows at the end of each dilution with its accompanying NaNO_3 crystals separation.

TABLE II— HNO_3 STRETCHING WITH NaNO_3 AND WATER AT 15° C. Total Addition per 100 G. Original 40° Bé. HNO_3

	NaNO_3 - HNO_3 Mixture	DILUTION		
		I	II	III
NaNO_3 in solution.....	3.24	3.45	4.15	4.83
Water in NaNO_3 solution.....	0.00	2.04	5.67	8.30
Total added matter.....	3.24	5.49	9.82	13.13
Sp. Gr. at this dilution.....	1.399	1.394	1.386	1.380
Bé. equivalent.....	41.4°	41.0°	40.4°	40.0°

Curve IV illustrates the gain in NaNO_3 content with falling density of mixture due to dilution with NaNO_3 solution and Curve V shows the rate of total gain in weight by diluting with NaNO_3 solution.



A similar series of results was accumulated at higher (ordinary) temperature as more practical working conditions. They may be summarized as follows:

The sodium nitrate solution used for dilution contained 48.33 g. nitrate per 100 g. solution, and its sp. gr. was 1.399 at 22.5° C. Separation of NaNO_3 crystals took place in each case upon using this solution for diluting the nitric acid-sodium nitrate mixture.

TABLE III— HNO_3 STRETCHING WITH NaNO_3 AND WATER AT 22.5° C. Total Addition per 100 G. Original 40° Bé. HNO_3

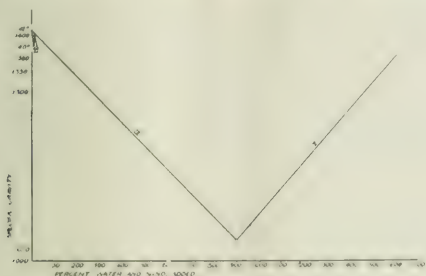
	NaNO_3 - HNO_3 Mixture	DILUTION	
		I	II
NaNO_3 in solution.....	3.96	4.26	5.08
Water in NaNO_3 solution.....	0.00	1.95	5.53
Total added matter.....	3.96	6.21	10.61
Sp. Gr. at this dilution.....	1.392	1.388	1.381
Bé. equivalent.....	40.8°	40.5°	40.0°

Curve VI illustrates the gain in weight and rise in density at 22.5° C. when NaNO_3 is dissolved in 40° Bé. HNO_3 ; Curve VII illustrates rise in NaNO_3 concentration with falling density due to dilution with

NaNO_3 solution; and Curve VIII gives rate of total gain in weight by this dilution.¹

Sodium nitrate is *very* soluble in dilute nitric acid. Actual experiment showed that 12.9 weight parts of 42° Bé. acid (sp. gr. 1.408) plus 116.1 weight parts of water had a sp. gr. of 1.037 at 15° C. This solution after saturation by warming with excess sodium nitrate and cooling to 15° C. had a sp. gr. of 1.366 (38.9° Bé.) and a NaNO_3 content of 70.94 g. per 100 g. of original diluted acid. In other words, 1 part of 42° Bé. acid plus 9 parts of water and 7.1 parts by weight of NaNO_3 give a solution of sp. gr. of 1.366 (38.9° Bé.), or 1 lb. of 42° Bé. acid would make 17.1 lbs. of this mixture.

Curve IX represents empirically the falling gravity, with the addition of 900 per cent of water to 42° Bé. acid and Curve X in the same way represents the rise in density (gain in weight) with the solution



of 710 per cent of NaNO_3 . Curve XI on behavior of 40° Bé. acid is drawn in for comparison of the possibilities as the acid used becomes more dilute. It had really initiated at 42° and is, therefore, so shown, otherwise it is identical with Curve III.

POSSIBILITIES USING SODIUM NITRATE SOLUTIONS

Since agitating and heating are desirable when dissolving sodium nitrate in nitric acid and as doing so would require special equipment, such equipment and some difficulties might be eliminated if nitrate were used as a strong or saturated solution, instead of as a solid.

Using C. P. nitric acid a number of solutions were prepared of 10, 30, 40 and 50 per cent strength determined by specific gravity or as high as 35° Bé. A strong solution of sodium nitrate was also prepared at 15°. Its sp. gr. was 1.37 and it contained 16.119 g. sodium nitrate per 100 g. solution or 62.971 g. per 100 cc. of solution. Starting with the same volume of nitric acid, 10 cc. in each case, as the sodium nitrate

Although these results amply confirm those in Table I in the case of experiments the total added matter is lower than was expected, such reversals of this kind though never serious, and also other interesting solubility phenomena also frequently encountered and the field is an interesting one for further study had one the opportunity. Difficulty in making nitrate solutions that were fully saturated and of cooling super-saturation even in presence of excess salt was striking at times. No effort was made to insure that solutions were saturated. They were merely made strong and care taken to avoid super-saturation as far as possible. In this particular case, as would be expected, more NaNO_3 dissolves in 40° Bé. HNO_3 at 25.3° than at 15° but the specific gravity is lower in the warmer case. This prevents, therefore, the addition of so much diluent as in the case with less NaNO_3 dissolved but with higher density.

solution was added the specific gravity rapidly increased until the quantity of sodium nitrate was somewhat greater than that of the nitric acid, when the specific gravity changed but slightly, approaching, but never reaching, the specific gravity of the original sodium nitrate solution. The highest gravity obtained was about 39.2° Bé., or 1.371 sp. gr., or not quite as high as the solution of sodium nitrate itself, 1.375 or 39.6° Bé. This was for the reason that in every case with these strengths of acid, excess sodium nitrate crystallized out upon addition of the nitric acid or the acid acted merely as a diluent as far as specific gravity of saturated sodium nitrate was concerned.

No analyses of the resulting solutions were made in these cases. Record was kept merely of the initial quantities used and the resulting specific gravities. Without taking up space with the details of the data the Curves XII to XV give an idea of the tendency of strong NaNO_3 solution to boost the specific gravity of the weaker nitric acid under this set of conditions.

These general conclusions were sustained even when stronger acid, 54.4 per cent, sp. gr. 1.343, or 37° Bé. was treated with progressive amounts of a stronger solution of NaNO_3 of sp. gr. 1.392 and NaNO_3 content of 46.8 g. per 100 g. solution, beginning with smaller amounts of nitrate than previously mentioned. It was found that for each 100 g. of acid, 5.15 g. of nitrate solution gave a sp. gr. of 1.348. Upon the addition of 10.2 g. nitrate solution, separation of sodium nitrate commenced and the highest specific gravity was obtained, 1.352. Progressive additions of nitrate solution were accompanied by continuous elimination of solid sodium nitrate and the specific gravity fell constantly as may be seen from Table IV. No determination of the concentration of nitrate in the resulting acid mixture was made but merely record kept of the progressive change in density after definite addition of nitrate solution.

TABLE IV. SPECIFIC GRAVITY COMPARISONS OF VARIOUS MIXTURES OF HNO_3 (SP. GR. 1.343) AND SATURATED NaNO_3 (SP. GR. 1.392)

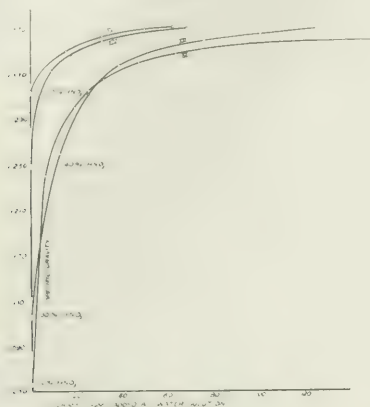
Sp. Gr. of Mixture	NaNO_3 Solution Added per 100 g. Original HNO_3	Total NaNO_3 Solution Added per 100 g. Original HNO_3
1.343	000.000	000.000
1.344	1.024	1.024
1.348	4.106	5.150
1.352(a)	5.052	10.202
1.343	15.263	1.343
1.324	26.2	27.544
1.311	37.3	64.8
1.316	107.53	214.23
1.339	200	434.80
1.357	332.12	666.92

(a) Crystallization began. A check on this point was as follows: sp. gr. 1.352, NaNO_3 solution added per 100 g. HNO_3 13.15. No more crystallization began addition of a small crystal of NaNO_3 and allowing the mixture to stand 12 hr. at 15° to 20° C.

Curve XVI shows graphically the increase and break in the specific gravity caused by the addition of strong NaNO_3 solution in HNO_3 under the above conditions.

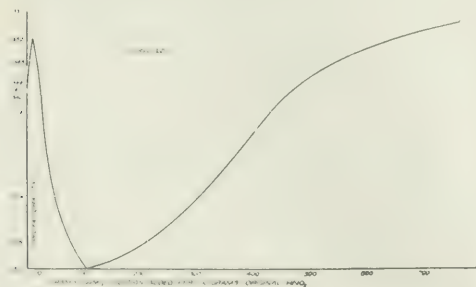
Using still stronger acid, a strong solution of sodium nitrate, 50 per cent, at 15° C. containing 46.8 g. salt per 100 g. of solution, and mixed in 900 cc. by weight of 42° Bé. nitric acid was added to the nitrate solution. This solution was allowed to stand 48 hours in contact with a crystal of sodium nitrate. A crop of about 4 g. of solid nitrate crystals was obtained thus preventing super-saturation. The spe-

inal acid had a sp. gr. of 1.408; the sodium nitrate solution a sp. gr. of 1.326; the final mixture stood 1.336 or 36.5° Bé. at 15° C. This final solution contained 32.6 g. of sodium nitrate per 100 g. of the solution plus 17.73 parts by weight of 42° Bé. HNO₃ and 49.67 parts of water exclusive of the water present



in the 42° Bé. nitric acid, or 1 part of 42° Bé. HNO₃ per 1.837 parts NaNO₃ and 2.79 parts of water. Curves XVII and XVIII show the gain in both NaNO₃ and water, respectively, during dilution with the NaNO₃ solution. The 42° Bé. acid used contained 18.8 g. of real HNO₃ and the final product (36.5° Bé.) has a specific gravity corresponding to 83 g. of real HNO₃ or a gain on this basis of over 340 per cent. This apparent gain was produced by adding less than 2.7 lbs. of sodium nitrate per lb. of original 42° acid.

Using a smaller quantity of strong acid, to 100 g. of a water solution of NaNO₃ (sp. gr. 1.393 or 41° Bé. at 15°) was added 2.56 g. HNO₃ (sp. gr. 1.408 or 42° Bé.). After standing for 24 hours at room temperature the solution was cooled to 15° C. and de-

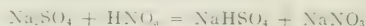


canted from the crystals which had precipitated. The sp. gr. of the solution at this point was 1.386, or 40.5° Bé.

The NaNO₃ content of a saturated water solution of NaNO₃ is 47.430 g. per 100 g. of solution. This means that our 3900 per cent of sodium nitrate solution added to 42° Bé. HNO₃ gives a mixture of 40.5° Bé.

SULFATE AND ACID SULFATE ADMIXTURE

The separation of nitrate crystals from nitric acid is by no means evidence that nitrate had been mixed with or added to the acid. The solution of sodium sulfate in strong nitric acid was found to deposit small white crystals which are clear cut rhombohedrons of sodium nitrate. This behavior might be expected from general considerations and in connection with the possibilities of the following equation:



The original admixture might have been, therefore, sodium sulfate and still have sodium nitrate separate from the acid.

Nitric acid (sp. gr. 1.381, 40° Bé.) was found to dissolve 12.62 g. of sodium sulfate per 100 g. of the acid at 15° C., giving a sp. gr. of 1.416 or 42.6° Bé. This was diluted with water in steps to 40° Bé. with results as follows:

TABLE V—HNO₃ STRETCHING WITH Na₂SO₄ AND WATER AT 15° C.
Total Addition per 100 G. Original 40° Bé. HNO₃

Na ₂ SO ₄ HNO ₃ Mixture	DILUTION—		
	I	II	III
Na ₂ SO ₄ in solution.....	12.62	12.62	12.62
Water in Na ₂ SO ₄ solution.....	0.00	2.31	7.91
Total matter added.....	12.62	14.93	20.53
Sp. Gr. at this dilution.....	1.416	1.392	1.374
Bé. equivalent.....	42.6°	42.2°	40.8°



It was also found that the addition of sodium sulfate to 40° Bé. nitric acid could raise it to 45° Bé.

Sodium acid sulfate separates apparently as such, together with some sodium nitrate when added to nitric acid. This acid of 40° Bé. strength was found to dissolve 12.62 g. of sodium acid sulfate per 100 g. of the acid at 15° C., giving a sp. gr. of 1.462 or 45.8° Bé. This was diluted in steps with water to 40° Bé. with the following results:

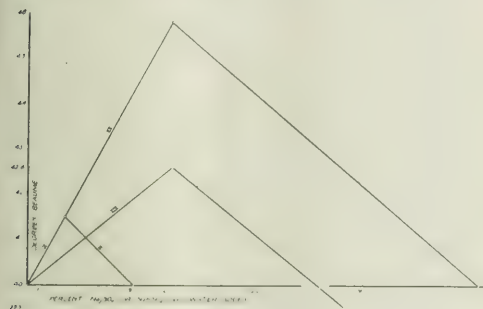
TABLE VI—HNO₃ STRETCHING WITH NaHSO₄ AND WATER AT 15° C.
Total per 100 G. Original 40° Bé. HNO₃

NaHSO ₄ HNO ₃ Mixture	DILUTION—		
	I	II	III
NaHSO ₄ in solution.....	12.62	12.62	12.62
Water in NaHSO ₄ solution.....	0.00	2.89	16.36
Total matter added.....	12.62	15.51	28.98
Sp. Gr. at this dilution.....	1.462	1.412	1.382
Bé. equivalent.....	45.8°	42.3°	40.0°

These results could very easily be obtained in using the nitre cake from the manufacture of nitric acid. This material is at hand and convenient and is a drug on the market at present. It is interesting to note that the solubility of sulfate and acid sulfate is the same in this strength acid if equilibrium actually was ob-

tained in both cases. Confirmatory work on this by different persons arrived at the same conclusions. In spite of this, however, the specific gravity is different in the case of the solutions of these two salts and, therefore, much more water can be added in the case of the acid sulfate without lowering the specific gravity below 40° B \acute{e} .

Curves XIX, Na_2SO_4 , and XX, NaHSO_4 , illustrate clearly the real danger to the consumer from the presence of even a little acid sulfate in his nitric acid. Its effect on the density is profound and a comparison with the effect of NaNO_3 (Curve III superimposed)



is edifying. It was interesting to note that the curve for NaNO_3 (III) lay exactly on that for NaHSO_4 (XX) as though NaNO_3 went into solution as an acid nitrate, for NaHSO_4 could hardly go into solution as a nitrate.

FINANCIAL BEARING

Enough results have been given to indicate the possibility of profitable sophistication of nitric acid and at any rate to warn against serious loss to consumers. The indication of a few financial possibilities will suffice to point out clearly the dangers of these opportunities for salt admixture in commercial acid.

Our contract called for "Aqua Fortis 40° Pale" at 9 cents f. o. b. (9.5 cents delivered). The *Oil, Paint and Drug Reporter's* quotations, June 16, 1916, were as follows:

Aqua Fortis	Extractions of Soda	Salt Cake (White)
80	70 per cent spot	0.00 per cent
80	70 per cent	0.00 per cent
80	80 per cent	0.00 per cent
80	80 per cent	0.00 per cent

These are, of course, war prices. The corresponding quotations, June 17, 1917, were:

Aqua Fortis	Extractions of Soda	Salt Cake
80	70 per cent	0.00 per cent
80	80 per cent	0.00 per cent
80	80 per cent	0.00 per cent
80	80 per cent	0.00 per cent

Nitric acid is quoted from a fraction to a full unit higher for the same strength.

If cost of materials be figured in the case where 40° B \acute{e} HNO_3 is diluted 3.4 per cent of its weight of NaNO_3 and then permitted the addition of 6.3 per cent of water before the gravity fell to 40° B \acute{e} again, we reach the following statement:

Buying always at top market and expecting on sale only bottom market,

100 lbs. 40° B \acute{e} Aqua Fortis at 8 c.	\$8.25
3.24 lbs. NaNO_3 at 3 c.	0.10
6.0 lbs. water	0.00
Total 109.24 lbs. 40° B \acute{e} mixture costing	8.35
109.24 lbs. 40° B \acute{e} Aqua Fortis at 8 c. brings	9.04
at 8 c.	9.04
Minimum Margin to producer per 100 lbs. initial acid	0.39
Minimum Excess (dead loss) paid by consumer at 8 c.	0.49
per 100 lbs. purchased	0.45
Minimum Excess at ante-bellum prices per 100 lbs. purchased at $4\frac{1}{4}$ c.	0.40

There would have been no excess paid by purchaser under extreme minimum condition at $4\frac{1}{4}$ cents in ante-bellum times.

In the case of the data where 40° B \acute{e} acid saturated with NaNO_3 permitted the addition of NaNO_3 solution to such an extent that a NaNO_3 total of 4.8 per cent of the weight of the original 40° B \acute{e} HNO_3 had been added and an addition of 8.3 per cent of water or a total of 13.1 per cent before 40° B \acute{e} was again reached, we have the following situation:

100 lbs. 40° B \acute{e} Aqua Fortis at $8\frac{1}{4}$ c.	\$8.25
4.8 lbs. NaNO_3 at 3 c.	0.14
8.3 lbs. water	0.00
Total 113.1 lbs. 40° B \acute{e} mixture costing	8.40
113.1 lbs. 40° B \acute{e} Aqua Fortis at 8 c. brings	9.33
at 8 c.	9.05
Minimum Margin to producer per 100 lbs. initial acid	0.65
Minimum Excess (loss) paid by consumer per 100 lbs. purchased at 8 c.	0.70
Minimum Excess at ante-bellum prices per 100 lbs. purchased at $4\frac{1}{4}$ c.	0.05
Minimum Excess at ante-bellum prices per 100 lbs. purchased at $4\frac{1}{4}$ c.	0.54

Cost of materials follows for the case where 42° HNO_3 was diluted with 9 parts of water and then saturated with 7.1 parts of NaNO_3 , giving a total of 17.1 parts of a mixture with specific gravity 1.366 or 38.9° B \acute{e} .

100 lbs. 42° B \acute{e} Aqua Fortis at 8 c.	\$8.40
7.10 lbs. NaNO_3 at 3.1 c.	22.01
100 lbs. water	0.00
Total 117.10 lbs. 38.9° B \acute{e} mixture costing	30.41
117.10 lbs. 38.9° B \acute{e} Aqua Fortis at 8 c. brings	9.33
Minimum Margin to producer per 100 lbs. initial acid	0.65
Minimum Excess (loss) paid by consumer per 100 lbs. purchased at 8 c.	0.70
Minimum Excess at ante-bellum prices per 100 lbs. purchased at $4\frac{1}{4}$ c.	0.05
Minimum Excess at ante-bellum prices per 100 lbs. purchased at $4\frac{1}{4}$ c.	0.54

This is a margin over cost of materials of \$102.02 on an investment of \$30.51, but it will be noticed that the margin is really greater than this for the mixture was 38.9° B \acute{e} , and it could stand much more dilution before it reached 38° B \acute{e} , the acid quoted at $7\frac{1}{4}$ cents, and this would materially increase the margin derived above.

The consumer in purchasing 1710 lbs. really received 100 lbs. of 42° B \acute{e} HNO_3 containing 16 lbs. of 38° B \acute{e} acid and 1024 lbs. of water, worth \$0.60 instead of \$1.32.53.

In normal times, 1710 pounds of mixture (10 percent over cost of all materials) could be sold for more than that of 42° B \acute{e} acid (purchased), and the consumer would pay \$06.40 for acid alone, and receive and have immediately \$1.32.

Cost of materials follows for the case where 40° HNO_3 was diluted with 3.4 parts of NaNO_3 and 6.3 of water, giving a mixture with a specific gravity of 1.366 or 38.9° B \acute{e} .

100 lbs. 42° Bé. <i>Aqua Fortis</i> at 8 1/2 c.....	\$8.50
197 lbs. NaNO ₃ at 3.1 c.....	6.11
313 lbs. water.....
Total 610 lbs. 36.5° Bé. mixture costing.....	\$14.61
610 lbs. 36° Bé. <i>Aqua Fortis</i> at 7 1/2 c brings.....	\$48.75
Minimum Margin to producer per 100 lbs. initial acid.....	\$81.14
Minimum Excess (loss) paid by consumer per 100 lbs. purchased at 7 1/2 c.....	\$ 6.10
Minimum Excess at ante-bellum prices (3 1/2 c.) per 100 lbs. purchased.....	2.80

Cost of materials follows for the case where 40° HNO₃ was mixed with 12.62 parts Na₂SO₄ and 15.15 parts of water, giving a 40° Bé. solution.

100 lbs. 40° Bé. <i>Aqua Fortis</i> at 8 1/4 c.....	\$ 8.25
12.62 lbs. Na ₂ SO ₄ at 0.7 c.....	0.09
15.15 lbs. water.....
Total 127.77 lbs. 40° Bé. mixture costing.....	\$ 8.34
127 lbs. 40° Bé. <i>Aqua Fortis</i> at 8 c brings.....	\$10.16
Minimum margin to producer per 100 lbs. initial acid.....	\$ 1.82
Minimum Excess (loss) paid by consumer per 100 lbs. purchased at 8 c.....	1.51
Minimum Excess at ante-bellum prices per 100 lbs. purchased at 4 1/4 c.....	0.51

In the case where NaHSO₄ (nitre cake) was used the total matter added was much higher than in the case of sodium sulfate without lowering the gravity below 40° Bé. The margin to the producer would be greater, therefore, than with the normal sulfate and particularly so since nitre cake is a drug on the market at present with most acid makers and usually is with many of them.

DISCUSSION

With these quotations in mind it is evident that it would be profitable to buy 42° acid at the top price, 8 1/2 or 5 cents in war or normal times, respectively, and add to it sodium nitrate or a strong nitrate of soda solution or either of the sulfates of soda in such a way as greatly to stretch the amount of acid on hand by diluting with water, and selling at even the lowest quotation for the particular specific gravity obtained.

Not as much salt and water need be present as in the extreme possible cases cited. The profit to the producer and the loss to the consumer can be of any size short of the maximum. It has been shown by the data given that even a casual boil-over of NaHSO₄ during distillation may entail an unnecessary loss to the consumer by unduly increasing the producers' yields at the expense of the consumer.

Even 1 cent per pound is a severe raise on the market in the case of 9 cent acid and may spell disaster to many operations.

It seems likely that no fraud was intended in the case which caused this investigation and, therefore, the name of the manufacturer has been withheld even in private conversation. Further deliveries, however, were refused. It would seem that the presence of the sulfuric radical in the nitrate separating from the acid shows either large amounts of sulfuric acid in the nitric acid or the results of a boil-over of nitre cake or "soup." The fact that the acid always arrived of the correct specific gravity does not signify intentional adulteration, for the final correction of the specific gravity might be made by an employee who had no knowledge that a boil-over had occurred.

The presence of SO₄ in reagent ("pure") HNO₃ has been long known though no commercial informa-

tion is published. In one case¹ the manufacturer suggested that it came from the "salt cake" used in making the bottles in which the acid was stored.

It is unlikely that adulteration of commercial acids is practiced to any extent. Obviously no reputable manufacturer would avail himself of the possibilities indicated in this paper. However, these possibilities must be kept in mind by consumers for even operating employees might at times fall to the temptation to better their yield record in this way.

The possibilities herein disclosed of varying amounts of contamination in commercial nitric acid are not of direct financial significance merely, though that phase is serious enough, for it is evident that the presence of salts in quantity may seriously impede processes as well as curtail yields of same. This last effect may be quite serious where the nitric acid failure even to the extent of a few per cent in one operation may cause a greatly magnified fall-off in the finished product, leaving all question of quality out of consideration.

It should be noticed by consumers of most commercial acids such as hydrochloric, sulfuric, and acetic, that similar possibilities exist in these cases. The solubility of salts in some of these is even greater than in the case of nitrates and with some of them little or no inspection is exercised other than specific gravity determinations. Obviously the determination of the acid radical in most cases would give little protection and titration is not satisfactory with some of them. An evaporation test for residual salt would be the only certain single test to eliminate the factor under discussion.

The author wishes to thank Messrs. F. R. Porter, W. J. Becker, H. Mersereau, S. L. Shenefield and T. A. Boyd for checking data by laboratory experiment at different times.

CONCLUSIONS

I—The strength of commercial nitric acid cannot be derived with safety from the specific gravity alone nor from the specific gravity and NO₂ content alone but titration will be necessary in addition provided always that sulfuric acid is found to be absent by qualitative tests. It seems desirable to combine a specific gravity or NO₂ determination with an evaporation test for residual salts.

II—Producers and consumers alike should inspect all commercial acids by an evaporation test.

LABORATORY OF INDUSTRIAL CHEMISTRY
THE OHIO STATE UNIVERSITY
COLUMBUS, OHIO

DETERMINATION OF THE EXPLOSIBILITY OF PYRITES AS WELL AS ITS AVAILABLE SULFUR AND THE SULFUR CONTENT OF ITS CINDERS

By C. R. GYZANDER
Received May 16, 1917

In buying pyrites as a source of sulfur in sulfuric acid manufacture, high content of sulfur in the ore is not necessarily a guarantee for its fitness, since other characteristics have a bearing on the amount of sulfur available for the production of sulfur dioxide. Thus,

¹ Chem. News, 61, 289 and 301.

for example, the explosive property of some varieties of pyrites while rather an aid to high efficiency when the ore is burned as fines, is a great drawback when the ore is to be burned as lump, since the dust caused by explosion of the ore fills up the interstices between the lumps and thus prevents the free access of air, in consequence of which combustion is incomplete, the resulting cinders high in sulfur, and the available sulfur low.

Again, some ores consist of small crystals or particles of pyrites and sand or silica, loosely cemented together and readily broken up during the process of combustion, thus forming dust which may clog and render the material unsuitable as a lump ore.

These two qualities are easily exhibited by heating a lump of the ore on a clay triangle over the naked flame of a Bunsen burner while a screen of fine netting is placed over the lump to prevent the scattering of the small pieces of ore if it does explode.

The quantitative determination of its explosibility or crumbling quality is accomplished by heating the ore in a covered dish at a high temperature, until crumbling or explosibility has ceased, then cooling, screening and weighing the ore, originally selected to remain on a certain size screen while passing through a next larger size. Calling the total weight of the burnt ore a , and the portion that passes through the smaller screen b , the per cent explosibility or crumbling of the ore is $100 \times b/a$. By the use of graded sieves, the percentage of the various sizes resulting from the explosion may be determined.

Some authorities claim to destroy or minimize the explosive effect by a gradual preheating of the ore, but the writer's observations in this direction do not confirm that statement, possibly because the exact conditions of a successful preheating were unknown. Twenty-four hours' preheating at temperatures from 120 to 340° C. (at which temperature explosibility seems to commence) has no apparent effect in diminishing the explosive quality.

Some users of ore have offered as an explanation for the explosibility of a pyrites that its mass is subject to an unequal internal strain, but the fact that preheating seems to have no effect in annealing or equalizing this strain, even up to temperatures at which explosion begins, seems to speak against this theory.

Dr. Lunge suggests that the explosibility is due to pockets of CO₂ gas, the expansion of which, during the process of combustion, causes the breakage of the lump with more or less explosive violence. The correctness of this view seems to be borne out by the fact that the explosibility diminishes as the ore is crushed down in size, a process which naturally would tend to destroy any existing pockets through cleavage.

If actual values with reference to explosibility are sought the ore should be heated in the same size that it is to be used in the burners, i. e., a definite weight of ore should be graded by screening and each portion tested separately, for explosibility. But this would involve the use of a cumbersome laboratory apparatus, while a relative explosibility, i. e., the ex-

plosibility of the ore of a uniform but small size, would be equally as valuable as a means of comparison of two grades of ore, while the laboratory apparatus would be more manageable.

For a comparative test, therefore, the ore may be crushed to pass a 7/16 but remain on a 5/16 round hole screen, when, after heating, what passes through the 5/16 screen is explosive ore. This portion may now be graded to determine dust qualities.

As an example of the application of this explosive test the following cases are quoted.

The ores tested were Spanish "Perrunal" and Rio Tinto washed ore: 240 g., crushed to pass a 7/16 but to remain on a 5/16 round hole screen, were heated in a covered agate wash bowl, placed in a suitable ring tripod and heated with a large Méker burner for 1/2 hr., when all cracking had ceased. After cooling, the ore was sifted with the result given in Table I.

ORE:		SPANISH "PERRUNAL"		RIO TINTO WASHED	
SCREEN ANALYSIS		Lot No. 1	Lot No. 2	Lot No. 1	Lot No. 2
On 5/16 round-hole Screen	232.5 g.	184.8 g.		209.5 g.	182.0 g.
On 10-mesh Sieve	3.8	20.8		9.2	40.0
On 20-mesh Sieve	0.2	4.7		1.0	1.0
Through 20-mesh Sieve	0.2	7.9		3.1	3.0
TOTAL	236.7 g.	218.2 g.		222.8 g.	226.0 g.
CORRESPONDING PERCENTAGES					
Non-explosive Ore	98.22	84.69		94.03	80.6
Explosive Ore	1.78	15.31		5.97	19.4
TOTAL	100.00	100.00		100.00	100.0
EXPLOSIVE ORE CLASSIFIED					
On 10-mesh Sieve	1.60	9.53		4.12	17.7
On 20-mesh Sieve	0.09	2.15		0.44	0.4
Through 20-mesh Sieve	0.09	3.63		1.41	1.3
TOTAL	1.78	15.31		5.97	19.4

This goes to show what a wide difference the same kind of ore does exhibit as to explosibility, and the same holds as to cinder tests which, with the "Perrunal" ore, vary from less than 1 per cent for a non-explosive ore up to 5 and 6 per cent for explosive ore, while the Rio Tinto cinders vary from 4 to 10 per cent, due to choking with dust; these cinder tests refer to the ores burnt as lump ore.

Though these explosive tests do not give absolute figures they indicate that one may reasonably look for a difference in the cinder values of such ores when burned as lump ore. What *exact* relation this relative explosion test bears to the cinder value is not known, since no systematic determinations have been carried out on separate lots, but, whatever relation does exist, it can be of only a local significance, since a lump burner with a large sectional area and shallow depth will be less affected by the dust than one of small sectional area and greater depth, as the chances are that the latter will retain more of the obstructive dust than the former. The figures in Table II may aid in judging the fitness of an ore for use in lump form in the production of SO₂. It might happen that the difference in sulfur content of the cinders of an explosive ore referred to burners of a certain construction, when compared with that of a non-explosive ore, would be the legitimate sulfur content of the pure ore if it were non-explosive, would more than pay for the cost of crushing the lump into fines, the most effective form in which an explosive ore can be handled.

That the size of the lump does cause a difference in the explosive test will be seen from the figures in Table II, which were obtained with a specially selected explosive "Perrunal" ore. The explosibility dropped from 100 to 7.71 per cent by varying the size of the lump from that of a hen egg to that of coarse fines.

TABLE II

No.	SIZE OF ORE	EXPLOSIBILITY
1	Lump, hen-egg size	100.00
2	Passing 1 in., remaining on 3/4 in. round hole Screen	89.01
3	Passing 3/4 in., remaining on 1/2 in. round hole Screen	37.42
4	Passing 6-mesh, remaining on 10-mesh Sieve	7.71

SERIES ANALYSIS OF EXPLOSIVE PARTS OF ORE				
PERCENTAGES	No. 1	No. 2	No. 3	No. 4
On 1/4 round-hole Screen	16.23	41.90
On 10-mesh Sieve	49.23	22.87	26.63	...
On 20-mesh Sieve	16.16	8.71	4.76	6.33
Through 20-mesh Sieve	18.38	15.53	6.03	1.38
TOTAL	100.00	89.01	37.42	8.71

But even though the ore is non-explosive or non-crumbling it still does not follow that it is economical as a source of sulfur, since its burning qualities may be poor, *i. e.*, the rate at which it gives up its sulfur, the rate of change of the ore, is low, or, as it is usually expressed, it burns more or less freely, and it is evident that, since the ore is subject to the process of burning, whatever it may be, for a definite length of time, the more freely burning ore will have less sulfur remaining unburnt in a given time, than the ore that burns more slowly, if such a quality does exist as an adjunct to a lot of pyrites.

Experience has proved that it does, and, therefore, the determination of the rate of change of combustion and its application to the determination of available sulfur as well as the sulfur content of the cinders will now be described.

METHOD PROPOSED

The method consists of burning a convenient amount of the ore, crushed to pass a 50-mesh sieve, in a standard size dish, under standard conditions of temperature, for various intervals of time, and determining the amount of unburnt sulfur in the resultant cinders, which furnishes the data necessary for the calculation of the rate of change of the ore.

Since the combustion of pyrites, like most other chemical reactions, is influenced by temperature, it is absolutely necessary to have the analytical temperature conditions constant at all times. Further, the ore which is used as a standard for comparison should be a fines ore, or, a non-explosive, non-crumbling lump ore, of which the sulfur value of its cinders is also known.

MANIPULATION

As a source of heat the author uses an electric furnace which attains a temperature of 1000° F. and heats 2 g. of ore, crushed to pass a 50-mesh sieve and accurately weighed, in small, thin-walled, electro-quartz dishes of uniform size and thickness. The ones the author uses hold 10 cc. and have a thickness of wall of 1/32 in.

Three of them are placed, close together, in a sheet-iron rack (with handle) the exact size of the furnace and having holes which fit the respective dishes so that they touch the bottom of the oven when placed there. After 15-minute intervals of time, or longer if necessary, each dish is lifted, separately, out from

the furnace with crucible tongs, while an empty dish replaces it in the furnace, so as to insure that the circulation of heat remains constant as nearly as possible. The reaction is stopped by placing 5 g. Na₂CO₃ on top of the dish as soon as it comes out of the furnace, and the dish is left to cool.

There thus results three samples of cinders, having been exposed for known intervals of time, say for 15, 30 and 45 minutes, respectively. The sulfur content of each is determined by transferring the dish of cinders and Na₂CO₃ to a roomy platinum dish, breaking up the cake of cinders with a flattened, thick, glass rod, adding 5 g. NaNO₃, mixing and fusing to oxidize the sulfur.

After cooling, it is lixiviated with water, filtered, the filtrate acidified with excess of HCl in a covered glass dish, CO₂ boiled off, the solution evaporated to dryness, the dry mass dissolved in water, acidified with HCl, filtered from SiO₂, precipitated by BaCl₂ and this washed, dried, ignited, cooled and weighed. From these weights we ascertain the sulfur content which corresponds to $a - x$ in Equation (1) below. Whether we regard the combustion of the pyrites merely as a distillation of its sulfur content, or as an oxidation process or both, the reaction may be treated as one of the first order, since, even in the case of the oxidation, both in the analytical and practical operation, the burning ore is continually being treated with fresh quantities of air, in consequence of which the oxygen phase of the reaction is constant and hence only the sulfur is undergoing change. The rate of change is, therefore, expressed by the differential equation

$$(1) \quad \frac{dx}{dt} = K(a - x)$$

which when integrated for $x = 0$ and $t = 0$ becomes

$$(2) \quad \frac{1}{t} \log_e \frac{a}{a - x} = K$$

Here a represents the amount of sulfur in the 2 g. of ore used.

From Equation (2) we see that, since the amount of action, or x , in a given time t , is proportional to a , other conditions being constant, m times as much ore, or ma g., would give m times as much action or mx in the time t ; hence the logarithmic factor of the equation becomes

$$\frac{ma}{ma - mx} = \frac{ma}{m(a - x)} = \frac{a}{a - x} \text{ or constant.}$$

Therefore, the value of K is independent of the value of a and so we may use the constant quantity 2 g. of ore, even if the samples do not always carry the same amount of sulfur. The value of K is still proportional to the velocity of the reaction, if the temperature conditions are constant, or any other conditions that may have an influence on the reaction are constant, like size and thickness of dishes used for the combustion.

As a sample for comparison the writer uses a non-explosive, non-crumbling variety of "Perrunal" ore which gave the tests noted below.

Sulfur in ore, 50.5%		Sulfur in cinders, 1.0%	
$2 \text{ g. ore} = \frac{50.5}{100} \times 2 = 1.01 \text{ g. sulfur} = a$			
t	$a - x$	K_{10}	
15	0.37163	0.38020	Av. K_{10} 0.03895
30	0.06351	0.04004	
45	0.01813	0.03879	

K_{10} represents the value of the velocity constant when referred to common logarithms in Equation (2). With reference to natural logs it is to be multiplied by 2.30259, hence $K = 2.30259 K_{10} = 0.089686$.

Since K is independent of the value of a , we may refer it to 100 g. of ore when determining available sulfur and cinder sulfur, in preference to using 2 g. or the analytical amount used in determining K .

The composition of the cinders is, in all probability, a mixture of Fe_2O_3 and Fe_3O_4 , but we will assume them to be Fe_2O_3 as sufficiently correct for our purpose.

The next question is, then, how long shall we have to burn 100 g. of the ore, under the same conditions of temperature and so on, as prevailed when determining K , in order that the cinders may contain 1 per cent sulfur?

If to do this, x g. of sulfur burn off, the cinders will be $100 - x + \frac{48}{128.24} x$, since for every 4 atoms of sulfur burnt off, 3 atoms of oxygen are taken up to form Fe_2O_3 , and we have the proportion

$$\frac{100 - x + \frac{48}{128.24} x}{50.5 - x} = \frac{1.0}{0.03895} \quad (50.5 - x) = 100 - 1$$

$$a \quad x = 0.69 \text{ per cent sulfur left in cinders}$$

$$x = 49.81 \text{ per cent available sulfur burnt off}$$

$$a = 50.50$$

Substituting these values in Equation 2 we have, when using common logs:

$$\frac{2.30259}{t} \log \frac{50.5}{0.69} = 0.089686 \text{ whence } t = 48 \text{ minutes}$$

That is to say, 48 minutes is the time to which we must refer the burning of all ores, so long as their rate of burning or the value of K , has been determined in the electric furnace.

If for some reason this has to be given up, the value of K , will have to be reestablished for the new con-

ditions, before we may make any computations as to cinder values or available sulfur.

Another lot of "Perrunal" ore tested as follows:

Sulfur in ore = 49.3 per cent Sulfur in cinder = 2.3 per cent

$$2 \text{ g. ore} = \frac{49.3}{100} \times 2 = 0.9860 = a$$

t	$a - x$	K_{20}	
15	0.37145	0.02826	Av. K_{10} 0.03239
30	0.10163	0.03296	
45	0.02373	0.03596	

$$K = 2.30259 K_{10} = 0.07458$$

100 g. of this ore, burning as above for 48 minutes, would leave $a - x$ sulfur for cinders and we have

$$\frac{2.30259}{48} \log \frac{49.3}{a - x} = 0.07458$$

$$a - x = 1.37 \text{ g. sulfur left in cinders}$$

$$x = 47.93 \text{ g. available sulfur}$$

$$a = 49.30$$

$$100 - 47.93 + \frac{48}{128.24} \times 47.93 = 50.00 \text{ g. Fe}_2\text{O}_3 \text{ cinders}$$

$$\frac{1.37}{50.01} \times 100 = 2.0 \text{ per cent sulfur in cinders}$$

$$\text{Found} = 2.3 \text{ per cent sulfur in cinders}$$

The above value of K_{10} is not in very good agreement as a constant, but the calculations show that it is near enough for this case. Had the sulfur value of the cinders been required before burning the ore it would have been a safer practice to repeat the analytical operation with a view to obtaining better agreeing values of K .

Four analyses are compared with actual tests of the materials in Table III. The results on No. 4 show that burnt as fines, the ore would have left only 1.33 per cent sulfur in the cinders, but on account of the explosive dust and clogging this rose to 4.10 per cent.

In August of 1908, Carridad lump ore was burned at one set of burners, giving high cinder sulfur, while Eustis lump was being burned at another set of burners with normal sulfur test in the cinders. As it happened that men with less experience were engaged on the Carridad ore it was not unreasonable to suspect that the men, either from laziness or ignorance, had not given the attention to breaking and charging that they should, so the author tried the determination of the rate of change of the two ores, with the expectation that

TABLE III.—COMPARISON OF ACTUAL ANALYSES WITH CALCULATED RESULTS			
1.—A sample of Eustis fine		2.—Another lot of Eustis fines	
ACTUAL ANALYSES		ACTUAL ANALYSES	
A. Sulfur in ore	49.8	A. Sulfur in ore	44.9
B. Sulfur in cinder	0.7	B. Sulfur in cinder	2.70
CALCULATION FROM A		CALCULATION FROM A	
$a = \frac{49.8}{100} \times 2 = 0.996$		$a = \frac{44.6}{100} \times 2 = 0.892$	
t	$a - x$	t	$a - x$
20	0.19761	15	0.43476
40	0.01957	30	0.18767
60	0.01468	45	0.04066
Average K_{10}	0.0377	Average K_{10}	0.01748
$K = 2.30259 K_{10} = 0.08780$		$K = 2.30259 K_{10} = 0.04044$	
Burning 48 min. in Fe cinder		Burning 48 min. in Fe cinder	
$\frac{2.30259}{48} \log \frac{49.8}{a - x} = 0.08780$		$\frac{2.30259}{48} \log \frac{44.9}{a - x} = 0.04044$	
$a - x = 1.60 \text{ sulfur in cinder}$		$a - x = 1.00 \text{ sulfur in cinder}$	
$x = 48.18 \text{ Available sulfur}$		$x = 43.90 \text{ Available sulfur}$	
$a = 49.8$		$a = 44.00$	
$100 - 48.18 + \frac{48}{128.24} \times 48.18$		$100 - 43.90 + \frac{48}{128.24} \times 43.90$	
$= 1.06 \text{ per cent sulfur in cinder}$		$= 3.83 \text{ per cent sulfur in cinder}$	
$\frac{1.60}{49.8} \times 100$		$\frac{1.00}{44.00} \times 100$	
$= 3.16 \text{ per cent sulfur in cinder}$		$= 2.50 \text{ per cent sulfur in cinder}$	

TABLE III.—COMPARISON OF ACTUAL ANALYSES WITH CALCULATED RESULTS			
3.—Carridad lump ore		4.—Eustis lump ore	
ACTUAL ANALYSES		ACTUAL ANALYSES	
A. Sulfur in ore	41.0	A. Sulfur in ore	41.0
B. Sulfur in cinder	3.00	B. Sulfur in cinder	4.10
CALCULATION FROM A		CALCULATION FROM A	
$a = \frac{41.0}{100} \times 2 = 0.820$		$a = \frac{41.0}{100} \times 2 = 0.820$	
t	$a - x$	t	$a - x$
15	0.60000	15	0.60000
30	0.34444	30	0.34444
45	0.20000	45	0.20000
Average K_{10}	0.0377	Average K_{10}	0.0377
$K = 2.30259 K_{10} = 0.08780$		$K = 2.30259 K_{10} = 0.08780$	
Burning 48 min. in Fe cinder		Burning 48 min. in Fe cinder	
$\frac{2.30259}{48} \log \frac{41.0}{a - x} = 0.08780$		$\frac{2.30259}{48} \log \frac{41.0}{a - x} = 0.08780$	
$a - x = 1.00 \text{ sulfur in cinder}$		$a - x = 1.00 \text{ sulfur in cinder}$	
$x = 40.00 \text{ Available sulfur}$		$x = 40.00 \text{ Available sulfur}$	
$a = 41.0$		$a = 41.0$	
$100 - 40.00 + \frac{48}{128.24} \times 40.00$		$100 - 40.00 + \frac{48}{128.24} \times 40.00$	
$= 1.00 \text{ per cent sulfur in cinder}$		$= 1.00 \text{ per cent sulfur in cinder}$	
$\frac{1.00}{41.0} \times 100$		$\frac{1.00}{41.0} \times 100$	
$= 2.44 \text{ per cent sulfur in cinder}$		$= 2.44 \text{ per cent sulfur in cinder}$	

the suspicions regarding the men's guilt would be confirmed.

The results, however, entirely exonerated the men from all blame and showed the cause to be due to the poor burning quality of the ore itself. At that time I did not have the electric furnace, but made the determinations in one and the same dish placed on a tripod and heated with a small Méker burner, shielded from draughts by a sheet iron hood. The results were as given in Table IV.

TABLE IV

EUSTIS LUMP ORE ACTUAL ANALYSIS			CARRIDAD ORE ACTUAL ANALYSIS		
A—Sulfur in ore.....	45.8%		A—Sulfur in ore.....	43.7%	
B—Sulfur in cinders.....	3.0%		B—Sulfur in cinders.....	9.7%	
CALCULATION FROM A			CALCULATION FROM A		
$a = \frac{45.8}{100} \times 2 = 0.9160$			$a = \frac{43.7}{100} \times 2 = 0.8740$		
t	$a - x$	K_{10}	t	$a - x$	K_{10}
15	0.3705	0.02620	15	0.5027	0.01601
30	0.1893	0.02282	30	0.3743	0.01435
45	0.0446	0.02916	45	0.1945	0.01450
Average K_{10}	0.02606		Average K_{10}	0.01495	
$\therefore K_p = 2.30259 K_{10} = 0.06001$			$\therefore K_p = 2.30259 K_{10} = 0.03442$		
$(100 - x + \frac{48}{128.24} x) : (45.8 - x)$			$\frac{2.30259}{51} \log \frac{33.7}{a - x} = 0.03442$		
$= 100 : 3$			$a - x = 7.55 \text{ g. Sulfur in cinders}$		
$a - x = 2.18 \text{ g. Sulfur in cinders}$			$x = 36.15 \text{ Available Sulfur}$		
$x = 43.62 \text{ g. Sulfur burnt off}$			$a = 43.70$		
$a = 45.80$			$100 - 36.15 + \frac{48}{128.24} \times 36.15$		
$\frac{2.30259}{t} \log \frac{45.8}{2.18} = 0.06001$			$= 76.91 \text{ per cent cinder}$		
$t = 51 \text{ minutes}$			$\frac{7.55}{76.91} \times 100$		
			$= 9.80 \text{ per cent sulfur in cinders}$		

Again in November that same year some of this Carridad ore was burned as fines with such unusual low sulfur test in the cinders, compared with the lump ore, that now the suspicion arose as to the accuracy of the cinder samples or the cinder test. Again, the determination of the rate of change of the fines ore exonerated the parties concerned, and placed the explanation on the better burning qualities of the fines ore. As it was not any surety that the flame could be adjusted to the exact conditions prevailing when the test of the lump ores was made the preceding August, I chose for comparison a sample of Bustis fines ore burned the same month as the Carridad fines. The results are given in Table V.

TABLE V

EUSTIS FINES ORE ACTUAL ANALYSIS			CARRIDAD FINES ACTUAL ANALYSIS		
A—Sulfur in ore.....	46.1%		A—Sulfur in ore.....	42.2%	
B—Sulfur in cinders.....	2.6%		B—Sulfur in cinders.....	2.1%	
CALCULATION			CALCULATION		
$a = \frac{46.1}{100} \times 2 = 0.9220$			$a = \frac{42.2}{100} \times 2 = 0.8440$		
t	$a - x$	K_{10}	t	$a - x$	K_{10}
15	0.3962	0.0247	15	0.3628	0.0245
30	0.2120	0.0214	30	0.1941	0.0213
45	0.0675	0.0253	45	0.0621	0.0252
Average K_{10}	0.0238		Average K_{10}	0.0236	
$\therefore K_p = 2.30259 K_{10} = 0.0548$			$\therefore K_p = 2.30259 K_{10} = 0.0543$		
$(100 - x + \frac{48}{128.24} x) : (46.1 - x)$			$\frac{2.30259}{58} \log \frac{42.2}{a - x} = 0.0543$		
$= 100 : 2.6$			$a - x = 1.80 \text{ g. Sulfur in cinders}$		
$x = 44.22 \text{ g. Sulfur burnt off}$			$x = 40.40 \text{ g. Available Sulfur}$		
$a - x = 1.88 \text{ Available Sulfur left in cinders}$			$a = 42.20$		
$a = 46.10$			$100 - 40.4 + \frac{48}{128.24} \times 40.4$		
$\frac{2.30259}{t} \log \frac{46.1}{1.88} = 0.0548$			$= 74.72 \text{ g. cinders}$		
$t = 58 \text{ minutes}$			$\frac{1.80}{74.72} \times 100$		
			$= 2.40 \text{ per cent sulfur in cinders}$		

CONCLUSION

It is well known that as regards available sulfur in pyrites no method has hitherto been presented that does at all agree with practice.

To account for the low yield of available sulfur it is the custom in some places at least, to determine such heavy metals as lead, copper and zinc and deduct from the total sulfur that equivalent to sulfates of these metals, but even so, there is usually no agreement with practical yields and as the sulfates of these heavy metals are all decomposable at a bright red heat, the temperature of the burners, it is evident that such a practice is faulty, even if it occasionally should seem to agree with practical results.

The only reliable method of arriving at the available sulfur content of a pyrites is, as has been shown, the determination of the rate of change of the ore, compared with some other ore that works normally and the available sulfur of which is known.

Furthermore, this determination serves as a check upon results already obtained and so helps to place the true explanation upon them instead of subjecting them to mere suspicions, which, though seemingly reasonable, may still be untrue.

THE MERRIMAC CHEMICAL COMPANY
EVERETT, MASSACHUSETTS

A CONVENIENT APPARATUS FOR ELECTROMETRIC TITRATION DEPENDING ON THE CHANGE OF OXIDATION POTENTIAL, AND ITS APPLICATION TO THE DETERMINATION OF SMALL QUANTITIES OF CHROMIUM IN STEEL

By G. L. KELLEY, J. R. ADAMS AND J. A. WILEY

Received January 17, 1917

THE APPARATUS

The apparatus for electrometric titration described by Hildebrand¹ and Forbes² and the modified form described by Kelley and Conant³ consisted of a number of separate parts, many of which were not well adapted to purposes to which they were put. In the present apparatus, which was made for us by Leeds and Northrup, the parts have been selected to give the greatest efficiency for such work and are combined as a unit in a single rugged instrument. The present instrument can be moved about the laboratory readily, requiring for its operation only the connection of a plug with an electric light socket. It is complete in that it carries a potentiometer system, a motor for the operation of the stirrer and the two burettes for the oxidizing and reducing solutions.

ILLUSTRATION

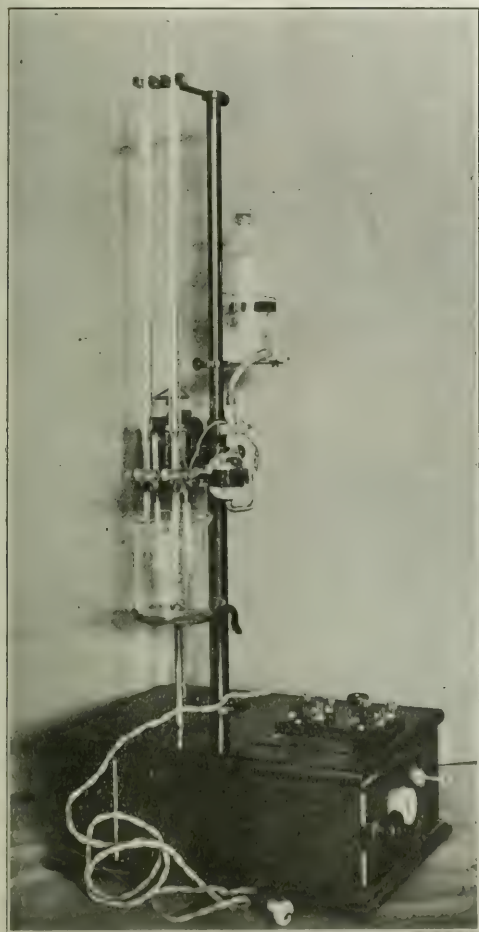
As will be seen in the illustration, the apparatus consists essentially of a wooden box with a metal upright carrying the motor, burettes and electrodes. In the box are two dry cells, an adjustable resistance and a Leeds and Northrup reflecting galvanometer of the form known as Type 2400. This galvanometer is sufficiently sensitive for the purpose and has the further advantage of a very short period. On the

¹ J. Am. Chem. Soc., **36** (1913), 869.

² Ibid., **35** (1913), 1527.

³ Ibid., **38** (1916), 341.

upper surface of the box is a ground glass plate on which the light from the galvanometer is thrown. This puts it in a position where it may be conveniently observed by the operator during titration. A knob on top of the box permits of adjusting the zero point of the galvanometer and one on the side controls the resistance. A plug and resistance coil, also on the side, make it possible to vary the resistance and so increase the range of potentials over which the adjustable resistance may be made to operate. The standard carries the burettes,



the electrodes, and the motor for driving the stirrer. In addition, provision has been made for a reservoir of the electrolyte which is used in the calomel cell (a concentrated solution of potassium or sodium nitrate and calomel) to make conveniently possible without change in its potential the displacement of the impure electrolyte which may have accumulated in the tip of the calomel electrode. This is accomplished by opening the stopcock at the top of the electrode enough

to let one or two drops pass. A hard rubber pan, carried on an adjustable support, serves to center the beaker in which the titration is made, and because of stops prevents carrying the beaker high enough to strike the electrodes or stirrer. Two switches are mounted on the box. One controls the motor and galvanometer light and the other throws in the potentiometer circuit. All connections, except to dry cells, are soldered and the insulation is designed to make as little as possible trouble from "leaks."

To operate the instrument, a beaker containing the solution to be analyzed is placed on the rubber pan, and the support raised and locked in position. The switch controlling the galvanometer light and motor is then closed. The other switch closes the potentiometer circuit and a slight turn of the knob controlling the resistance is sufficient to bring the beam of light from the galvanometer onto the scale. In titrating a series of solutions at one time this latter adjustment need be made only once. During the operation, which is quick, certain and convenient, the analyst watches the beam of light until a permanent change of potential is noted. The apparatus has been in satisfactory daily use in this laboratory for several months for the determination of chromium and vanadium in steel and ferro alloys.

THE DETERMINATION OF SMALL AMOUNTS OF CHROMIUM IN STEEL

Many methods for the determination of chromium in steel make possible the determination of this element to within 0.01 or 0.02 per cent of the weight of the sample. Other more rapid methods show variations amounting to 0.10 per cent. In this paper we give figures showing that determinations may be made which agree within 0.001 per cent and which are probably accurate to nearly this degree. This has been made possible by the development of the instrument described above. In a paper by one of us¹ chromium determinations on a given sample are shown as varying by several hundredths of a per cent. With this instrument and solutions of the same strength, these differences have been reduced to 0.01 per cent. By using more dilute solutions in the analysis of samples containing small amounts of chromium, the determinations were made with a corresponding degree of accuracy.

A standard chromate solution was prepared of such strength that one liter of solution contained 1 gram of chromium. Twice crystallizing potassium dichromate of C. P. grade, powdering and drying it at 150° for several hours gives a product from which solutions may be made accurate to 1 part in 100,000. If it is desired to standardize such a solution with permanganate to a color end-point, the most convenient procedure is to standardize the permanganate by titration against sodium oxalate. This is then accompanied with ferrous sulfate and the chromate is finally titrated by adding an excess of ferrous sulfate and titrating back with permanganate. Care must be taken to obtain corrections on blank titrations for all end-points. With-

out such corrections, the error may amount to 7 to 10 parts in 1000, the figure for chromium appearing too low by this amount. Even when sodium phosphate is used the correction is necessary. It has been the custom in this laboratory to prepare a blank by reducing the chromate solution with SO_2 in hot solution, after which it is boiled gently for 15 min. while a stream of CO_2 is passed in. The solution is then cooled, diluted to the proper volume and permanganate added gradually to the first permanent change in color. During the reduction material reducible by SO_2 other than chromates must be carefully excluded and the presence of halogens is to be avoided also because of the action on the permanganate. Another method of finding this blank consists in adding a quantity of standard ferrous sulfate solution to the solution of chromic salt, which upon titration will be found to have required an amount of permanganate too large by the amount of the correction. The end-point obtained has a color which is described as blue by some and as gray by others. It appears much earlier than the first pink color and it is a more definite point. This method of obtaining the blank is somewhat questionable because the color of the solution of chromic salts is noticeably different from that which results from the reduction of chromates by ferrous sulfate.

If all titrations, except the titration of sodium oxalate with permanganate, are made on the electrometric apparatus, better results are obtained. On this apparatus one may titrate, (1) permanganate and ferrous sulfate, (2) chromate and ferrous sulfate, and (3) chromate, using an excess of ferrous sulfate with respect to the chromate, completing the titration with permanganate and ferrous sulfate. In working with different combinations of oxidizing and reducing reagents on this apparatus, we have noted certain characteristic differences at the end-point. Allowance must be made for this if full advantage is to be taken of the accuracy of which the instrument is capable. In titrating a chromate solution the addition of ferrous sulfate almost invariably produces what Forbes describes as an anomalous rise. In titrating a permanganate solution, this phenomenon does not appear with quite the same regularity and is always less marked. In titrating chromate, the change in potential is always abrupt when the end-point is reached, but with permanganate the addition of as many as 0.2 to 0.4 cc. of ferrous sulfate after the disappearance of the pink color often causes only a gradual change. If now permanganate be added drop by drop the return of the original potential is delayed until one or two drops cause a marked change. One or two additional drops of permanganate are now sufficient to produce a pink color. From this point the titration of the permanganate with ferrous sulfate closely resembles the titration of chromates, in that no change occurs until the end-point is reached when the change is abrupt. It has occurred to us that in adding ferrous sulfate gradually to an excess of permanganate, a suspension of manganese dioxide is built up which requires an appreciable excess of ferrous sulfate for its reduction. On titrating back with permanganate, either the condition is overcome,

or it is so much less marked as to have no appreciable effect upon the behavior of the electrodes. It is our custom to add ferrous sulfate in excess until there is a marked change of potential. Permanganate is then added gradually until the original potential is reached which existed immediately before the fall in potential began or until the further addition of two or three drops causes no further change. The drop-wise addition of ferrous sulfate then gives a sharp and definite end-point.

In connection with the analyses given in this paper 100 cc. of the solution of chromate containing 1 g. Cr in a liter was diluted to 1000 cc. A solution of ferrous sulfate of equivalent strength was similarly diluted. When these solutions were compared their relation was found to be unchanged. These solutions were of such strength that 0.1 cc. corresponded to 0.001 per cent of Cr in a 1 g. sample of steel or to 0.0005 per cent in a sample weighing 2 g. The samples were prepared for titration exactly as described elsewhere.¹

In the table below, we give analyses for chromium on samples of steel issued by the Bureau of Standards. The column marked "Certif. Value" contains the percentage of chromium given on the certificate: it is not known what accuracy is claimed for these figures, but it is probably not greater than 0.003 or 0.004 per cent. In the case of Sample 33, one analyst reports 0.11 and another 0.12.

SAMPLE PER CENT CHROMIUM				SAMPLE PER CENT CHROMIUM			
B. of S. No.	Grams Taken	Certif. Value	Found Electr. Titr.	B. of S. No.	Grams Taken	Certif. Value	Found Electr. Titr.
106.....	2	0.005	0.007(2)	33..	2	0.11	0.113(5)
	2		0.007(2)		2	and 0.12	0.113(5)
	3		0.007(0)		3		0.113(3)
	3		0.007(7)		3		0.113(7)
16a.....	2	0.008	0.009(5)		2		0.011(5)
	2		0.009(5)		3		0.011(3)
19a.....	2	0.08	0.076(8)	34..	2	0.01	0.011(5)
	2		0.076(7)		2		0.011(5)
	3		0.076(5)		3		0.011(3)
	3		0.076(3)		3		0.011(5)

We believe this to be the most sensitive and accurate method known for the determination of small amounts of chromium in complex solutions. Of substances ordinarily present in steel, only vanadium interferes.

RESEARCH DEPARTMENT
THE MIDVALE STEEL COMPANY
PHILADELPHIA

THE PHOTOMICROGRAPHY OF PAPER STRUCTURE

By MILLARD B. HODGSON

Received May 16, 1917

In the study of the ultimate structure of paper, much valuable information can be obtained by photomicrographs of cross-sections of the paper stocks.

Some published accounts have appeared from time to time illustrating the matting together of fibers in paper stocks, but little has been done in the direction of a more intimate study of the subject, and the possibility of data to be obtained from photomicrographs of cross-sections of paper has scarcely been touched upon, one reason for the lack of work in this last direction probably being the difficulty of making cross-sections of paper.

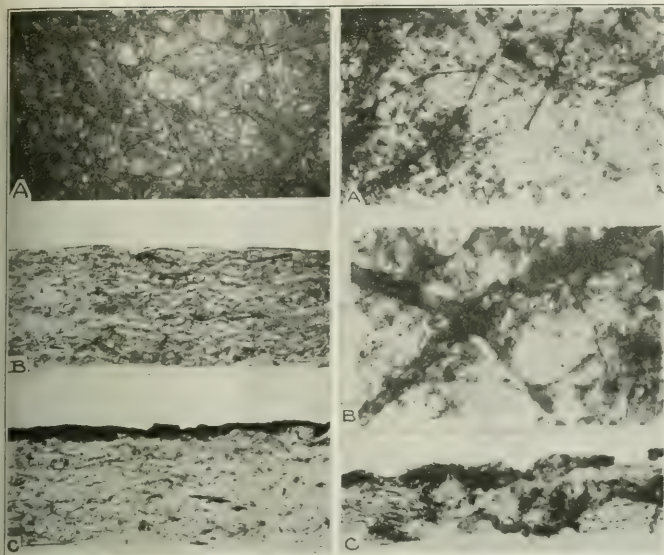


FIG. I—HOT PRESSED DRAWING PAPER
A, Horizontal Section $\times 88$
B, Vertical Section $\times 175$
C, Vertical Section Showing Mark made by Ruhig Pen with India Ink

FIG. III—"LILY OF THE VALLEY" PAPER
(Plant Fiber)
A, Horizontal Section $\times 10$
B, Part of Same Section $\times 88$
C, Vertical Section $\times 175$

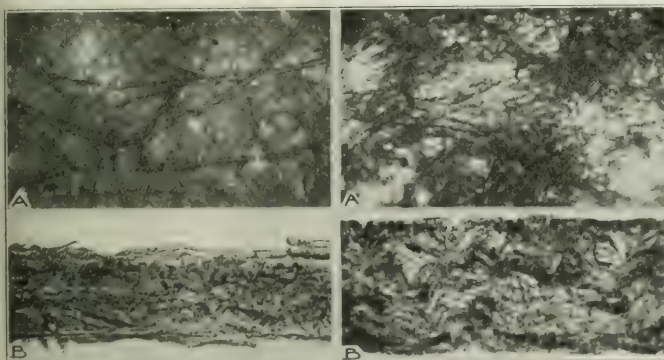


FIG. II—FLAX PAPER

FIG. IV—BROWNS WRAPPING PAPER

In some recent work on the penetration of various materials into paper stocks the writer found it necessary to develop a technique for making sections of paper stocks as thin as 0.05 mm. Considerable difficulty was experienced in obtaining satisfactory results, but the following method was finally adopted:

The particular microtome used was one made by the Spencer Lens Company, of Buffalo, with a micrometer adjustment, enabling cuts from 0.001 to 0.050 mm. to be made.

The paper of which a section is desired is mounted between two pieces of gelatine-coated film, ordinary Kodak NC film being used, the gelatine being moistened to cause it to adhere to the paper, and the paper,

held between the pieces of film, is then placed between two pieces of moderately dry castile soap, the latter being placed in the chuck of the microtome with the paper edge normal to the razor edge. The use of the gelatine is very important as it forms a firm but slightly resilient binder for the paper and prevents the tearing of the surface fibers.

The microtome blade should be sharpened on an Arkansas (fine) stone, with frequent use of a piece of commercial fine soap to keep it from becoming too dull. The saw-tooth edge peculiar to such sharpening is fatal to the cutting of good sections.

Great care should be taken in the microtome work to obtain a satisfactory result in obtaining good sections.

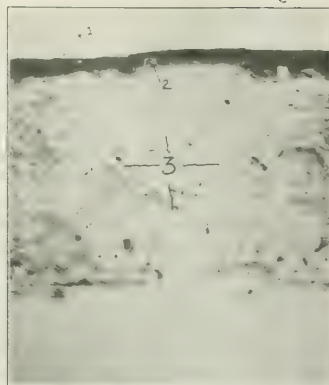


FIG. V—PHOTOGRAPHIC PRINT PAPER (Velox)

VERTICAL SECTION $\times 175$
1, Emulsion Layer Fixed out
2, Substratum of Baryta
3, Paper Stock

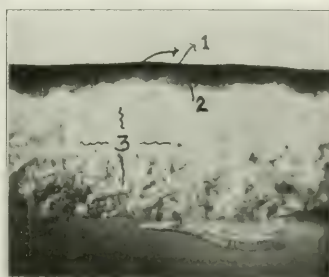


FIG. VI—PHOTOGRAPHIC PRINT PAPER (Thin Stock)

VERTICAL SECTION $\times 175$
1, Silver Deposit
2, Substratum of Baryta
3, Paper Stock

FIGS. II AND IV

A, Horizontal Section $\times 88$
B, Horizontal Section $\times 175$

(The above microphotographs have been reduced to three-fifths of the original size.)

sections. The movement should be kept smooth at all times and the entire mechanism carefully screened from dust. The blades must be kept sharpened to an exact edge, that is, until under fifty diameters of magnification the detectable flaws are negligible.

In cutting, the micro adjustment is set for a 0.03 mm. cut, the action is started slowly, the cut off "specimen" being guided with the finger tip or a bit of card to prevent curling. A good start being assured, the finish of the cut is made in a quick, steady manner. About ten or twenty of such cuts are collected and a few good ones selected for mounting with the aid of a pocket microscope and a small pair of tweezers. The specimens are then mounted on the usual micro slides in Canada balsam diluted with xylol.

Photomicrographs of such sections are easy to make, the best results being obtained by the use of orthochromatic plates with a yellow filter. In the present case, Standard Orthonon plates were used with the Wratten G filter, normal development adjusted to obtain considerable contrast being employed. In some cases the illumination of the camera system was totally direct so that the photographs were taken by light transmitted through the specimen, while in other cases the lighting was partially transmitted and partially reflected from the surface of the paper.

Some of the results obtained are shown in the illustrations. Fig. I, C, shows the way in which the mark of the pen carrying India ink penetrates the paper. Fig. III, "Lily of the Valley" paper, from Brazil, shows the long plant fibers. Figs. V and VI are sections through a Velox print; this photograph was taken by transmitted light so that we see on it first the transparent emulsion layer, only about 6μ thick, then the baryta substratum, which is white by reflected light but absorbs the transmitted light and so appears black, and then finally the paper stock itself.

EASTMAN KODAK COMPANY
ROCHESTER, NEW YORK

A PHOTOMETER FOR THE MEASUREMENT OF THE TRANSLUCENT EFFECT OF PAPER

By C. FRANK SAMMET

Received July 3, 1917

In a previous publication¹ a new method was explained for the measurement of the translucent effect of paper. The instrument therein described, however, is somewhat complicated and expensive and has not proven entirely practical for extensive use.

A much simpler instrument has been devised for industrial use which meets the necessities of small cost of construction and easy manipulation, and has the added advantages of being sensitive to very small differences in translucent effects. It gives strictly comparable results, although perhaps not absolute values.

The principle of the method is that used in making photometric measurements. Two movable standard white backgrounds are mounted on a track (see Fig. 1). In order to avoid surface glare they are inclined from

the perpendicular at an angle of 30° toward the source of illumination which is placed between and slightly below them. The distances of the backgrounds from the zero point over the source of illumination are read on scales engraved on the track, the scales reading in millimeters from 0 to 300. The centers



Fig. I

of the areas reflected from the backgrounds should come directly over the 300 mm. marks when the backgrounds are at the ends of the scales. Above the light and the zero point is supported a specially constructed prism and eyepiece so placed as to reflect the surfaces of the backgrounds into adjacent fields. A Lummer-Brodthum prism is more satisfactory, as it eliminates the dividing line between the fields.

The instrument is set by placing the right-hand block at the 300 mm. mark. The left-hand block is then moved until a position is found where the fields appear matched in luminosity. Five readings should be made to determine the average position. This average reading may be considered constant for any set of papers, provided the position of the light remains unchanged. The left-hand block is then locked in this position.

A single sheet of paper of which the translucent effect is to be measured is then placed over the left-hand block. Another piece is placed over the other block with black velvet between. The black velvet¹ absorbs practically all of the light which the paper transmits, thus allowing only the light from the surface of the paper to reach the corresponding field in

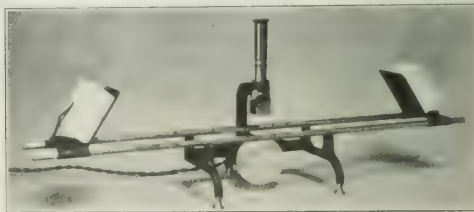


Fig. II

the eyepiece. In consequence this field is the darker since the other is illuminated by the light reflected from the surface of the paper plus that reflected by the standard white background. When the former block has been advanced toward the light it becomes brighter and finally a position is reached where the fields appear matched. The distance this block has

¹ Black velvet is sufficiently black and the fresh surfaces of the magnesium carbonate blocks sufficiently white for the sensitiveness of the instrument to come far within the distinction of differences of translucent effect desired by practical workers.

¹ U. S. Dept. Agr., Bureau of Chemistry, *Circ.* 96, 1912.

been moved is an expression of an amount of light transmitted by the paper to the velvet and then absorbed. This scale reading furnishes a basis for expressing the translucent effect of paper since this effect is dependent upon the light transmitted.

The essential construction of the instrument is shown in the photograph. It must be used in a darkened room and for illumination a frosted 100-watt stereopticon bulb (Mazda) is preferable, as it gives a centralized light. One of materially more watts is too brilliant for accurate work.

The character of results obtained is shown in Table I, in which the papers are arranged in the order of translucent effect to the naked eye, and the original and check scale readings and the percentages of translucent effects are recorded.

KIND OF PAPER Arranged by Naked Eye	AVERAGE OF—		TRANSLUCENT EFFECT 100(1 - b^2/a^2) Per cent
	1st 5 Readings Mm.	2nd 5 Readings Mm.	
Pergamyn.....	130	129	81.4
Tissue.....	156	155	73.1
Tracing.....	165	165	69.7
Onion Skin.....	211	213	50.1
Manifold (Green).....	216	218	47.7
Manifold (White).....	220	222	45.7
Typewriter.....	233	235	39.1
Printing.....	262	265	22.8
Bible.....	264	265	22.3
Bond.....	265	265	22.0
Bond (Pink).....	277	277	14.7
Printing.....	280	278	13.5
Bond (Blue).....	283	283	11.0
Writing.....	286	288	9.5

It is difficult for the naked eye to distinguish between green manifold and white manifold, and also between pink bond and printing. The instrument, however, places them with greater certainty. The order by the naked eye was confirmed by three independent observers.

The backgrounds of magnesium carbonate blocks give very satisfactory smooth, clean, reproducible white surfaces. Only a small area of paper should be exposed since it can be more readily held in close contact with the surface of the block or the black velvet, thus aiding greatly the sensitiveness of the instrument. The blocks must move freely on the tracks for ease of manipulation and accuracy.

Since the intensity of light varies inversely as the square of the distance from the luminous point, the reading, on any paper, substituted in the formula $100(1 - \frac{b^2}{a^2})$ gives a value for comparison of the approximate percentage loss of light due to absorption by the black velvet. In the formula, a is the total scale reading and b is the distance that the block is removed from zero.

The prisms of the eyepiece are cut at 45° angles to reflect adjacent fields and the eyepiece is long to permit the comparisons to be made with the least fatigue. A collar of metal or cardboard may be placed on the eyepiece to shade the eyes from the light of the bulb. A strip may be similarly placed across the track directly over the bulb so the instrument may be constructed with the eyepiece horizontal.

In the measurement of the translucent effect of the paper an exact match of color cannot be realized as there is a difference due to the absorption of light by

the black velvet. This difficulty is overcome by making the comparisons through a colored glass, either green or brown, placed on the eyepiece.

A colored paper should always be matched through a glass of its predominating hue.

When experience is gained in judging the luminosity match, rather than the color, the method and instrument give results which are satisfactory for all industrial purposes. The instrument should prove practical because of its sensitiveness, low cost, and ease of manipulation over other instruments.

CRANE & COMPANY
DALTON, MASS.

A PRACTICAL REVISION OF THE COBALTI-NITRITE METHOD FOR THE DETERMINATION OF POTASH

By R. C. HAPPEL and E. H. SCHWARTZ

Received July 9, 1917

Some years ago, there appeared in *THIS JOURNAL*² the method for the determination of potash by the use of cobalti-nitrite.

About a year ago, when the Security Cement & Lime Company began actual operations with their new treater plant with the idea of collecting and selling the dust on account of its high content of water-soluble potash, we were called upon to make a very large number of determinations for potash, not only on our own materials but on many other cement and foreign materials as well.

Since many of these determinations, on which total potash was also required, were made along research lines, mainly, the more laborious and very tedious J. Lawrence Smith method, while it proved very satisfactory as to accuracy of results, was found to be quite impracticable, due to the large laboratory force required and the time consumed in getting our final results.

Upon receipt of information that the cobalti-nitrite method was employed in the laboratories of the Western Precipitation Company, at Los Angeles, Cal., and in those of Mr. Charles Catlett, at Staunton, Va., we decided to attempt to employ it at Security with the idea of perfecting it in a more uniform laboratory routine, providing we could rely upon the results to check satisfactorily those obtained when employing the recognized Official methods.

The early work with this method required a very great number of duplicate determinations on all grades of material, and particular stress was laid upon the accuracy and reliability of "total potash" results, since all duplicate results on raw material and clinker, in particular, had to be accurate within 0.20 per cent K₂O.

This method has been employed in our laboratory at Security for about six months and has been found to give most satisfactory results on "total potash" when checked against the J. Lawrence Smith method and on "water-soluble potash" when checked against the Official method employed and recommended by the American Chemical Association.

CRANE & COMPANY, and SECURITY CEMENT & LIME COMPANY, at the Western Precipitation Company, Los Angeles, California.
Received July 9, 1917.

METHOD IN DETAIL

I—Weigh out a 2 gram sample of raw material (or clinker) or a 0.5 gram sample of treater dust and add to the former 0.5 g. of ammonium chloride and to the latter 0.25 g. of ammonium chloride. Transfer to a mortar, mix thoroughly and grind. Transfer the contents of the mortar to a 20 cc. platinum crucible, the bottom of which has been covered with a generous layer of calcium carbonate—about 2 grams. Cover contents of crucible with about 2 grams of calcium carbonate and proceed with heating and sintering as in the J. Lawrence Smith method.

After the mass has been slaked in a small casserole, place on the hot plate and heat to boiling. Filter into a flat-bottomed porcelain dish and wash the precipitate 3 or 4 times with very hot water. Add to the filtrate an excess of acetic acid (5 to 10 cc.) and evaporate on a steam bath until no odor of acetic acid remains. Take up with a little hot water, using the precaution to wash the sides of the dish *thoroughly*. Now add from 10 to 15 cc. of cobalt reagent (see below) and evaporate on steam bath to pasty consistency. Remove from bath and when precipitate has *cooled*, take up with about 30 cc. of *cold water*, breaking up precipitate thoroughly.

Filter through an asbestos padded Gooch crucible and wash precipitate once with *cold water*.¹

Wash contents of crucible into a 400 cc. beaker (containing an excess of standard *N/5* potassium permanganate solution)² with hot water and dilute to 250 cc.

Place on steam bath for about 15 minutes or until a decided black color appears. Acidulate with 10 cc. 1 : 1 sulfuric acid. With a standard pipette (10 cc.) neutralize the excess potassium permanganate with *N/5* oxalic acid solution, the potassium permanganate equivalent of which has been determined. When the final solution has cleared, titrate with standard potassium permanganate solution.

COBALT-NITRITE SOLUTION—(1) Dissolve 220 g. of sodium nitrite in 400 cc. of water.

(2) Dissolve 113 g. of cobalt acetate in a mixture of 300 cc. of water and 100 cc. of glacial acetic acid.

(3) Mix the above solutions and place under vacuum over night. Filter and dilute to 1000 cc. Keep the solution in a dark bottle. Never use a solution over two weeks old.

II—When determining “water-soluble” potash by this method, weigh 10 g. of the material into a 600 cc. beaker, cover with about 250 cc. of water and boil for 30 minutes. Pour into a 500 cc. flask. Cool to room temperature. Make solution to mark. After shaking well, filter a portion of the solution through a dry paper. Draw off 50 cc. (1 gram equivalent) and place in a platinum or porcelain dish. Then proceed as in the above method, beginning with “Add to the filtrate an excess of acetic acid (5 to 10 cc.) and evaporate on steam bath until no odor of acetic acid remains.”

¹ Water poured from a beaker causes less disturbance in the crucible and gives better results.

² 10 cc. for each 1 per cent K_2O equivalent in the sample.

ILLUSTRATION—RESULTS ON SAMPLE OF RAW MATERIAL

DATA—20 cc. Permanganate originally used;
10 cc. Oxalic acid used to neutralize excess Permanganate;
10 cc. Oxalic acid found to equal 11.2 cc. Permanganate;
5 cc. Permanganate used to neutralize excess Oxalic acid.
Now (20 cc. + 5 cc.) — 11.2 cc. (Oxalic acid equivalent)
= No. of cc. of Permanganate used to complete titration.
Therefore (No. of cc. of Permanganate) \times Factor
= per cent K_2O .

CALCULATION OF K_2O FACTOR—

$\frac{CaO \text{ Factor}}{2} : 0.0056 = X : 0.00171$, where $X = K_2O$ factor.

Regular *N/5* Permanganate is used where the calcium oxide factor is based on 0.5 gram. To calculate the K_2O factor to 1 gram, one-half of the calcium oxide factor must be used in the above proportion.

SECURITY CEMENT & LIME COMPANY
HAGERSTOWN, MARYLAND

DETERMINATION OF CARBONATES IN LIMESTONE AND OTHER MATERIALS

By J. F. BARKER

Received May 18, 1917

Results obtained in the determination of carbonates by the apparatus herein described compare favorably with results from the use of any standard laboratory method. The advantage of this method over others is that no mechanical balance or scale is required and there are no long calculations to be made. Anyone with some aptitude for accuracy can, with this instrument, make as reliable a determination in home or office as a skilled chemist in a well-equipped laboratory using complicated apparatus.

The invention depends upon the principle of the hydrometer, which takes account of the law that when an object is immersed in a liquid it is buoyed up by a force equal to the weight of the liquid displaced by the object. In this apparatus the carbon dioxide gas set free from the sample decreases the weight; and the rise of the graduation scale tube above the water records the percentage of carbonates from which the gas was released.

PROCEDURE

To analyze a sample of limestone for carbonates, measure out 40 cc. of HCl (sp. gr. 1.15), using a small graduate; pour this into the acid reservoir through the opening *A*. With graduated stem disconnected hang a 10-g. weight at *B*. The hydrometer should then float in a cylinder of water and be immersed to some point at *C*. Remove the 10-g. weight and introduce pulverized limestone until instrument is immersed to exactly the same point. Now connect up graduated stem and add water a drop at a time, through the funnel-shaped top, until immersed to zero point. Raise hydrometer out of water and open stopcock *D* until acid drops slowly into reaction chamber, decomposing the limestone. As the reaction proceeds the instrument rises slowly and at the conclusion the point on stem at the surface of the water gives the per cent of calcium carbonate equivalent to the carbon dioxide in the sample. This figure is the *calcium carbonate equivalent* so often mentioned in connection with limestone analyses.

A Fahrenheit thermometer accompanies each instrument and is hung inside the floating cylinder. Its reading is taken before and after each determination to allow for any error due to change in temperature. To the figure for calcium carbonate equivalent add 0.5 for each degree rise, or subtract 0.5 for each degree fall in temperature between the two readings. This temperature change need seldom amount to more than a fraction of a degree.

DEGREE OF ACCURACY

The following table of results illustrates what may be expected as to degree of accuracy. They represent all of the determinations made by one person, a boy without laboratory training and who has never studied chemistry. The standard method mentioned is by use of the Parr carbon apparatus.

Limestone No.	Author's Method	Standard Method
200	80.0	80.0
201	81.5	81.8
220	78.5	78.6
221	71.0	71.1
223	78.5	78.7
224	83.0	84.0
226	82.5	82.9
230	83.5	83.2
240	99.5	99.0
244	98.5	98.5
254	97.5	97.7
256	89.0	88.9
257	95.5	95.8
Calcite	99.5	

SOME DETAILS

To those who care to examine the method critically it should be said that sources of error have been eliminated until the method is accurate to the degree that the graduated stem can easily be read: this means about 0.25 per cent. The limestone can be weighed to an accuracy of 0.02 g. The weight of CO_2 remaining in the apparatus tends to offset the loss due to moisture escaping with the gas, but the difference, together with any other possible sources of error, has been accounted for in the graduation of the reading stem.

This graduation was first determined theoretically and then tested by checking against pure calcite. Small corrections were found necessary and subsequent instruments have been so graduated that their reading need no correction save for change in temperature occurring during the progress of the determination.

Each outfit of this apparatus includes a glass cylinder

for floating the hydrometer, a small Fahrenheit thermometer, 500 cc. of hydrochloric acid (sp. gr. 1.15), a 50 cc. graduate, a small dropping pipette and a scoop for convenience in transferring the sample. The manufacturer's price for a single outfit, it seems now, will be less than \$10.00.

APPLICATION OF THE METHOD

For analyzing carbonates other than limestone and similar materials, this instrument is fitted with a graduated stem which reads percentage of carbon dioxide, an arrangement which greatly extends its use. It will be found especially suited to determining the comparative strengths of baking powders and considering speed and accuracy is more suitable than any other device now employed for that purpose.

The method is adapted for use in all chemical laboratories, college, experiment station, or commercial laboratories. However, it is devised for use outside of chemical laboratories, also. Limestone companies can employ it to check up on every carload of their goods, or to locate the stone in their quarry most suitable for grinding. County agricultural agents will use it to keep posted on the quality of limestone being sold in their territory and to determine the composition of local limestone deposits. Many an individual farmer or some member of his household will no doubt wish to own the apparatus.

NEW YORK AGRICULTURAL EXPERIMENT STATION
GENEVA, NEW YORK

CARBONATION STUDIES: I—A MECHANICAL STIRRER FOR CARBONATION DIRECT IN THE BOTTLE

BY HARRISON E. PATTON AND GERALD H. MAHES

Received March 3, 1917

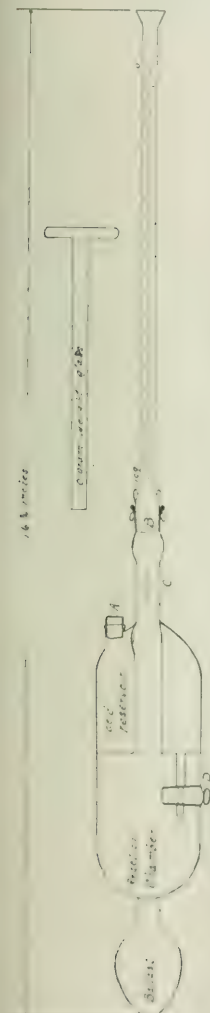
In connection with an attempt to distinguish between naturally charged or bottle-fermented wines, and artificially carbonated wines, the need was felt for a machine which would enable one to carbonate direct in the bottle, and in a measure to control the purity of the carbon dioxide gas.

After extended experiments the machine described below was devised.¹

A detachable stirring-head enables one to pass carbon dioxide (or other gas) through a side tube into the bottle containing liquid to be impregnated. This liquid is agitated by tines rotated by a shaft attached by pulley and belt to a motor. The complete assembly is shown in Fig. 1.

DETAILS OF CONSTRUCTION

The stirring-head (Fig. 11) consists of a stirrer with clock spring (pieces *A* and *B*) mounted in a shaft-chamber, *F*. The upper end of the stirrer-shaft *B* is fitted with a pulley *H*, serving to connect it by belt to a source of power. The shaft-chamber through which *B* passes is sealed with a stuffing-box packed with oil-packed hemp, which can be removed, either to place the upper end of a heated metal-disk *G*, thus expelling the air between the shaft and shaft-chamber packing. As opening toward the stuffing-box has been made, the shaft *B*, so that there is free gas circulation between the motor and the



HYDROMETER FOR DETERMINATION OF CARBON DIOXIDE IN LIMESTONE AND OTHER MATERIALS

Each outfit of this apparatus includes a glass cylinder

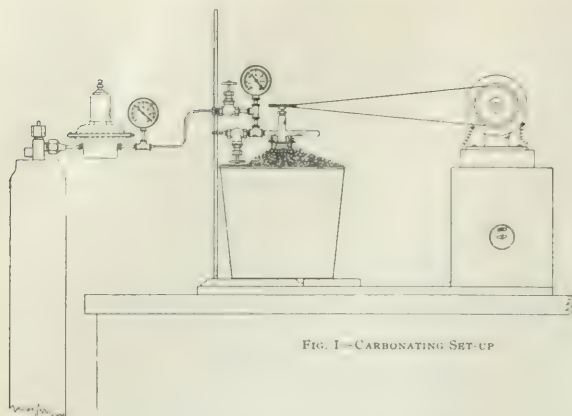


FIG. I—CARBONATING SET-UP

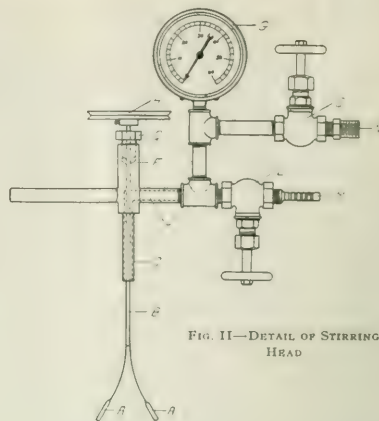


FIG. II—DETAIL OF STIRRING HEAD

stirrer-shaft. This gas inlet through *J* is connected with a pressure gauge, *G*, and also with a union, *N*, serving to connect with a source of compressed carbon dioxide gas. The globe-valve *O* controls the admission of gas.

A continuation of *J* through control-valve *L* leads to exit tube *M*, where gas may be withdrawn as desired.

OPERATION

The apparatus used for impregnating with carbon dioxide consists of a carbon dioxide cylinder, pressure-reducing valve, the stirring apparatus described above, a champagne bottle, and a small motor, as shown in Fig. I.

First, the liquid is placed in the bottle, and chilled, if desired.

Attachment of the stirring-head to the bottle is made as follows: Holding the tines *AA* together they are passed through the central hole of a slotted plate, which then slides on up over sleeve *C*, and is held firmly in place by a one-hole rubber stopper which serves as a heavy gasket closing air-tight the mouth of the bottle when the standard-clamp screws are brought up into the slots of the plate (120° apart) and screwed tight to place as shown in Fig. I. The bottle with attached stirring-head is packed in ice and the pail is placed in position, the bottle being held securely by a clamp. (Upward thrust of the pulley due to gas pressure in the bottle is prevented by a glass rod which acts as a top-bearing.) A flexible pipe from the carbon dioxide cylinder is connected with the union *N*, and a belt run from the pulley-wheel *H* of the stirring-head to the motor. Gas is turned on by opening the cylinder-valve and the globe-valve *O*, the motor started and carbonation continued as long as desired for the experiment. During the process of carbonation, the collar *Q* is turned back sufficiently to allow free rotation of the shaft *B*. This entails a slight gas leak, but the source of pressure being practically infinite by comparison, the operation of the machine is not affected.

If a high degree of purity of carbon dioxide in the finished liquid is desired, control-valve *O* should be

closed, valve *L* opened and gas allowed to run out of exit tube *M*. The valve *L* is then closed, valve *O* opened, and carbonation resumed. This "blow-off" of top gas from the bottle sweeps out foreign gases, especially nitrogen and oxygen collected above the liquid and should be repeated several times to secure the best carbonation.

As soon as the carbonation process is finished, the collar *Q* is screwed down tight and the valve *O* closed.

In practice we have found that with the packing used in the stuffing-box and valves we are able to hold a pressure of 75 lbs. per sq. in. for several weeks.

DEPARTMENT OF AGRICULTURE
BUREAU OF CHEMISTRY, WASHINGTON, D. C.

A SAMPLING PRESS¹

By W. BLAIR CLARK²

Received March 16, 1917

Any device used in the preparation of samples for the ordinary run of analytical work should meet each of the following conditions as completely as possible: it should reduce all the constituents of the substance under investigation to particles of approximately equal size, and these particles should be fine enough to be acted upon promptly by whatever solvents or extractive liquids are to be used subsequently; in the process of reduction no part of the sample should be lost by spurting or otherwise; a minimum of the sample should be retained in the mechanism, and it should be possible to remove this minimum without contamination and in such a manner that, if desired, it may be added to the main bulk of the sample; the apparatus should be capable of rapid operation; and, finally, it should be easily taken apart for cleaning.

It is believed that the press here described fulfills these requirements quite satisfactorily as applied to the sampling of roots, tubers, melons, and such fruits as are easily separated from the seeds and skins, especially when the last mentioned are of the tough, thick sort.

¹ Published by permission of the Secretary of Agriculture.

² Biochemist, Office of Cotton, Truck and Forage Crop Disease Investigations.

There are two general types of sampling apparatus used for these classes of materials. One type reduces the substance by cutting or rasping. It is exemplified in the various meat and vegetable cutters and in boring and other forms of rasps. The other type reduces the sample by crushing. This ordinarily involves the use of some form of press in which the power may be applied through a lever, a screw, or hydraulic mechanism. One of the earliest of this type to combine good results with simplicity of construction and operation was the "Sans Pareille" press, manufactured in France. This, being a screw press, is rather slow in operation where many samples are to be prepared.

In the course of some work on sugar beets done during the fall of 1913, use was made of a press in which the plunger was actuated by a lever. This press was built in Austria, and while in many ways a marked advance over any other beet sampling device which had come to the writer's notice, it possessed some defects of design. In the new form these have been eliminated, it is hoped, without the introduction of any new faults.

The photographs reproduced in Figs. 1 and 2 show the construction of the press clearly. The essential parts are a plunger and a cylinder, the latter having a stout sieve bottom. The remainder of the apparatus is simply a supporting framework for these two parts and the lever which actuates the plunger as it is forced into or withdrawn from the cylinder. Fig. 1 shows the plunger raised and the cylinder yoke thrown to one side for charging or removal of the cylinder. In operation, pieces of the material to be analyzed, preferably but not necessarily in the shape of cylindrical plugs, are placed in the cylinder, the cylinder yoke is swung into place under the plunger and locked, and the plunger is then forced to the bottom of the cylinder. The relative position of the parts is now that shown in Fig. 2.

By reference to Figs. 3 and 4 it will be observed that in reality what has been called the cylinder consists of two cylinders, one within the other. The outer one, *C*, is of steel, while the inner one, *A*, is made of brass. One of the serious defects of the foreign-built press was the loss of juice through the joint where the cylinder was screwed into the sieve support. By having two cylinders fitted snugly together, as shown, and by removing the threaded part of the joint to the top of the combination, this loss has been completely eliminated. When the inner cylinder is screwed down tightly against the sieve, the contact surface between the two cylinders does not become even moist for more than $\frac{1}{2}$ to $\frac{3}{4}$ in. above the sieve, unless a large number of samples are run without stopping to clean the press.

This style of construction also permits making the threads quite coarse, thereby facilitating the quick separation of the two cylinders for cleaning. To the same end the enlarged parts of the cylinders, at *K* and *Z*, should be knurled or otherwise roughened so as to be readily gripped.

The sieve *D*, which is of steel, should have the $\frac{1}{16}$ in. holes slightly countersunk on one side. For all

except the most refractory materials, which are to be passed through the press, a very fine, "mushy" pulp can be obtained by placing a disk of thin perforated copper over the steel sieve, the latter being put with its countersunk side next to the copper. A product described in the trade as "16-oz. o-mesh, perforated sheet copper" has been used very effectively. The holes in this are $\frac{1}{16}$ in. in diameter, and run 24 to the inch in both directions. This fine sieve has been used regularly in the preparation of Irish potato samples, and tests have shown equally good results with sugar beets, sweet potatoes, and apples.

Even with such a fine sieve as that described it has not been found necessary to remove the skins from the ends of the plugs in the case of any of the materials mentioned, although the nature of an investigation may be such as to make the removal desirable for other reasons.

Where one wishes to use cylindrical plugs, they may be cut either with a cork borer or with a butter and cheese trier. These implements may be secured in suitable sizes for the dimensions given.

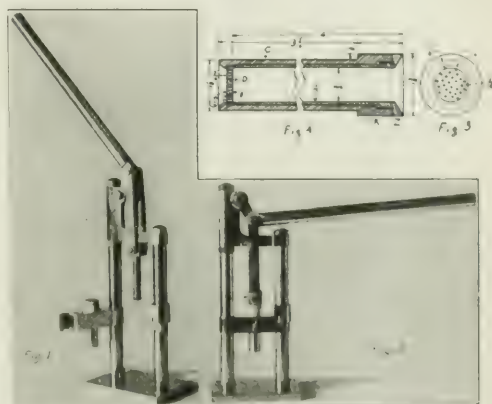


FIG. 1. SAMPLING PRESS WITH PLUNGER RAISED AND CYLINDER YOKE THROWN TO ONE SIDE FOR REMOVAL OR CHARGING OF CYLINDER.

FIG. 2. SAMPLING PRESS CLOSED, WITH PLUNGER FORCED TO BOTTOM OF CYLINDER.

FIGS. 3 AND 4—DETAILS OF CYLINDER.

The lower end of the plunger is provided with two leather washers (Fig. 1), held in place by a flat-headed screw countersunk into the lower washer. These washers must be replaced when worn sufficiently to let juice work up past them in appreciable quantity.

The upper yoke is drilled to serve as one bearing for the plunger and also supports the release for the lever. The cylinder makes a snug slip fit in the operating yoke, the wing top or upper arm of the sliding yoke following the plunger as the latter is withdrawn. The yoke is at sufficient depth to hold the cylinder firmly in place, so that the latter constitutes a second bearing for the plunger. The top of the cylinder just above the bottom of the plunger when the latter is at its highest point. When the cylinder is in proper position to receive the plunger the whole is held steady by slipping over its top and the clamp screw on the

front support in Figs. 1 and 2. The swinging yoke is kept from vertical movement by pieces of tubing slipped over the rear standard, one below and one above the yoke. These are clamped with just sufficient tightness by the lock nut immediately underneath the upper yoke. The tube over the front standard is in one continuous piece from the base to the upper yoke, a portion, however, being cut away in such a manner as to form a support for the free end of the swinging yoke when the latter is in position for the operation of the plunger. The two standards are screwed into the base and when the nuts at their tops are drawn tight, the framework of the press is locked solidly together.

The pulp may be received either in open vessels, as beakers, or in wide-mouth bottles or flasks. In any case, the top of the receiving vessel should be raised high enough around the lower part of the cylinder to insure against loss from spurting sidewise. In the writer's practice, potato samples are received directly into weighing bottles about 45 mm. in diameter by 65 mm. high. The bottles are immediately stoppered and the samples thus held without possibility of loss by evaporation until after weighing.

In some analyses the pulp is delivered directly into a tared vessel containing the solvent to be used for extraction or digestion. A second weighing then gives the amount of the sample. This procedure minimizes the possibility of chemical changes due to contact of the finely divided sample with the air. It also enables the instantaneous inhibition of enzymatic action.

For certain work in this laboratory there have been desired raw cultures of finely divided substance, sterile, except for such inoculations as may already exist in the interior of the material. The press herein described has been found to be well adapted to the making of such culture preparations. The cylinder may be removed, wrapped and placed in the sterilizer, while the plunger may either be treated similarly or be sterilized without removal by immersing its entire working portion in a suitable sterilizing fluid. The balance of the press may also be readily sprayed with any suitable noncorrosive liquid. Plugs of the culture material are then prepared with flamed tools and slipped into sterile test tubes, which are closed with cotton plugs until the moment for insertion of the plugs into the press cylinder. The pulp will, of course, be received directly into the sterilized tubes or flasks in which the cultures are to be grown. This work has not been fully developed as yet, but preliminary trials with only ordinary precautions have resulted very satisfactorily.

From the writer's experience with a number of sampling devices it is believed that the press which has been described possesses distinct points of superiority which would make it especially useful to Experiment Station chemists as well as to others having much work with the class of materials to which it is applicable. The finely divided pulp produced by this process can be extracted in a small fraction of the time required where the pieces are merely chopped or minced by hand or in a vegetable grinder.

For convenience in packing for transportation the handle of the lever may be unscrewed at a point near the bend. Where much variety of analytical work is to be done, it will also be found convenient to have two handles, one about 30 in. long for tough, fibrous roots, and one not over 15 to 20 in. long for use with softer materials.

The press now being used by the writer was made at the Government Navy Yard in Washington at a cost of about \$55.00. However, it would not be possible for other than Government laboratories to have work done at the Navy Yard. As yet no arrangements have been completed for the commercial production of the press, but pending such arrangements blue prints of the complete working drawings will be furnished upon request from interested parties. The materials required in building the press are such as may be found in stock in almost any machine shop.

U. S. DEPARTMENT OF AGRICULTURE
BUREAU OF PLANT INDUSTRY
WASHINGTON, D. C.

DETERMINATION OF GAS DENSITY¹

By JAMES DAVID EDWARDS

Received April 11, 1917

Because of its importance in orifice meter measurements, as well as to the gas industry in general, the problem of determining the density of gases has been investigated at the Bureau of Standards. The complete results of this investigation are to be published as Technologic Papers Nos. 89 and 94, entitled "A Specific Gravity Balance for Gases" and "Effusion Method of Determining Gas Density." The present paper presents a summary of the results and conclusions of the work.

The direct method of determining gas density and the one capable of yielding the most accurate results is to weigh in a closed glass globe a known volume of the gas at a definite temperature and pressure. When conducted with every refinement of technique and apparatus, this method may be made to give results accurate to 1 part in 10,000 or 20,000. To secure an accuracy of even a part in 1000, is, however, a tedious and delicate operation.

In order to secure precise results with convenience and rapidity, a specific gravity balance employing an indirect weighing method was developed. The principle of the method is based upon the laws of the compressibility and the buoyant effect of gas. According to Boyle's law the density of a gas is proportional to its pressure, and the buoyant force exerted upon a body suspended in a gas is proportional to the density of the gas and therefore to its pressure. Therefore, if the buoyant force exerted upon a body is made the same when suspended successively in two gases, then the densities of the two gases must be the same at these pressures; or the densities of the two gases at

¹Published with the permission of the Director of the Bureau of Standards.

normal pressure are in inverse ratio to the pressures when of equal buoyant force.

The construction of the specific gravity balance is shown in Fig. 1. The central water-jacketed gas

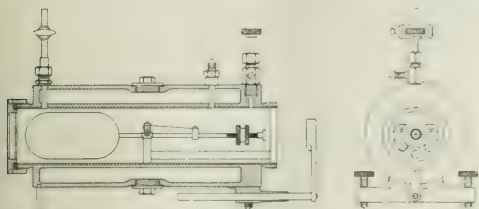


FIG. 1—DETAILS OF CONSTRUCTION OF EDWARDS GAS-DENSITY BALANCE

chamber is closed gas-tight by screw caps, one of which is shown at the left, and is provided with a gas inlet, a connection for attaching a mercury U-gauge, and a needle valve. The balance beam carries on one

glass tubing. In operation the gas chamber is filled with air and the pressure accurately adjusted by means of the needle valve until the beam just balances at a predetermined point. This is judged by observing the position of a pair of cross lines, on the end of the beam, with respect to a fixed mark on a small glass window (shown in end view). A small magnifying glass mounted on a movable arm aids in reading the position of the beam. The operation is then repeated with the gas whose density is to be determined. The specific gravity of the gas is the ratio of the total pressure (gauge plus atmospheric pressure) at which the beam balances in the air to the total pressure at which it balances in the gas.

The success obtained in the use of this apparatus is mainly due to the high sensibility afforded by the needles which support the balance beam. The needles are easily adjustable and, in contrast with a metal or quartz knife edge, can be obtained readily at low cost; they also can be replaced as often as necessary. The beam is left on its support when not in use, although it may be removed for transportation. The balance is capable of giving results accurate to about 0.2 per cent and requires no calibration.

The effusion method, which has been widely used for technical work, is based upon the fact that the times of escape of equal volumes of two gases under the same pressure and through the same small orifice in a thin plate are approximately proportional to the square roots of the densities of the gases. Experiments made at the Bureau in cooperation with experienced observers using effusion apparatus, showed that results in error by 10 per cent or more were not unusual. In order to discover the sources of error in the method, the theory of the effusion process was investigated. However, the number of factors involved, such as the ratio of the specific heats, the vis-

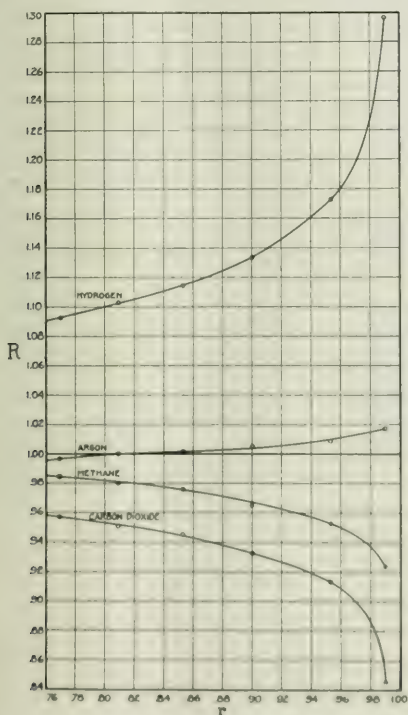


FIG. 2—CURVES SHOWING THE VARIATION IN THE APPARENT SPECIFIC GRAVITIES REFERRED TO AIR OF DIFFERENT GASES AS DETERMINED WITH THE SAME ORIFICE AND AT DIFFERENT PRESSURES

cosity, the thermal conductivity, etc., make the problem very complex; it will be discussed in full in another paper.

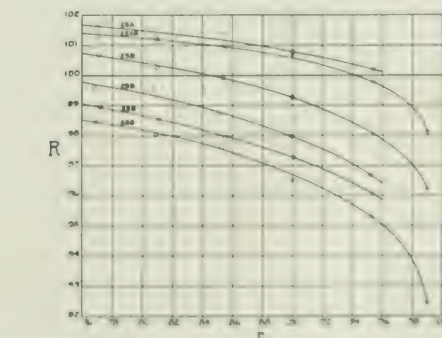


FIG. 3—CURVES SHOWING THE APPARENT SPECIFIC GRAVITY REFERRED TO AIR OF METHANE AS DETERMINED WITH DIFFERENT ORIFICES

cosity, the thermal conductivity, etc., make the problem very complex; it will be discussed in full in another paper.

The apparent specific gravity of a gas as determined by the effusion method is affected by the character

of the orifice used, the effusion pressure and the confining medium. The effect of different effusion pressures with the same orifice and different gases is shown in Fig. 2, where R is the ratio of the apparent specific gravity to the true specific gravity and the effusion pressure r is expressed as the ratio of the atmospheric pressure to the total effusion pressure. Different orifices give curves for the same gas which are similar in form but have different values for the apparent specific gravity. This is shown by the curves in Fig. 3 for six different orifices when using methane.

The results may be summarized as follows: In general, the deviations are greatest at the lowest effusion pressures (highest values of r) and a low effusion pressure should be avoided; but it is not necessarily true that the higher the effusion pressure the more nearly correct will be the results. Although there may be a pressure at which a certain orifice will give correct results (*i. e.*, correct ratio to air) with a certain gas, there is no pressure at which it will give correct results with all gases. The combination of factors which produces such a low result in the case of carbon dioxide or methane produces just the opposite effect with hydrogen.

Decreasing the diameter of the orifice or increasing the thickness of the orifice plate tends to give a lower apparent specific gravity with methane or carbon dioxide; the same changes give a higher result with hydrogen, as previously explained. Examination of the results obtained with 30 orifices shows that orifices of the following characteristics give the most satisfactory results: the orifice should be round and smooth, with all burr and ragged edges carefully removed. For apparatus using a mean effusion pressure ratio of 0.90 (with mercury as a confining liquid) an orifice 0.15 mm. to 0.30 mm. in diameter in a plate 0.05 mm. or less in thickness should prove satisfactory. For apparatus using a mean effusion pressure ratio of 0.99 (with water as a confining liquid) an orifice 0.18 mm. to 0.30 mm. in diameter in a plate 0.04 mm. or less in thickness may be used. These limits are merely given as a guide to aid in constructing suitable orifices, as such orifices do not necessarily give accurate results, although they can probably be relied on to within a few per cent.

Mercury and water have been the two confining mediums most widely used in effusion apparatus. When using water, the gas must be measured saturated with water vapor; and under these circumstances, erratic results are often produced by condensation of water vapor in the orifice. This trouble is eliminated by the use of mercury. Lower effusion pressures are usually obtained with water; but the pressure should not be allowed to fall below 2 in. of water in any case, even at the end of the test.

The effusion method, although not adapted to securing absolute results, should prove well adapted for control work or other uses where only relative values are desired. It is suggested that the apparatus be calibrated for use with a gas of the character under test. The method will give results accurate to 1

or 2 per cent when properly carried out and a somewhat greater precision can be secured by the calibration recommended. Suitable forms of apparatus, operating directions and precautions as well as other details will be found in the Bureau of Standards, Technologic Paper No. 94.

BUREAU OF STANDARDS
WASHINGTON, D. C.

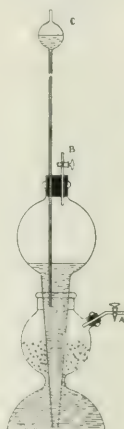
A SIMPLE IMPROVED APPARATUS FOR HYDROGEN SULFIDE PRECIPITATION UNDER PRESSURE

BY AUBREY VAIL FULLER

Received April 20, 1917

The ordinary method of conducting hydrogen sulfide precipitations by allowing the gas to bubble through the solution is at once time-consuming, wasteful, and uncleanly from both chemical and hygienic standpoints.

In order to obviate these objections attending the customary practice, the writer has constructed the apparatus pictured.



A 500 cc. Kipp generator is provided with a two-holed rubber stopper which carries a one-way stopcock, B , and a small-bore glass tube about 3 feet long which terminates at its upper end in the reservoir bulb C , of about 100 cc. capacity and whose lower end extends several inches below the acid level. The gas outlet is fitted with a rubber stopper carrying a two-way stopcock, A .

The operation of the device is as follows: the flask in which the precipitation is to be conducted is closed with a rubber stopper carrying two glass tubes, one of which is provided with a short length of rubber tubing and spring pinchcock, the other being connected by means of rubber tubing to the gas wash-bottle (not shown).

Cock B is opened and the gas passed through the flask in order to sweep out the air, the pinchcock of course having been removed.

The gas is then shut off, the pinchcock replaced, and the two-way cock A is opened to the air until the acid level rises almost to the tubulature, when the cock is turned so as to connect the flask with the generator, and cock B is closed.

The acid level is thus caused to sink in the reservoir of the generator proper and to rise in the tube as shown in the figure. When through using the generator, the cock B is opened in order to relieve the pressure, and is allowed to remain open while the apparatus is idle.

It is evident that with an effective pressure column of 1 meter height and employing 1 : 3 hydrochloric

acid, a pressure of something over 100 g. per cm². will be attained.

The precipitates obtained with this apparatus appear very granular, and settle and filter readily. Furthermore, the point of saturation is easily determined by rotating the flask and noting an absence of gas bubbles in the wash-bottle.

BIOCHEMICAL DIVISION, BUREAU OF ANIMAL INDUSTRY
U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON

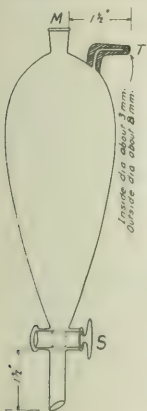
A NEW FILTER FLASK

By Jos. A. SHAW

Received June 11, 1917

Most chemists, I am sure, have wished many times for a suction filter flask that was less awkward than the various forms of apparatus now in use for suction filtering. The old-fashioned side-outlet flask and the bell jar and ground glass plate are the two forms of apparatus most used at the present time for this purpose. They both have decided shortcomings. It is believed by the writer that the filter flask here described will overcome most of these objections. The idea is simple, but it is believed original in its application. At least it is listed in none of the catalogs of scientific apparatus published at the present time.

The flask is pear-shaped with a wide-mouthed stopcock, *S*, at the bottom and a heavy glass tubing, *T*, leading off to the suction pump from near the flask mouth, which is of a size suitable to take the filtering funnel adjusted with a No. 5 rubber stopper. Owing to its shape, this flask is readily washed free from filtrates and may be permanently mounted on an iron support. It may be put in place over a drain in order that, if desired, the filtrate may be readily discarded by simply opening the stopcock. If the operator



wishes, a three-way cock may be inserted in the suction line to cut off the pump and let air into the flask to facilitate emptying it.

The writer has found this design to be very satisfactory for all sorts of analytical work requiring a suction flask, and it is believed by him that to users of this apparatus the following points will establish themselves:

(1) The air seals are at least as good as those in the ordinary type of filter flask and are fewer and very much better than those of the bell jar type, for as soon as any grit gets upon the ground glass plate the air seal between the jar and the plate is at least partially spoiled.

(2) The filtrate can be removed from the flask with greater facility than in the other types because of a smaller number of operations.

(3) It is easier to wash free from filtrates than the ordinary filter flask and there is no great danger of contaminating the analysis as is so liable to be done when lifting the bell jar from the plate, if the plate has gotten any water upon it, as is so often the case in routine work. It may be mentioned here that if the filter funnel has a short tube arranged so that the filtrate and wash water can run down the sides of the flask it will be found that with most filtrates the upper layer of liquid will be practically pure wash water, and when the stopcock is opened to drain the flask the wash water coming down last will wash the flask nearly free from the filtrate, so that if a fine rinsing jet is used the flask may be washed clean in many instances with as little as 10 cc. of liquid. Lastly, this flask is of course much more readily kept clean than the bell jar type because of the absence of the vaseline used to form the seal in the latter piece of apparatus.

This flask can be obtained from Messrs. Eimer & Amend, and it is confidently believed by the writer that it will satisfy a long felt want for a neater, more readily manipulated piece of filtering apparatus.

LABORATORY OF PITTSBURGH CRUCIBLE STEEL COMPANY
MIDLAND, PENNSYLVANIA

ADDRESSES

THE CHEMICAL DEVELOPMENT AT BERLIN, N. H.

By ELLWOOD HENDERICK

Received May 14, 1917

In 1852 the late W. W. Brown established himself in the lumber business with a small sawmill along the Androscoggin River at Berlin, N. H. It was a bleak place, high up in the White Mountains, along the Presidential Range, with a very short annual growing season and no natural resources except water power and some timber. Nearly all the timber except white birch had long ago disappeared from the country to the south. But Mr. Brown was a man of parts, and with the aid of his four sons his business grew and prospered. His lumbering operations followed up the Androscoggin River and in time paper mills were added to the plant. In time also a sulfite pulp mill was built on adjoining property under other than Brown management. By the close of

the last century Berlin had become an important producing center of these commodities.

The class of 1807 of the Massachusetts Institute of Technology included Hugh Nelson Moore, who as a result of his studies on the production of chlorine and soda by the decomposition of salt, devised an unsubmerged diaphragm cell which was put upon the market in 1898. In 1890 the sulfite mill at Berlin, with a view to getting cheaper bleach, installed the Moore cell in the plant and the inventor went there to put it into operation. When the work was completed he left.

At the end of a very long (fifteen) period, Mr. Moore in 1901 determined to get into chemical work connected with pulp making and bleaching. Through the acquaintance of a friend of the superintendent of the sulfite mill at Berlin, he was only able to secure a position in the wood yard at very low wages, but while very uncommensurate the position offered ap-
proach-

tunities for observing many serious wastes that were continuously taking place. For example, it was evident that there was unnecessary loss of pulp in the waste water; by wiring the sewers it was proved that the loss amounted to approximately 19 tons of pulp per day. This loss was largely eliminated. Again it was noted that the product or the mill was uneven, and further that it was weaker after a humid than after a dry day.

The unusual character of the services rendered by such a laborer in the wood yard led to quite a change in the personnel of the mill force and Moore finally obtained an appointment as an analytical chemist in the mill; the value of a research chemist was not so well recognized then as now.

COUNTERACTING ATMOSPHERIC HUMIDITY

Meanwhile, the weakness of the pulp after a humid day persisted. The trouble was finally traced to the sulfur kilns. In the presence of moisture a greater quantity of sulfuric acid is formed from the burning of the sulfur thereby hydrolyzing a portion of the pulp to sugars. Precautions which eliminated this moisture proved partly responsible for the complete cure of the weakness of the pulp.

The analytical chemist saw innumerable things to improve, but he lacked the time. He had introduced chemical control and that prevented research. Too much bleach was being used, for instance, and caustic soda was going to waste, yet he had no chance to work out the solutions to the problems. The president was a practical man who knew how overhead charges can eat up profits; and the idea of a lot of chemists fuddling away in a laboratory on theoretical problems paid for out of the profits of the mill did not appeal to him, at first. But he was also a good business man who was not ashamed to change his mind, and finally he saw clearly that chemical research is a function of chemical control. The result was that Moore at last secured an assistant for the routine work.

Some time after this the Brown interests bought out the sulfite mill and the duties of chief chemist of all the various enterprises were given to their erstwhile analyst.

Chemical control and the regulation of the sulfur room were but the beginnings of a series of improvements in the art of making sulfite pulp. These were introduced at different times as the result of research by Hugh K. Moore and Robert B. Wolf, who was the superintendent of the mill. The production of a stronger acid made under refrigeration for cooking, and operating under lower temperatures than theretofore, produced a stronger pulp, and as a vast destruction of fiber was avoided, much less wood was required to produce the same quantity of pulp. Ocular demonstration of this was a goodly mountain of wood at the end of a season, whereas the pile, based upon the output of pulp according to previous figures, should have been used up. Detailed figures are not given, but such is the fact.

So significant is this improvement obtained by the use of better acid that in the event now of low water power another mill is shut down at intervals with a view to using the available power for refrigeration rather than to proceed by the former methods of making the weaker acid. So important indeed is refrigeration in this and other processes that the capacity of the apparatus in operation at Berlin is over 2,000 tons of ice per day.

The air around Berlin is clear and the usual odor of a sulfite mill cannot be noticed until one gets almost into the plant, and even then it is very slight, for the spent fumes are recovered, the SO_2 saved, and offense is avoided.

THE BLEACH PROBLEM

Another problem was bleach. Excess of bleach is no more desired in pulp than it is in the weekly wash, and it costs money withal. It was observed that the amount of available bleach required increased as its content of chlorate. The plotted lines on graphs show very clearly a tendency toward parallelism between the available bleach required and the chlorate in the bleach. The production of the chlorate was avoided by

refrigeration. By complete chemical control of the bleaching process from start to finish the minimum quantity of chlorine is employed, the color control is absolute and the resultant fiber far stronger than that produced by rule-of-thumb methods.

Early in 1907, through an accident in the mill, Mr. Moore lost three fingers of his right hand, and during his convalescence addressed himself to a problem that had been teasing him for a long time, and which seriously affected the appearance and consequently the value of the pulp. The finished product showed no less than 10,000 specks per square foot, and with the aid of his left hand and some helpful assistance, he proceeded to work with his microscope. Bark, rosin, coal, hair, cement and the almost innumerable other things that may and do constitute specks required long and patient classification before they were recognized. Proper precautions in factory practice and devices of remarkable ingenuity overcame everything except the specks consisting of minute particles of bark, and these finally gave way to improvements in cooking in the digesters and to a special bleaching process. Specks were reduced from 10,000 per sq. ft. to 15 or 20 per sq. ft.

The sequel to these improvements is that the entire capacity of the mill is devoted to making bleached pulp of an unusually fine and strong quality.

CAUSTIC SODA SAVINGS

Another problem at Berlin was the saving of the caustic soda, which theretofore ran down the river. The separation of salt and problems of evaporation, involving higher temperatures as concentration increases, were full of troubles which were finally met by the design of new evaporators in which the liquor is introduced into the last effect and proceeds against the steam instead of with it. These are the patented Moore evaporators, which now work with great success, and give a product which is very pure and even.

The same interests have a great—in fact the largest in existence—sulfate pulp mill at La Tuque, Canada, in which kraft pulp is made for kraft paper; used for wrapping automobile tires and other objects requiring a sturdy wrapper and also employed for making twine and for use in furniture in the place of cane. The greatest technical trouble in connection with this process lay in the evaporation of the waste pulp liquors from which the soda must be regained. Intense foaming is characteristic of such liquors.

The usual method of evaporation is to employ revolving discs which dip into the liquor and are heated by furnace gases while covered with a film of it. The evaporated liquor, which contains 45 per cent soda and lignin compounds, polymerizes at high temperatures and becomes gummy. This is run through a revolving drum for incineration by means of hot gases from the smelting furnaces. The black ash comes out of the lower end of the inclined, revolving incinerator upon the floor. It is then mixed with more sodium sulfate and smelted in the furnace with the formation of the sodium sulfide. During evaporation and charring in the incinerator, the soda from the black liquor is liable to form rings around the inside of it which act as a dam. This holds back the lignin liquor on one side of the dam while on the other is molten soda and black ash. When this ring breaks the mixture of molten alkali and black liquor explodes. If the ring forms near the end, accidents are likely to occur. The cure of the trouble was accomplished only by working out an entirely new method of evaporation through the employment of Stefan's law of radiant heat, which is developed as follows:

$$B. t. u. \text{ per sq. ft. per min. radiant heat} \\ = 2.66 \times 10^{-11} (T_2^4 - T_1^4)$$

By the use of radiant heat (which is projected without imparting heat to the medium through which it travels) and with an entirely original design of apparatus, all under constant control, remarkable results are obtained.

By this method a far greater amount of soda is recovered as Na_2CO_3 and Na_2S , particularly as the sulfide. There are no

revolving discs, no accidents and there is no revolving incinerator drum and no black ash. Where formerly large quantities of fuel were required, 1600 available H. P. is obtained from the operation, the labor of many men is saved and the product is increased and improved.

A new application of a certain grade of sulfate pulp was worked out at Berlin by Mr. Parker on the mechanical side and Mr. Moore and his associates on the chemical side. This is a very strong, water-tight and machinable pipe made at present chiefly in 4 in. sizes. It is of about the weight of hardwood, takes beautiful threads and withstands 400 lbs. pressure to the sq. in. It forms an ideal conduit for electric wires and the entire output is sold ahead for an indefinite time.

At the La Tuque sulfate pulp mill a saving is also made of large quantities of turpentine obtained from digesters during the process of cooking. This is equal to the best gum turpentine, except for a slight odor.

THE SEMI-COMMERCIAL PLAN OF TESTING NEW PRODUCTS

So far we have been dealing with the pulp and paper industry and incidentally with the caustic soda plant. The beginning of this in 1909 was the beginning of a method of chemical development that is now the practice in the introduction of every new product. The chemical director was ready to produce caustic soda and asked for an appropriation of \$100,000 to begin. This was refused, but \$5,000 was appropriated for a test plant. The test plant succeeded and then the works were built which have since been greatly enlarged. The method was correct and now every new product is worked out on a semi-commercial scale before a permanent plant is built. The term semi-commercial, however, needs a little explanation. It involves often the expenditure of large sums and it always signifies a more or less improvised layout of sufficient capacity to turn out the material in marketable quantity. Until this is so adjusted that it not only runs smoothly but pays for itself, the process is regarded as not yet complete and general building and construction operations are not begun. In the developments which are recorded below, some are in the commercial stage, some are semi-commercial in its large or completed sense and are in operation while more adequate housing is in preparation, and some are at the inception of the semi-commercial phase.

UTILIZING WASTE CHLORINE

By 1910 the establishment was apparently well balanced, the caustic soda industry established and everything running full. But a demand arose for sulfite pulp bleached more on the side of yellow than of blue. In the largest sulfite pulp mill in the world (which the Berlin plant is) the amount of chlorine released by such a change in product is very great. The new problem was to utilize it. This was partly solved by leading the hydrogen and the chlorine from a number of electrolytic cells according to the requirement into a small apparatus in which they are combined to form hydrochloric acid.

Still there was chlorine to spare, owing to the growing installations for the increased demand for bleached pulp and the contrast for caustic soda.

We shall note first a great plant in process of construction and past the semi-commercial stage, for making dry bleach by a new continuous process. This is under H. K. Moore's patent and provides an amorphous dry powder, free from lumps, with the substantial elimination of chlorates and improvement in keeping qualities. The process consists of constant agitation of lime at a temperature below freezing, in the presence of chlorine and is fully described in the United States Patent No. 1,344,705, issued October 3, 1915.

One of the early chlorination products was chloroform from acetone and at present it is said that about six per cent of that consumed in the United States is made at Berlin. Through the activity of the Berlin Mills staff of chemists, especially of George

Richter, further developments have taken place, based upon the utilization of excess chlorine. As typical of these developments the manufacture of carbon disulfide was begun. This product, while sold as such in part, forms also the starting point for the manufacture of carbon tetrachloride and sulfur chloride. Processes for ethylene trichloride and acetylene tetrachloride are past the laboratory stage, as are also those for a number of other chlorinated products.

FEATURES IN COURSE OF DEVELOPMENT

A semi-commercial plant is under construction for making liquid SO_2 and this is to be followed by another for liquid chlorine. Another now under way is for the production of glucose from sawdust and bark, available from the original lumber mills which are in active operation: this contains an extension for working the remainder over into oxalic acid. An additional extension to the semi-commercial scale, planned, but not yet erected, is to carry the glucose over into alcohol or to lactic acid.

As soon as labor is available a semi-commercial plant will be erected for the production of synthetic formic acid. Another process that is promising but not yet ready for the semi-commercial tryout is the fixation of nitrogen, of which 400,000 lbs. are daily available from the sulfite mill. A semi-commercial plant is installed for waste liquor recovery from which the concentrate is shipped for core compounds, road binders, to tannin extractors, and small amounts to perfumery manufacturers. A kyanizing plant for ties using mercuric chloride has been in operation for some time and plans are ready to begin with tin tetrachloride as soon as this is feasible.

EFFECT OF REFRIGERATION ON HYDROGENATION

With the frequent use of refrigeration first in the laboratory and later on a large scale in practice, a situation was finally met, in which for purposes of research a lower temperature was needed than was conveniently available. In connection with a problem that Mr. Moore was working out in conjunction with Professor Muliken of the Massachusetts Institute of Technology, ethane was wanted for refrigeration, but was not to be obtained. Sabatier and Senderens had shown how it might be produced by the catalysis of hydrogen with ethylene or acetylene and by following the French savants closely they obtained exactly the yields prescribed. The yield is far from rich, however, and the method gave little promise of sufficient ethane for the purposes of the investigation. While discussing this, Mr. Moore remarked that ethylene was endothermic, and that it had more heat than the same amount of carbon and hydrogen has. Why, then, and more heat? All the extra heat must go off with the ethane as it is made. Why not cool it instead of heating it? The argument seemed sound enough to neglect the question as to whether Sabatier and Senderens had warmed themselves up as a part of their research or from sheer chemical habit, and they proceeded to refrigerate with salt and ice, which was the only means they had handy. The result was surprising. They increased the yield over 100,000 times that of Sabatier and Senderens and the only reason why they did not obtain more was because the water overflowed the gasometer. There was no trouble about getting all the ethane they needed from that first batch. A thermometer in a test tube inserted into the hydrogen stream was showing plus showed over 100° C. above the set and had.

Another conclusion reached from this experiment is that some of the poison of nickel dissolved by solution are also neutralizing from its own process. As with a catalyst and from the hydrolysis of gases to the hydrochlorination, and Mr. Moore, who had been at the time of the experiment with regard to some of the details of the chlorination process, was depressed and carried over a letter suggesting how to make out the others and some results, we shall send you a few tables. The process is in the state of a small scale plant and a small factory with hydrochlorination and temperature control. This is a standard

over the catalyst by a revolving arm so that, for a given moment of time, so much of the catalyst as rests upon the segment of the bed just underneath the arm gives up part of its hydrogen, thus hydrogenating the oil in contact with it. Hydrogen is constantly sweeping through all the rest of the catalyst, which has the effect of revivifying it. As the oil-spraying arm revolves, the sector in which oil is in process of hydrogenation is constantly moving. The same, of course, also holds true of that part of the catalyst filter bed which is being revivified.

The plant is of a very highly developed semi-commercial nature with a capacity of 30,000 lbs. daily.

CHEMICAL CONTROL IN PLANTS

The entire works in all departments are under constant chemical control, being intense in the sulfite pulp and chemical works and less observable in the lumber and paper mills which we shall not even undertake to describe. An interesting feature of the sulfite mill is the automatic analysis of the flue gases as worked out by Moore. The apparatus collects the gases from flues and boilers and from mains, cools and compresses to a pre-determined pressure and temperature, measures out a given volume, analyzes it by absorption, remeasures at the same pressure and temperature, records analysis, empties itself and begins again. It can be regulated to any frequency desired. In this mill they average one gas analysis each every 4 or 5 minutes. The apparatus is entirely automatic and the records are very plain and clear. A large number of these in different portions of the plant automatically keep data on the gas from one operation to another.

These automatic analyses constitute a part of the "chemical graphics" of the mill, the purpose of which is to form a picture of the chemical operation which may be understood by the men at work. For instance, the big digesters at the sulfite mill are 54 ft. high and 20 ft. in diameter. They are operated at 75 lbs. pressure at the top. Of course the process may not be watched as in a test tube, but recording thermometers and pressure gauges may be installed, and this is done. Every 15 minutes the temperatures are read and the workman looks up on a chart to determine the corresponding steam pressure. He reads also the gauge pressure and the computed steam pressure subtracted from the gauge pressure gives the gas pressure. Now SO_2 is the gas with which they are cooking, and the plotted chart prepared in the laboratory and set as the standard picture or graph of the reaction, shows just where the computed steam pressure and the gas pressure should cross, so as to obtain the best results. The workman also plots from his readings and if the picture is right, well and good. But if the picture is wrong; if, for instance, the plotted lines showing the computed steam pressure and the gas pressure cross too soon, then the cooking is incorrectly done, steam is wasted and the quality is inferior. This system enables the man in the mill to know whether the temperature is adequate for the reaction or not and if not to make it so, and it gives him knowledge and control of the process right through the reaction.

COOKING PULP SCIENTIFICALLY

Cooking pulp is not a simple operation, and when it was done by rule-of-thumb, six men could close down the great works by going on strike. Now, with pre-determined graphs, the personal equation in the cooking has been eliminated. There are production charts, bleach charts, humidity records, etc.; indeed over 1350 graphs are daily recorded in the sulfite mill alone. A considerable force of clerks collect figures and carry them to the office where they are averaged for each variable, calculated, plotted and finally studied. Then every six months they have a "scrap day," on which, after a conference, the useless curves are discarded.

RESEARCH FACILITIES

The research laboratory of the company now houses nineteen chemists and is about to be enlarged to over twice its present

size. It contains a considerable amount of small scale iron apparatus and a few testing devices of too general use to have place in local testing laboratories in the various works. A fleeting impression of the laboratory is of a busy but cheerful place. There is greater indulgence in mathematical habits of thought than some of us are accustomed to, for calculus is used like arithmetic. The chief assistant is George Richter, who bids fair to let us hear more of him some day. Another valued assistant who has been of distinguished aid by his clear vision of the mathematics of what happens is W. B. van Arsdel.

ADMINISTRATION OF MILLS

The Berlin Mills with its subsidiaries, the Brown Corporation and the Burgess Sulfite Fibre Company, is still a family affair, although the founder, Mr. W. W. Brown, died several years ago. His four sons now in control are Messrs. H. J. Brown, President; O. B. Brown, Vice-President and Treasurer; W. R. Brown, in charge of woods; and D. P. Brown, in charge of the La Tuque mill.

A few notes on the administration of the property may be of interest. The establishment is run on a 3-shift, 8-hr. basis. The highest current wages are paid. On Sundays there is a general shutdown for repairs. A company store is maintained in competition with village stores. A health and accident fund is maintained in which any man working in the mills may join, and which is supplementary to the workmen's compensation laws. Officers are elected by the men insured. Full wages are thus provided for those who are injured or ill and the surplus is returned annually in dividends. Besides the obligations of superintendents and managers, there is a safety committee appointed from among the men to report all points of danger and need of repair for safety's sake. District nurses are maintained. A large Y. M. C. A. was provided for under the will of the late W. W. Brown. In every mill there is a smoking room where men may gather for rest and recreation. A large baseball field is available and in active use in season for factory and forest workers. Any man that wants to can "see Mr. Brown." In the woods, the company does not "cut clean," except where necessary, so that reforestation is in large part continuous.

WATER POWER

There is about 30,000 horse power developed at Berlin Falls of which the Brown interests use the major portion and a large news mill of the International Paper Company the rest. This power may be increased by a proposed engineering undertaking that will not disturb existing industries. At La Tuque 110,000 H. P. is already developed which will be increased to 160,000 on completion of a new dam, while further up the river there is still more available to the Brown interests, bringing the total up to about 200,000 H. P.

CONCLUSION

In the Berlin Mills we have an example of the birth and growth of an important chemical center from a sulfite pulp mill, previously operated under rule-of-thumb methods. Aside from water power, mostly needed in the lumber, pulp and paper industries already established, there was nothing to invite chemical development. There was no coal, no limestone, no pyrites, nothing except a great pulp mill that was behaving badly. What happened was that a chemist with the gift of vision and creative genius came there and in the course of time was backed by capital in the hands of genuine administrative ability.

In all the developments there has hardly been a single lucky strike. Every improvement has been based upon natural laws that were at once both known and neglected. The men who did it were awake. How many of us go our ways, sleeping? The whole establishment is the answer made to difficulties by well-trained scientific ability of the first rank coupled with capital in the hands of administrators of the first rank.

THE PROFESSIONAL STATUS OF THE CHEMIST¹

By RAYMOND F. BACON

"Ahead of us are problems still more crucial and complex; their solutions [may perhaps be neither individualistic nor collectivistic, but they must be applications of a policy scientifically conceived.]"

The success of many of our most important industries can only be attributed to the centralized, coordinated work of operation with chemical research, and it is generally conceded that the accomplishments of industrial research have eventuated in the recognition by our manufacturers of the essentiality of the chemist.

The results of an investigation carried out by me last fall revealed the fact that certain of our research laboratory forces have been increased from 250 to 400 per cent in the last ten years, and that, since August 1914, the staffs of a number of the largest laboratories have been enlarged from 25 to 100 per cent. One great American corporation now employs about 500 men who have been trained as chemists. In the principal research laboratory of this organization 62 researchers are now at work, whereas in 1914 only 30 were employed and in 1906 but 17. At least five other organizations have 60 or more research chemists. However, the growth of the appreciation of research by American industrialists is inadequately indicated by the number of research chemists employed at various periods. There are numerous instances where the research work has only kept pace with the extent of the operations involved, although these companies have grown partly because they have constantly endeavored to progress with the advancement in knowledge. Their present conception of original investigation as a necessary accompaniment of manufacturing in no way differs from that which they held a decade ago. It is, accordingly, impossible to measure their appreciation of research by the extent of the facilities set apart for the purpose rather than by the degree with which the organizations are imbued with the investigative idea.

In addition to research chemists, three other general classes of chemically trained men are engaged in the service of industry. I refer to analytical chemists engineer-chemists (properly, applied physical chemists) and chemical engineers. The two last mentioned are frequently confused, and the industrialist does not usually draw a decided distinction between the analyst and plant, or engineer, chemist as to preliminary training. Strictly speaking, from the manufacturer's viewpoint, the chemists in his employ are either research or analytical.

AN INDUSTRIAL APPRAISAL OF THE CHEMICAL TRAINING OF TO-DAY

"Our industries need ideas, good ideas, and good men to execute them."

There exists a diversity of opinion among the directors of corporation laboratories of this country regarding both the industrial usefulness of present-day chemical instruction and the defects of academic training in chemistry. In order to demonstrate the actuality of this, I shall summarize the results of an inquiry, preliminary in nature, which was initiated during the past winter, as to whether American industrialists are satisfied with the training of the young chemists who have been taken into their employ during the past three years. In presenting these conclusions, it is necessary, both because of the large scope of the subject and because the quotation of individual instances would be offensive, to proceed in a spirit of broad generalization, and the validity of these general applications will be dependent upon their contextual reasonableness.

The results of the preliminary investigation are illuminating

¹ An address delivered before the New York Section of the American Chemical Society on May 11, 1917.

of the improvement over the conditions which obtained in factory laboratories six years ago. From the replies received in response to my questionnaire, approximately 30 per cent of the chief chemists and research directors expressed no real dissatisfaction with the chemical training of to-day. These officials conceded that a perfect training could hardly exist, and indicated that very much depended upon the traits of character of the young graduate, independent of the training. They thought that our large, well-equipped institutions of learning gave their chemical students fundamental knowledge which constituted a sort of inventory with which the men began work; but they pointed out that it was largely a question of active optimism and continuity of effort of the man in the position, coupled, perhaps, with the selection of subject of work, and that accordingly some gifted young men, with very little academic training, often accomplished fully as much.

It may be interesting to know that the college graduates in our steel works laboratories, both analytical and research, are regarded in general as well qualified. In fact, one chief chemist who had employed 25 young chemists since the beginning of the European war, stated that these men had "a more intimate knowledge of general conditions" in such plants "than those of five years ago." In another domain of industry, the laboratory director, an employer of 45 chemists, regarded the training of the men received into his department as "sufficient for the purpose." To quote further from his communication, the "training at the present time appears to be very good, but, of course, many men are taking the courses who are not fitted by nature and temperament to make a success of applied chemistry." Several chief chemists agreed that "if a man does not do satisfactory work in industrial chemistry, it is more his fault than the shortcoming of the training he has received." A prominent manufacturing chemist who requires twice the number of chemists employed five years ago, reported that he had noticed no difference in the training of young chemists during the past three years, but that "like all human beings, some are more efficient than others and some have taken better advantage of their opportunities than others." This industrialist retains only the diligent, earnest and loyal laboratory employees. The technical director of a large oil refinery endorsed the satisfactory nature of present-day chemical training, but alluded to the failure of chemists to win for themselves leading positions in their respective industries; he accounted for this, in a measure, by the experienced deficiency in "sticking qualities": "young men expect rapid promotion, and, if such is not forthcoming at once, they leave our employ in the hope of finding a more rapid advancement elsewhere." Still another technologist, the supervisor of 12 researchers, gave the opinion that "the quality of the men has improved greatly in the last five years and their knowledge of theoretical chemistry is greater, but they are very much lacking in even semi-practical work, having no knowledge of even the smallest form of industrial apparatus." His new chemical employees therefore receive an apprenticeship procedure which has become so general in scientific training, chemistry that it will be considered at more length later. Finally, mention may be made here of the complaint of those chemists who, while entirely satisfied with the adequacy of our chemical curricula, receive fewer applications for positions from well-trained chemists than they did three years ago. One employer of 45 chemists stated that the chemical types of twenty years ago seemed to be bred better generation by the "best Indians" "who offer higher salaries than the chemical institutions and working for export would necessarily." It has become increasingly difficult for such men to attract to their plants the men required for filling vacancies created by advancement of the members of their staffs.

On the other hand, the inquiry revealed the fact that about

70 per cent of the heads of important industrial laboratories are dissatisfied over the type of instruction that in many cases is offered young men who, after graduation, enter plant laboratories in positional capacities. There is dissatisfaction with the methods that are taught and with the neglect of the time factor in conducting analyses—dissatisfaction also with the omission of chemical literature from the course of study, with the failure to give instruction of a practical nature in chemical apparatus, and with the neglect to teach some sense of proportion in distinguishing between accuracy and practical accuracy. Then, too, those directors who have given the subject careful deliberation point to the lack of resourcefulness and optimism in the average graduate of to-day, and advise that, wherever possible, young men be selected for training in chemistry.

One great corporation, which now employs 70 chemists, replied that the young graduates taken into its laboratories during the last several years did not fully meet requirements. The opinion of the head of the research department of this company is the outcome of thoughtful consideration during the last decade, and is supported in general by the findings of the Subcommittee on Research in Industrial Laboratories of the Committee of One Hundred on Scientific Research of the American Association for the Advancement of Science;¹ it is therefore presented in full.

"They are nearly all deficient in the fundamentals, especially quantitative analysis; they have not received in the university the thorough drilling in analysis which its importance warrants, and, as a result, it is necessary to put the young men through an extended drill in the general analytical laboratory lasting for six months to a year before reliable work can be obtained from them. Obviously it would facilitate matters if this drill were given in the university. We believe more time should be devoted in the university to the making of complete analyses of natural substances; as, for instance, a heavy metal sulfide, such as pyrites, and a silicate, such as feldspar, everything present being determined quantitatively.

"Another criticism which can be made of the average young chemist is that he is lacking in a knowledge of chemical literature. In many cases he knows few chemical books and journals and may not even know the standard books on analysis. His ideas on where to find methods for his work are often vague, and consequently, when he gets into difficulties, as all chemists will, he is unable to work himself out. It may be remarked that lack of knowledge of chemical literature occurs probably most often with men from the smaller colleges.

"It is suggested that it would be profitable to pay more attention to teaching the student to work out his own methods of analysis; for instance, if he were given a sample of clay for complete analysis and required to locate the method for himself, he would be better prepared to meet a similar situation when it occurred outside of the university walls, as it certainly will a year or two later. We appreciate that this method of instruction is used to some extent, but we believe that the average student does not get enough of it."

This contention is corroborated by the experience of many other managers of research departments. One of the real personalities in industry remarked that,

"The young men of to-day do not have a thorough training in analytical chemistry, the desired laboratory accuracy, nor do they seem to think closely along strictly chemical lines."

Another director replied that,

"It has been our observation that those universities that aim to give broad training in the fundamentals of chemistry, and that neglect no department of analytical work, turn out men who more quickly become valuable to us in research work than do institutions that endeavor to specialize in producing so-called chemical engineers."

However, in such highly specialized industries as the manufacture of aniline colors, somewhat different, and preferably more elaborate, training is expected. It is the united opinion that in such an industry every chemist who is to do more than

routine work should have had a thorough training in research work; in other words, the man with the bachelor's degree is unsatisfactory unless he be given the research training under factory guidance, and obviously the man with the experience of a Ph.D. is the type most wanted. From the viewpoint of the coal products industrialist our universities are most weak in the direction of the various allied branches of science and engineering. For example, men are needed who are well grounded in electrochemistry, physical chemistry, physics and the engineering subjects, and who at the same time are conversant with the fundamentals of organic chemistry, so they can apply their specific knowledge to the development of this industry. As explained by an expert in dyes, much of the time spent in industrial chemistry as well as in certain lines of analytical chemistry does not bear the fruit it would if devoted to the study of the fundamental lines of the above allied subjects. "The most practical thing which the university can do for its students is to ground them thoroughly in the theory of chemistry and at the same time give them some insight into the fundamentals of the above-mentioned subjects."

Of course, it is essential that every chemist learn the manipulation peculiar to chemistry, but it is questionable if this cannot be done in less time than most institutions take for it. It seems to be the opinion of the men engaged in manufacturing organic chemistry that the industry itself can train the man best in industrial chemistry providing he has some groundwork upon which reliance can be placed and that this groundwork should be taught in the university. One thing is certain: the industrialists in that field are demanding that the chemist be able to conduct investigations, and every student should be made to realize that he must have graduate work to give him training which is absolutely essential to his success.

Another group of research directors holds firmly to the view that character and natural ability are of infinitely more consequence than training, and that in regard to the latter by far the most important part is that received after entering industrial work. That is, each important branch of industry demands its own special type of chemist and consequently no course of university training can cover all the requisite ground. Most of the profitable work in industry is the outcome of intimate contact with factory practice and manufacturing difficulties, and one of the most valuable assets that a young chemist can possess is the ability to get close to factory workmen and secure their cooperation. This group accordingly regards the young chemist as undertrained, not so much in chemistry, but in the every-day affairs in industrial practice, and considers the young graduate most useful who possesses a sense of how to do things in a direct way ("factory sense"), which is, of course, *resourcefulness*. The difficulty experienced is in knowing how to select the right man for the place.

One of our leading manufacturers, himself a chemist, informed me that he had never found a chemist who had sufficient training to take up his particular line of work, and that factory training was invariably necessary before the young graduate became sufficiently efficient to earn his salary. This technologist did not approve of the methods in use in teaching chemistry in this country: "Our system, with perhaps one or two exceptions, is like teaching the grammar of a foreign language exclusively without teaching the language. The student knows all about the language excepting how to talk." This is, no doubt, an extreme view, for my inquiry shows that it is far from being representative, but it is the outcome of a varied experience and therefore merits mention. The general opinion among manufacturers who are alone in a field of industrial chemistry or who are engaged in a highly specialized branch thereof, is that it would be expecting too much of the universities to ask them to supply trained men. As one chemical director has expressed this condition, "If the man has a good university training, and has

¹ See Bacon, *Supra*, N. S., 45 (1913) 31.

learned to think for himself and use inherited common sense, we usually can make a pretty good industrial chemist out of him in a year or two." This director has, in fact, even gone to the extreme of placing men with no chemical training in charge of chemical operations because of their ability to exercise independent thought and to act wisely in an emergency; of course, he has always supplemented such men by others with chemical training, in order to reply to chemical queries as they arise and not obligate those in charge to ascertain the answers themselves at a great waste of time.

Supplemental laboratory training for young graduates is a general practice in the explosives industry. One company has found that university-trained chemists are satisfactory after six or eight months training in its own laboratories, while in the chemical department of another corporation the newer men usually work under chemists who have had several years' experience in both research and in the adaptation of laboratory processes to works operations. "If a man has a good grounding in chemistry and is the right kind of man, we put him under older men in the laboratory to help in their investigations, and he in time becomes able to carry on research himself, that is, if he has the right kind of brains for that kind of work."

The following system of training is in operation by a company which manufactures over 40 products and employs about 60 chemists:

The carefully selected young graduates are first placed in the routine laboratory, the head of which eventually transfers the most capable chemists to the research laboratory. There are always a number of investigations in progress in the research laboratory, and one of the relatively new men is placed in charge of a process undergoing development. If he "makes good" under the general supervision of the research director, he later becomes superintendent of a plant erected for the purpose of applying the process. The method of getting into a new line of manufacture is as follows: a process is tested out with ordinary laboratory apparatus, and then, if the yields and prospects are such that it is decided to go into that line of manufacture, a small plant is built. A small amount of material is made in this way, and then the apparatus is improved upon according to the judgment of the man in charge, until finally it is got into working shape. It may then have a capacity of only a few ounces or a few pounds per day. This equipment is then used by the engineering department as a basis of design for a commercial plant. The first commercial unit itself is usually made on a small scale, and in as cheap a building as possible, and is expanded and elaborated as experience indicates. In other words, the processes and equipment are the products of slow but steady evolution, and the desired type of works chemist also results from this systematic development. When taken into the company's employ, the chemists are not competent to do anything but assist, but they are advanced to positions of leadership as rapidly as they are fully able to hold the jobs—at least, that is the aim.

Finally, reference should be made in this section to the recommendation of a chemical works manager of wide experience. In his opinion, one provision should be made in our educational system for the training of boys during the high school period in such technical subjects that they will be fitted for positions as "Chemical Apprentices," if such a term may be used. By chemical apprentice is meant boys who have had the equivalent of a high school course devoted almost exclusively to:

Arithmetic through Elementary Algebra
Elementary Physics
Elementary Chemistry
Elementary Mechanics
A little Mechanical Drawing
Considerable Manual Training, especially Wood Working and Machine Tool Work of the simplest sort

"We like to provide most of our chemists with one or more of such apprentices. By so doing we enormously increase the output of the trained chemist and at the same time we train up a valuable corps of assistants, who, for some purposes, are more satisfactory than the college graduate. We fully appreciate that the educational problem involved is purely a local problem; for, according to this plan, each community must shape its technical high schools, or trade schools, according to the needs of the industries of that particular section."

THE SELECTION AND TRAINING OF STUDENTS FOR INDUSTRIAL RESEARCH¹

"Our schools are called upon now not to record and systematize but to instill the active germ of a conscious, creative evolution."

Research leading to the discovery of new ideas requires not only intellect and training, but also initiative or genius; it can come only from an individual who possesses unusual intuition and insight. It follows, therefore, that there is a scarcity of men gifted with the genius for industrial research, and that it requires much experience in selecting suitable men and in training them to the desirable degree of efficiency, after having determined the particular qualities required.

It is considered advisable, in view of the experience of American manufacturers,² that in the beginning of his senior year the chemical student should branch more or less to a special study of the line of industrial work with which he anticipates he will later be associated. Those students possessing mechanical aptitude and those gifted for research work should be carefully selected with a view of suggesting specialization. Generally speaking, students qualified upon the completion of their undergraduate work to become engineers and research chemists, should be advised to devote two or three years to post-graduate study with the object in view of qualifying them for service in specific branches in the domain of chemical industry. These chosen students should be advised against accepting positions of an isolated nature.

Important qualifications in industrial research are the following:

Adequate training.	} Success
Scientific acumen. ³	
Active optimism. ⁴	
Intellectual honesty.	
Unobtrusiveness.	
Tact.	
Creative power. ⁵	
Enterprised. ⁶	
Impulsivity. ⁷	

Some directors of research place active optimism above scholarship, for they maintain that, without it, little that is novel will be accomplished except by accident. One is more likely to grant that knowledge may sometimes be a detriment to a type of searcher imbued merely with a need of solving new problems. However, the determinable nature of scholarly culture is

Read in part, and in part, to be given in the 45th volume of the *Proceedings of the American Chemical Society*, published in the preliminary volume as well as from the results of previous discussion.

¹ Especially in view of the recognition that the great industrial research centers in this work are now being established in the United States and that the country is becoming more and more dependent upon its own resources.

² The American Chemical Society, *Proceedings*, 43rd volume, 1915, p. 100.

³ Active optimism is a quality which is essential to the success of the research worker.

⁴ Active optimism is a quality which is essential to the success of the research worker.

⁵ Creative power is a quality which is essential to the success of the research worker.

⁶ Enterprised is a quality which is essential to the success of the research worker.

⁷ Impulsivity is a quality which is essential to the success of the research worker.

primary consideration in this place. It is scarcely necessary to mention that in no other human endeavor do the personal traits protrude so much as in concerted research; but the successful administration of research always presupposes the utmost faith in human nature, and it frequently requires some time for a display of optimism, poise, or fair play to become evident among qualified research chemists, especially when they are engaged on separate problems.

The important requisites for industrial research are frequently given no consideration by manufacturers, who, in endeavoring to select a research chemist—particularly their first researcher—are likely to regard every chemist as qualified for investigatory work. The supply of men capable of working at high efficiency as researchers is well below the demand, and chemists having the requisites and spirit of the investigator are indeed difficult to find even by those experienced in the direction of research. All research professors know that the location of a skilled private assistant—one who possesses not only originality, but also sound judgment and intellectual honesty—is not easy, because it frequently involves the gift of prophecy on the part of the searcher.¹ It has been truly said that the "seeds of great discoveries are constantly floating around us, but they take root only in minds well prepared to receive them."

On account of the extraordinary technologic importance of new ideas, particular emphasis should always be laid upon finding and supporting brilliant researchers. Such individuals can best be found in the universities. The function of the university is to work with the beneficent idea of increasing the sum of human knowledge, and among its most valuable products are those who will work for the exercise of the investigative instinct and the pleasure of overcoming difficulties.

The examination of the training necessary for those proposing to take up industrial research which is common with all scientifically trained men, is too extensive a subject to be discussed here. It is, however, appropriate to consider those subjects to which it seems desirable for the prospective researcher to devote specific attention; reference is, of course, had to subjects other than those required by the average student of the sciences as distinguished from their industrial application, but the assumption is not made that what is desirable for research work should not also be available for all.

Research men in the service of our industries frequently possess adequate training and scientific acumen, but fail in their ability to use it. There is no question that the chemical graduate of to-day is most noticeably deficient in *resourcefulness*. A qualified research chemist who possesses initiative is usually a creator, but, owing to the neglect of existing difficulties in chemical pedagogy, the present-day graduates of our schools of chemistry are too often deficient in inspiration, ingenuity and insight.

The failure to provide adequate and systematic instruction in chemical literature is illustrative of this contention.

Before commencing laboratory work upon any problem, it is obviously necessary to digest intelligently the important contributions which have been made upon the subject and to take advantage of what other workers have done in the same field. The average graduate is usually almost helpless when attempting to do this and consequently requires close supervision. The main difficulties are:

(a) He does not know how to go about it; he does not know where to look as the most probable source; and he is not familiar with the standard treatises and important journals.

(b) He fails to analyze the subject into its factors and hence generally looks for topics which are too general. Because he does not find any reference to the problem as a whole, as he has it in mind, he assumes that nothing has been done upon it and that there is nothing in the literature which will be of aid to him in the investigation. Were he to separate his subject into its

essential parts and then to consult the literature on each factor, he would find considerable information which he otherwise would miss.

(c) He does not critically digest the articles under examination, but often he makes only a few disconnected quotations and fails to interpret the work done.

The solution is to be found in the provision in the chemical curriculum, preferably in the junior year, of a course of lectures (one hour per week) on the literature of chemistry, with particular reference to the character of the writings and the status of the authors. The purpose of this course should be to present a general survey of the voluminous literature and to impart an accurate, systematic working knowledge of chemical bibliography. A concurrent seminar (at least two hours per week) should be devoted to indexing and tracing chemical literature, to the cultivation of an acquaintanceship with authorities, and to the solution of bibliographic problems. This training should continue through the senior year in order that it could be put into practice in thesis work.

Pedagogic attention should also be given to the arrangement of a course of study in the principles of technical reporting and in the criteria of literary excellence in the preparation of reports of researches and professional reports. The completion of such a subject, with its accompanying analysis, practice and criticism, would usefully supplement the training received in chemical bibliography and would develop a capability which is much needed by chemical graduates.

It may be noted in passing that, during the academic year 1914-15, distinct courses in chemical literature and in technical reporting were established at the University of Pittsburgh. Much success has attended this pedagogic innovation. Training in chemical literature for juniors has been provided at the University of Illinois since 1913, and there has been observed a marked difference in the ability of the seniors to handle literature with discrimination.

The chemical graduate of to-day is also deplorably deficient in resourcefulness in planning research. While this is an extensive subject, a research student may be trained in correct methods of attack, namely:

ANALYTICAL METHODS—Almost all investigations require analytical control. In no feature of chemical work is there more apparent an inability to use the analytical training which the young chemist has received.

PLANNING THE INVESTIGATION—Resourcefulness in separating a problem into its essential factors and in clearly grasping the interrelationship of these factors is most important. Too many men desire to start in at once, hoping thus to solve the problem at the first attempt. This tendency could be overcome by instruction in "methods of research."

APPARATUS—Unfamiliarity with apparatus, both laboratory and plant, is a marked weakness in the average graduate. While cleverness in this respect is doubtless innate, and not made, it should be possible to give the undergraduate some training in the use of his mental equipment in designing and planning apparatus which is to accomplish definite desired results.

THE STATUS OF THE CHEMICAL CONSULTANT

"Our chemical house must be in order."

At the present time the practice of chemistry savors of a profession, but it has not become a well-defined and established profession. Indeed, some consider it doubtful whether it can attain a higher standard until the cloak of legislative protection has been thrown around it. It is true that our chemical organizations can endeavor to protect the public against impostors and unqualified consultants, but their power is limited and eventually, according to this viewpoint, it will become necessary for the public to resort to the legislature for protection. It

¹ See discussion in *S. 1006*, N. S., 41 (1915), 319.

is contended that chemical liberality has opened the doors to merely interested and even ignorant persons—a condition which can be remedied only by legislation.

The actual profession of the consulting chemist should require very careful preparation by one who seeks to enter it; but while many may have occasion to consult him, comparatively few can determine the qualifications of learning and skill which he possesses. This is the basis of the argument that reliance should therefore be placed upon the assurance given by a license, issued by an authority competent to judge in that respect, that he has the requisite training.

The wisdom underlying the statutes requiring a definite preliminary education, supplemented by special study at accredited schools, as qualifications precedent to the application for license to practice medicine, dentistry, or pharmacy, cannot be questioned. The legislation of the several states of the United States in this respect has been approved by the courts in holding those statutes constitutional which prohibit the practice of those professions by unlicensed persons. The profession of the chemist, of inestimable importance to society, has not, however, found a place in our legislatures.

While the chemist does not have to deal with the influences upon which health and life depend, he has been active in the protection of public health, of vital moment in modern government, and it is therefore surprising, perhaps, that society has not taken advantage of the right to prescribe rules of conduct for the chemist which would attempt to conduce to the general welfare. But the condition may be explained by the fact that, logically, as it now exists, the chemical profession is constituted of varied specialists and assistants responsible thereto, and it is a well-established principle of law that—

"In all those employments where peculiar skill is requisite, the one who offers his services is understood as holding himself out to the public as possessing the degree of skill commonly possessed by others in the same employment."

Then, too, as in the case of the engineer, the great majority of chemists are definite employees whose qualifications have been passed upon by the organizations they serve and which are responsible therefor, and admittedly the skill and knowledge possessed by these representatives are not for the determination of society in general. Important elements of this nature serve to differentiate the status of the non-consulting chemist from that of the general medical practitioner. The question when a chemist becomes a specialist or expert will never be one of law, but one of fact for his own determination and for the recognition of his employers or colleagues; but when he holds himself out as a consulting specialist in some subject of chemistry, he assumes the obligation to use that degree of skill which such an expert should necessarily possess in the opinion of the profession. Statutory licensure would therefore appear to be unnecessary. The reasoning in this contention is predicated upon the law relating to the liability of the medical specialist.

The fact that there have been so few damage suits involving consulting chemists is a monument to the general high integrity of the chemical profession. Indeed, the rarity of chemical quackery is convincing testimony that there is no moral need for legislative protection of the public. Society must, however, look to professional organizations of the type of the American Institute of Chemical Engineers, to raise constantly the ethical and scientific standards of chemical consultants, discouraging and prohibiting unprofessional conduct. No one should be regarded as a chemical engineering consultant until he can qualify for membership in the American Institute of Chemical Engineers.¹

It is not contended that every chemical engineer should be expected to seek membership in the American Institute of Chemical Engineers, but it is reasonably maintained that every one who holds himself out as a consulting chemical engineer should be able to comply with the standard established by that organization and that the qualification should be employed legally in connection with expert and opinion evidence.

and it is highly desirable that an institute of analysts also be established, in order to advance the cause of analytical chemistry and to give the analyst such standing before the community as will justify the complete recognition of his profession by municipal, state and federal authorities in public works.

Those engaged in the practice of chemistry have become conscious of their work as a social service and their devotion to this work is intensified by the recognition that they are united in a sort of invisible brotherhood. It is therefore a natural result that their personal pride in individual achievements has become so elevated by consciousness of class that it has been converted into an abiding professional pride. The industrial chemist has been obliged to contend with infinite diversity of institution and with empiricism, but the introduction of scientific methods is providing a new center of interest for him as well as for the organization which he serves.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH
UNIVERSITY OF PITTSBURGH, PITTSBURGH, PENNSYLVANIA

THE INSPECTION AND TESTING OF TRINITROTOLUENE

By K. K. STEVENS

Received May 22, 1917

Trinitrotoluene, although long known to chemists, is comparatively new in the field as a military explosive, and for brevity is designated by various trade names, such as "Trotyl," "Tritol," "Trinol," "Tolite," "Trilit," and commonly known as TNT.

Picric acid or trinitrophenol was, and is still, used to a large extent as the principal explosive of this class, under the names of "Lyddite" and "Shimose." Picric acid and TNT belong to the "brisant" or shattering class, and are used largely in the manufacture of shells, torpedoes, mines, and, either alone or as components, in detonators or "exploders." The chief disadvantage in the use of picric acid is its tendency to form very sensitive picrates with the metals of shells, etc., and necessitates strict specifications for these materials.

TNT has several advantages over picric acid, viz.:

(1) Inertness towards heavy metals, in direct contrast to the picric acid, although caustic potash or soda will form compounds with TNT which will cause it to explode at even 160° C.

(2)—Lower fusion temperature, which allows pouring to be done at 81° C. or lower, while picric acid requires a temperature of 115 to 120° C.

(3)—Stability in storage; it can be stored indefinitely without change in composition.

(4)—Insensitiveness to shock of impact or friction, so that it can be safely handled and transported. A rifle bullet fired through a case of TNT had no explosive effect, and mixing with ether and/or water has no effect on its explosive force.

The velocity of detonation is less than that of picric acid, 1000 meters per second against 1300.

The explosive force test shows that the "Humboldt" method gives for TNT 1.5 or 1.6 g. of picric acid per g. of TNT. These figures may vary with different grades of material, and are given only for comparison.

The lower explosive or shattering force is a relative advantage, for, except in shell fuses or torpedoes, picric acid will not have the disastrous effect produced if the fuse or torpedoes are larger.

Used in detonators, TNT requires the same quantity of fulminate, e. g., 10 g. of TNT will replace 10 g. of fulminate, 10 g. of TNT will replace 10 g. of fulminate.

TNT is also used as component of many explosive mixtures, having greater effect if combined with compounds like chlorates and nitrates, which furnish oxygen for complete combustion of the TNT, which is decidedly lacking in oxygen, and when exploded alone gives a dense black smoke.

INSPECTION

TNT is on the market in two grades, primarily, *crude* and *refined*. The crude has not been recrystallized from solvents, while the refined has. Of these two grades, there may be several other grades based on the melting point (M.P.) or usually the solidification point (S.P.).

The crude TNT is the more common in the U. S. and when purchased by foreign governments is shipped crude and either refined or blended with other substances. The greater bulk of TNT made, up to very recently, has been shipped crude, probably only three plants in the U. S. manufacturing the refined grade in any quantity. In the different plants the product is obtained in lots of approximately 2200 lbs. each, called "runs."

The specifications usually call for containers, such as cases or kegs, which hold from 60 to 100 lbs., are lined with oiled paper, and numbered as to shipment, "run" and case. The inspector may be expected to check the weights, and take samples for analysis.

SAMPLING

Samples should represent amounts of 4000 lbs., and for convenience a composite sample from two runs is often taken. The cases are selected, opened, the samples taken from different parts of the case, mixed, and three 1-lb. bottles filled: one each for buyer, seller, and referee, the latter's bottle being sealed by the buyer's inspector.

TESTING

COLOR should be light yellow, for crude, cream for refined.

Comment—The color changes rapidly when exposed to strong light, sunlight changing it from yellow to orange in 15 to 20 minutes, although usually the deeper shades of yellow are not an indication of impurity. The brownish grades should be inspected, though not necessarily condemned in the crude grade without confirmatory tests.

In the refined grade the color may vary with the solvent used in recrystallizing, but should usually be of a light cream, melting to a clear light brown, not darkening appreciably at 100° C. for 2 hours.

FINENESS—For crude, 90 per cent shall pass through a 10-mesh sieve. For refined, 99 per cent shall pass through a 12-mesh sieve. For exploders, all shall pass through a 30-mesh sieve.

Comment—The crude may contain frequently 7 to 8 per cent of lumps larger than specified, but usually is O. K., always being sieved before packing, and the lumps forming on the sides of the crystallizing tub have been allowed, intentionally or accidentally, to get into the sieved product.

MOISTURE shall not be more than 0.10 per cent for crude or refined (some specifications allow 0.15 per cent) and shall be determined by drying 2 g. over sulfuric acid for 24 hours.

Comment—The method is efficient and will remove as much as 30 per cent moisture in the time specified.

ACIDITY—There must be no acidity. This determination is made by shaking 10 g., melted, with 100 cc. boiling distilled water, allowing to cool, pouring off the water extract into a flask, and reserving; the operation is repeated with 50 cc. water, adding the second extract to the first. The combined extraction is titrated with *N*/20 caustic alkali, using phenolphthalein as indicator.

Other specifications less definite are as follows: Shake 5 g. with 100 cc. of distilled water in a 100 cc. graduated cylinder one minute, add blue litmus paper and stand 30 minutes, with occasional shaking. The paper must not show any acid reaction at the end of this time.

One specification allows 0.03 per cent acid calculated as sulfuric.

Comment—The method of the first specification seems better, although any sodium bicarbonate washing (not used at present) will give acid reaction at this point, whereas methyl orange will give only the mineral acids. The litmus paper shows acidity with phenolic compounds as well as acids, but if the determination is carried out as specified, there will be no color to the litmus paper, it having been completely bleached, and any acid reaction is more or less doubtful. The method may be modified as follows: Shake 5 g. with 400 cc. distilled water 1 minute, filter, stand 5 minutes and add the litmus paper; any acid reaction will be detected in 2 minutes. The litmus might be used instead of titrating in the first method.

INSOLUBLE MATTER must not exceed 0.15 per cent, as determined by boiling 10 g. with 150 cc. of 95 per cent alcohol, collecting on weighed Gooch crucible, washing with not more than 150 cc. of 95 per cent alcohol, drying at 95° C. 1 hour and weighing.

Some specifications call for benzene as the solvent and allow 0.1 per cent for refined, 0.15 per cent for medium, and 0.2 per cent for crude.

Comments—The method is efficient.

Turbidity in the wash water is one cause for high insoluble matter, and another is allowing the TNT to stand too long in the lead-lined wash tanks, the acid attacking the lead and forming lead salts.

ASH IN CRUDE TNT must not exceed 0.10 per cent, determined by igniting 1 g. in a platinum crucible, allowing to burn slowly and igniting completely, precaution being taken to prevent loss of ash.

Comments—The sample should be heated, ignited directly with the flame and allowed to burn without first melting; if melted and then heated further the sudden combustion will expel it from the crucible.

The size of the sample should be about 2 g., taking into consideration the low percentage of ash present.

The residue called "insoluble matter" might be conveniently used for the ash determination.

Some specifications called for sulfated ash, probably to avoid loss of potassium or sodium salts during ignition.

ASH IN REFINED TNT for exploders must be less than 0.05 per cent.

NITROGEN—Crude TNT must not contain less than 18.00 per cent nitrogen determined by the Dumas combustion method. Refined TNT must not contain less than 18.2 nitrogen determined by the Dumas combustion method.

Comments—The Dumas method, standard for nitrogen, requires little comment, results being very satisfactory, although it is necessary to make determinations on a substance of standard nitrogen content.

The method requires from 1½ to 2 hours, and unless the chemist possesses several furnaces, not very many determinations can be made daily.

For the nitrogen determination on many organic compounds, the Gunning-Arnold method or modification of it has been used. The only modifications reported to be satisfactory for trinitrotoluene or other nitro compounds are the zinc-dust reduction by W. C. Cope, U. S. Bureau of Mines, and the use of nitron as reagent, by W. C. Cope and J. Barub, *J. Am. Chem. Soc.*, 39 (1914), 504-14.

The nitrogen determination is important, although if the melting point or solidification point is up to specifications, the nitrogen is seldom below.

In many instances it is common practice to average several samples for the determination of nitrogen.

DIPHENYLAMINE TEST—Crude TNT shall contain no products which will give the nitric acid reaction with a sulfuric acid solution of diphenylamine. The determination is made by shaking with 50 cc. distilled water in a graduated glass stoppered cylinder, standing 15 minutes, filtering and testing a few drops of the filtrate by adding to the diphenylamine solution. No nitric acid reaction should be obtained.

Comments—The blue color characteristic of this reaction is readily recognized and the test is extremely delicate.

Care must be taken that vessels are free from traces of nitric acid or nitrates.

Since other oxidizing agents, such as chlorine, chlorates, bromates, etc., will respond to this test, it is of more value, as a negative test, and fairly positive, because the oxidizing agents mentioned are not likely to be found in trinitrotoluene. A pale blue color is not confirmative; the color should be deep blue.

MELTING POINT

The MELTING POINT of crude TNT must be 75.5° C. or higher.

Note—This is the mean, some specifications calling for a melting point of 74.5° C., others 76.5° C.

Medium TNT must have a melting point of 79.5° to 81.5° C. Refined TNT for exploders must melt from 80 to 81.5° C.

Comments—Methods for obtaining melting points are not usually given in the specifications, but it is absolutely necessary that a definite procedure and definite apparatus be agreed upon. The following points should be taken into consideration: calibration and stem correction of thermometers, size of tubes, amount of substance taken, degrees of melting at which reading is to be taken, rate of melting and vessel or liquid to be used as bath.

The following is given by H. B. P. Humphries, Engineer:

APPARATUS AND METHOD—A beaker of 1500 cc. capacity should be filled $\frac{3}{4}$ full with distilled water, heated by an adjustable Bunsen, arranged with a mechanical stirrer with the center of the blade level with the thermometer bulb, clearing it by $\frac{1}{2}$ in. The thermometer should be graduated in tenths of a degree, and lowered so that the bulb is $\frac{1}{2}$ the height of the beaker from the bottom and 1 inch from the side.

Tubes should be made from thin-walled 6 m. s. $\frac{1}{2}$ in. test tubes drawn out into $\frac{1}{8}$ in. internal diameter, cut into 3 in. lengths, and sealed at one end.

Set stirrer going and heat until the temperature is about 15° C. below the melting point. Meanwhile introduce a $\frac{1}{4}$ to $\frac{1}{2}$ in. column of the powdered sample (previously dried at suitable temperature) into a tube and tap and tamp down gently. Attach the tube to the thermometer by a rubber ring so that the center of the column of material is level with the center of the thermometer bulb, and replace thermometer as before. Reduce the heat so that the temperature rises 1° in 2 or 3 minutes. The slower rate should be adopted if several determinations are made at the same time.

Readings. Note the temperature when

a. The first globule of melted material is observed.

b. The material is half molten and half unmelted.

c. The melting is complete and the clear liquid is obtained in the tube.

Record these readings and call a the uncorrected melting point.

CORRECTED M.P.—Correct the readings for exposed mercury stem as follows: while the thermometer is registering approximately the melting point, place a drop of melted diphenylamine on the stem and allow to flow down. For a small distance above the water surface the diphenylamine will remain molten; above this it will solidify. Note the point separating the solid from melted diphenylamine.

Then, if N = No. of degrees of mercury stem exposed above this point.

T_a = Surrounding air temperature and T_m = Melting point the correction is, $N(T_m - T_a) \times 0.000154$.

Add this correction to the recorded temperature (b) for the corrected M.P.

The grading of the TNT being almost entirely dependent upon this determination, the method should be carefully followed.

Comments—The tubes above mentioned seem too large in diameter, and a tube 1 mm. or less in diameter would give a result closer to the real melting point.

One quarter inch of substance is sufficient, because the higher the column, the more difficult it is to decide when half is melted completely since this compound does not always melt in one place in the tube, but often at the top and bottom simultaneously and it is left to the operator's judgment, at which point the reading is to be taken.

The three readings are usually taken as a check on each other.

SOLIDIFYING POINT

The uncertainty of the M.P. is avoided to a great degree, when the solidifying point is determined. Only one set of specifications gives the method which is given by E. M. Weaver, Brig.-General U. S. A. and Chief of Coast Artillery, in his book "Notes on Military Explosives."

METHOD—Place 200 to 250 g. TNT in a dry porcelain dish of 15 cm. diameter and 500 cc. capacity. Melt below 90° C., remove heat and stir with thermometer. The temperature falls gradually until TNT begins to crystallize, when it rises. Continue stirring until the highest temperature is reached: this is the solidifying point.

Comments—This determination is more apt to give consistent results, and is simple enough so that the different operators usually check closely.

It is more accurate, since a larger sample is used, and the point of taking the reading more certain than in the M.P. determination.

The above method is followed, without adhering to the size or form of dish. The majority of chemists use smaller dishes, test tubes and beakers without varying results.

Although the M.P. and S.P. are generally considered the same, there is some difference, reports from different chemists showing the S.P. to be in some instances higher and in others lower than the M.P. Some report identical results for the two.

The writer has noted that where the M.P. was higher the TNT had been dried at 60° C., and where lower the material sample had been used. Further evidence is necessary for a decision on this point.

STABILITY TESTS are not usually required on crude material, although some specifications have required it as follows:

The substance, about 5 g., is suspended in a test tube having a strip of potassium iodide starch paper suspended on a glass hook which passes through the stopper. The tube with contents is placed in a bath and heated to 100° C. for about 10 to 15 minutes (depending on concentration). No blue color showing presence of nitric acid should develop.

Copyright 1917 by American Chemical Society

PITTSBURGH, PA.

Printed by the American Chemical Society, 529 North Dearborn Street, Chicago, Ill.

CURRENT INDUSTRIAL NEWS

AGRICULTURAL MACHINERY AND IMPLEMENTS IN USE IN PALESTINE

The British Commissioner in Egypt has forwarded a memorandum on the subject of agriculture and supplies in Palestine, of which the following extract is given in the *Board of Trade Journal*: In the neighborhood of Jerusalem a good deal of scientific dry farming is carried on, the ground being kept loose by continual tillage. The Arabs do not use harrows, but the Jewish colonists have introduced the harrow and American pulverizers with very beneficial results. The ploughs chiefly in use in Palestine are the primitive Arab ploughs and the German ploughs used throughout the German and Jewish colonies. British ploughs are said to be too heavy and the shape not quite suitable. In the orangeries and other plantations, American ploughs are used exclusively and the American zig-zag harrows are also employed. The use of the American disc harrow is common and the American harvesters are in fairly general use even among the Arabs, while the Jews employ American binders. A hoe made in Philadelphia has been fairly widely introduced, but sowing drills are rare. In the Jaffa orange district, the irrigation of the new groves is effected by means of pumps operated by oil engines which were first introduced by the Jews. Most of these engines are of British make (3 to 8 H. P.) and it is estimated that there are about 300 of them in the orange groves. There is a great shortage of spare parts. The water is raised by small bore (4 in.) tubes sunk vertically into the sand strata to a depth of between 40 to 60 m., the water rising to a height of 12 m. in the pipes. The pumps raise from 25 to 40 cu. m. per hour. In 1915, the above-mentioned engines were transformed into charcoal gas engines, as no supplies of oil were available. Of the pumps employed, from 80 to 90 per cent are of local manufacture, mostly at the two factories in Jaffa (one of which is German, the other Jewish) where there are a number of good Jewish mechanics.—A. MACMILLAN.

ENGINE FOR MOTOR PLOUGHS

A new type of twin-cylinder, two-stroke cycle engine which Messrs. Petters (Ltd.), of Yeovil, have designed for use in motor tractors and ploughs is of 10 to 12 B. H. P., the cylinders having a bore of $4\frac{3}{4}$ in. and a stroke of $4\frac{1}{2}$ in. A feature of interest in this engine is that the fuel oil, consisting of ordinary paraffin, is not admitted into the crank chamber, as is usual with two-stroke engines, but is injected direct into the cylinder with the fresh air at the end of the firing cycle. On starting, the engine runs for two or three minutes on a small quantity of petrol, but afterwards works with paraffin. The ignition is by high-tension magneto, and a throttle governor is provided.—M.

DESULFURING PETROLEUM

In the course of an interesting paper on "Sulfur in Petroleum Oils," read recently before the Institute of Petroleum Technologists, London, Dr. F. Mollwo Perkin said that Messrs. Lucas, Palmer, and himself had devised a desulfurizing process which was as yet in its initial stages. It consisted in the treatment of the oil at high temperatures with gaseous ammonia. The oil may be either in the liquid or gaseous state. If the oil is liquid, the pressure must be kept sufficiently high to prevent the oil gasifying at the temperature to which it is subjected. On the other hand, the temperature should be sufficiently high to cause the ammonia to dissociate. When the oil is treated in the form of vapor, it is passed through a heating system together with the ammonia before being condensed. It has been found that sulfuretted hydrogen is given off from oils containing sulfur when treated in this way.—M.

THE ANALYSIS OF SPICES

The *Oil and Color Trade Journal*, 51 (1917), 1308, quoting from a Swiss contemporary, gives the following methods for the determination of water and essential oils in spices. For the estimation of water, 10 grains of the powdered substance are weighed out and 60 cc. of oil of turpentine, perfectly free from water, added. The mixture is distilled rapidly so that the distillation should take only about 10 to 12 minutes, the distillate being collected in a 50 cc. centrifuge tube to within 1 cc. of the graduation mark. The receiver is sealed, centrifuged for 15 minutes and then placed in a water bath at 15° C. The amount of separated water is then read off. It is claimed that this method gives the true amount of moisture, as distinct from "volatile matter." The fat and essential oil are determined by weighing out 10 grains and placing the sample in a desiccator for 6 hrs. The sample is then exhausted with ether which has been dried over calcium chloride. The ether is then distilled away at a low temperature at the rate of one drop per second from a tared flask until no more comes over. Ether vapor is then removed by a current of air and, on cooling, the residue is weighed. This is returned as fat and essential oil. This residue is then steam-distilled until 250 cc. are collected. The residue left after this distillation is dissolved in 40 cc. ether, and the ether driven off on a water bath, and what is left behind weighed. This is calculated as fat and deducted from the previous result which gives the amount of essential oil.—M.

DETERMINATION OF FREE ALKALI IN PETROLEUM SOAP

According to K. Charitschkow, says *Oil and Color Trade Journal*, 51 (1917), 1707, the usual methods of dissolving in methyl alcohol and titrating with normal acid or of dissolving in water, treating with barium chloride and titrating the filtrate fail to give concordant results in consequence of the hydrolysis or alcoholysis which takes place. He, therefore, proposes to treat the aqueous solution with copper sulfate or iron alum, dissolve the naphthalene salt in benzene, and determine the residue, oxide of iron or copper, expressing the result as free alkali. In filtering, it is advisable to use an elutriator or to treat the soap solution with aniline sulfate, quinoline, etc., in presence of benzene. The method is claimed to be applicable to all soaps.—M.

BRITISH BOARD OF TRADE

During the month of May, the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.

CHEMICALS:

Alum powder
Calcium permanganate
Potassium permanganate
Powdered red arsenic
Saponified stearine (for matches)
Soda
Sodium nitrate (20 tons)
Sodium nitrate
Sodium permanganate
Sulfur, ground for matches

Aeroplane cloth (linen)
Air-tight stoppers for jars
Asbestos, pulp and powder
Asbestos, corrugated for roofing
Asbestos, yarn for braiding electrical cables
Bone-black
Bone shields for feeding bottles
Dairy churns, glass
Glass balls for mineral water bottles
Glass for making glass paper
Impalpable glass
Needles, flexible
Paper, blue, for match-boxes
Pipe-cleaners
Stoneware jars (7 lb.)

MACHINERY AND PLANT for

cutting out sewing fabric gloves
making sealing wax
fixing metal lids to small glass jars
making wood-pulp jars
making veneered wood
boot-lace tagging

—M.

TUNGSTEN FILAMENTS

A peculiar way of preparing tungsten filaments which are ductile in spite of being squirted, was described by Dr. W. Böttger before the December meeting of the Bunsen Gesellschaft. The process is due to Messrs. O. Schaller and Orbig, and members of the Society were able to watch the process in the works after the meeting. The metallic powder is mixed with 2 per cent of thoria and kneaded into a paste with the addition of a binding agent; a thread is then squirted. The thread is first preheated and then rapidly heated up to 2,400 or 2,600° C., the object being to make the crystallization of the metal more rapid than the passage of the wire through the hot zone. The first apparatus used for this delicate operation had the dimensions of several meters; the actual apparatus is now a few centimeters in height. The resulting wire is said to contain crystals several meters in length, though only a few hundredths of a millimeter in thickness; the cross-section of the wire comes out octagonal rather than circular. There are very few joints in a wire while the first tungsten wires, it will be remembered, were really thin rods built up of very short sections. A recrystallization of the filament after long-continued use of the lamp is said not to occur. Why the thoria favors crystallization in so remarkable a way is not as yet understood.—M.

COLD WORK ON BRASS ALLOYS

A point apt to be overlooked, says *Practical Engineer*, 55 (1917), 220, in handling brass alloys was mentioned in a paper on "Brass and Other Copper Alloys Used in Marine Engineering" read before the Institute of Marine Engineers by Mr. J. T. Milton. The lecturer said that, although valuable properties were given to these brass alloys by cold work, such as increase of strength and elastic limit, it must not be forgotten that the ductility is much reduced at the same time. When brass is subjected to much cold work, it is liable to spontaneous fracture. Cases are not unknown of condenser tubing spontaneously cracking longitudinally and of cold-rolled brass rods being found split after being stored for some time. Such occurrences are sometimes called "season cracking." The cause is, to some extent, obscure, but the fact that it occurs shows how unwise it would be to rely upon what may be termed an artificial strength produced by cold rolling for articles in which a failure would cause disaster. This is sometimes not sufficiently realized by engineers who think they are securing a better article by specifying stringent conditions of high tensile strength and high elastic limit which can be obtained only by cold rolling.—M.

THE INDIAN RAW HIDE TRADE

According to an official statement issued by the Government of India, the lucrative Indian trade in raw hides had, for several years before the war, passed largely into German hands. Firms, consisting of Germans and with German trade connections, centered and formed an effective ring for the control of trade in Indian hides. Before the war, Germany held a predominant position in the cow-hide trade of Calcutta, the chief port of shipment for this trade in India. Italy, Austria-Hungary and Spain were the next largest buyers; but, while hides taken by Germany and Austria averaged about 9½ lbs. in weight, those taken by Italy and Spain were from 8½ to 6 lbs. Since the outbreak of the war, through the elimination of Germany and Austrian business, the most notable movements of the trade have been (1) the 100 per cent increase of the trade with Italy and (2) the growth of the trade with the United States which has taken hides averaging 11½ lbs. The United Kingdom has increased its takings average weight about 12 lbs. net; but its share of the trade was still only 6 per cent of the total in 1915-16.—M.

COAL-TAR RESEARCH

Development of the coal-tar color research scheme at Huddersfield, England, says the *Dyer and Calico Printer*, will be greatly stimulated by the decision of the local authority to proceed at once with the extension of the Technical College premises. Research work has been pushed forward energetically since the scheme was launched but the need for more accommodation existed even at that time and since then has grown more urgent. All the necessary preparations were made at the time for the erection of modern laboratories and the work of actual construction was sanctioned at the last meeting of the Town Council. The extension of the present premises is to be general but the council has specifically stated that the section for coal-tar color chemistry will be proceeded with first. This scheme has received a great measure of support, not only locally, but from all parts of the country and subscriptions were promised from many quarters.—M.

JAPANESE EXPORTS AND IMPORTS

During 1916 the exports from Japan included the following products; the unit of quantity, unless otherwise stated, is 1000 kin (1 kin equals 1.3 lbs.): camphor 5,574, valued at \$3,014,400; vegetable isinglass 2,786, valued at \$1,214,640; matches 41,222,000 gross, valued at \$10,129,440; menthol crystals 386, valued at \$1,157,280; sulfur 137,812, valued at \$2,983,680. Camphor, isinglass, menthol and sulfur showed increases both in quantity and value while the quantity of matches was less but the value greater than for the previous year.

The following table shows how the imports of manufactured articles have decreased since the outbreak of the war, while those of raw materials have made vast increases. The values given are for the last three years.

ARTICLE	1914	1915	1916
Raw cotton.....	\$218,975,000	\$217,316,000	\$276,009,000
Para-rubber.....	2,147,000	3,432,000	7,146,000
Hemp.....	7,939,000	8,423,000	9,124,000
Wool.....	14,784,000	80,584,000	33,507,000
Leather.....	1,952,000	1,908,000	2,781,000
Pulp.....	4,574,000	5,978,000	9,017,000
Aniline dyes.....	2,741,000	2,828,000	3,382,000
Iron ore.....	8,047,000	7,949,000	16,721,000
Iron bar.....	24,144,000	19,793,000	57,546,000
Iron tube.....	4,130,000	1,380,000	3,467,000
Zinc ore.....	2,950,000	2,910,000	7,463,000
TOTAL.....	\$292,383,000	\$485,501,000	\$426,163,000

For convenience the value of the amount imported alone is given above, but, owing to the rise in price of the various articles, there are some which have decreased in quantity yet increased in value, e. g., aniline dyes imported in 1914 were estimated at 4,831,000 kin and in 1915 1,429,000 kin while in 1916 the amount was 527,000 kin. Other imports show the same trend.—M.

GREASE RECOVERY FROM SEWAGE

Gratifying results, says *Chemical Trade Journal*, 60 (1917), 382, have attended the activities of the Corporation of Bradford, England, in the work of the recovery of grease from the city's sewage. Mr. F. Gordon Whiteley points out in his report that last year it was estimated to run \$250,000 from grease but the receipts have actually amounted to \$250,000 and it is estimated that \$250,000 will be provided from this source in the coming year in addition to \$14,000 from the sale of manure made from the precipitated sludge after the grease has been extracted. A substantial saving has also been made in regards the chemicals used in the process of precipitation. In normal times, sulfuric acid was used for this purpose but less supply of this chemical are now prepared for the government and the Bradford Corporation have made large purchases of material to take its place.—M.

CASE-HARDENING BY BORON

At the spring meeting of the Iron and Steel Institute held in London, Professor N. Tschischewsky contributed a paper on case-hardening of iron by boron. The author remarked that the fact that, on the cooling of iron-boron alloys, the boron is not wholly combined in the form of borides of iron, a proportion being left in the form of a hard solution, suggests the possibility of case-hardening steel by boron, in a similar way to the case-hardening of iron by carbon. Alloys of boron with iron are so hard that they can scarcely be treated on an emery wheel, and the technical application of case-hardening by boron may be a feasible industrial operation. The use of boron is not perhaps suitable for armor-plates, because of its comparative scarcity, but for some machine parts and generally speaking where much wear occurs, boron can be applied with success; while annealing is required to confer the necessary hardness on articles case-hardened by carbon, boron confers hardness without the need for any special heat treatment. Experiments had been carried out by filling holes drilled in cubes of soft iron with fine amorphous boron or with powdered ferro-boron, the holes being closed with stoppers of the same iron, pressed home by means of a hydraulic press. After heating for two hours at 950° the boron had penetrated the iron to the depth of 1 mm. Cementation by powdered ferro-boron proceeds more easily and more rapidly than with amorphous boron. Case-hardening at a lower temperature yields an alloy containing less boron and not so hard and brittle.—M.

AGRICULTURAL IMPLEMENTS FOR PORTUGAL

If there is any surplus of agricultural implements, says the *Times Trade Supplement* No. 14, 34, available for export to one of the allies after home requirements have been met, manufacturers of these goods would do well to turn their attention to the Portuguese market. In any case, some preliminary cultivation of the market might be made now with a view to reaping the benefit as soon as circumstances allow. Increased cost of farm labor is inducing Portuguese landowners to adopt more modern methods with the result that up-to-date farm implements are being eagerly sought. Formerly Germany headed the list as supplier of these articles. Now a local industry of some importance has been developed and this supplies much of the simpler and cheaper farming tools and implements. Still, pitchforks, manure-forks, sickles, hoes, scythes, sheep-shears, corn-knives, hay-knives, and hay-forks could be sold in Portugal, also small tractors, ploughs, harrows, harvesters, threshing machines, hay-baling presses, manure-spreaders and feed-grinders. It is suggested that the best method of selling is to establish a central warehouse in charge of expert salesmen, as the average Portuguese farmer requires to see an article before he decides to purchase. Descriptive matter is of little use without actual samples.—M.

SPUN GLASS AS INSULATING MATERIAL

Spun glass, says a contemporary, has been used with success in Germany as an insulating material to cover steam pipes. The method of installation is to wind the spun glass loosely around the pipes, between rings of asbestos placed at intervals, the insulation being then inclosed in asbestos braid and sailcloth and painted over with paint or tar. The spun glass, consisting of fine glass threads, makes a loose, light and porous wadding which adds little to the weight of the pipes and makes a good insulating material because of the presence of air between the threads. It is not affected by the vibration of the pipes, by high temperatures, steam, water or acids, and retains its insulating power indefinitely.—M.

TESTING ACETYSALICYLIC ACID

When incinerated, acetylsalicylic acid should leave no ash. During the process, it should form no caramel, nor give off the odor of burning tartaric acid, nor the characteristic odor of burning quinine. The test for free salicylic acid should be applied as follows: A dilution of four drops of ferric chloride solution 1:5 in 20 cc. of distilled water is first prepared. Into this, 0.5 g. of acetylsalicylic acid is dropped. No violet color should appear during the first minute of contact. The melting point should be taken thus: An oil (paraffin) bath should be used and two thermometers—one to register the heat of the bath, the other to carry the capillary tube of acetylsalicylic acid. The flame is regulated so that the temperature of the bath rises 1° C. per minute. When this reaches 125° C., the other thermometer carrying the tube is introduced. Under these conditions, the melting point should be 132° C. The statement of Codex that the melting point is 135° C. seems incorrect. Tsakalotos has previously shown that acetylsalicylic acid is very sensitive to decomposition by heat. By the above method, it is exposed to a high temperature for a relatively short time. At the present time, says the *Pharmaceutical Journal* quoting from *Pharm. Chim.*, much of the acetylsalicylic acid of French commerce is adulterated or impure. The author, who writes in the above-quoted journal, states that he has met a specimen of "so-called" aspirin which consisted of a mixture of approximately 46 parts magnesium sulfate, 46 parts lactose, and 8 parts of undetermined salicylic products.—M.

REMOVAL OF PITCH FROM SULFITE PULP

The following abstract from an article by K. H. Knadsen appeared in the *Journal of Chemical Industry*. The precise cause of the trouble experienced from the presence of resin in sulfite pulp has not yet been determined, but the evidence points to the fact that it is not necessary to remove the whole of the resin from the pulp provided that it can be evenly distributed. A pulp with a low resin content may cause trouble, whereas one with higher content may be satisfactory. The deleterious effects of resin are especially noticeable in the manufacture of thin paper and occasionally the resin gives rise to considerable trouble in the bleaching of the pulp; the bleaching process seems to favor the agglomeration of the resin particles.

The author states that he has examined a number of bleached pulp sheets containing resin spots and has always found sulfur and lime present in these spots. Further examination showed that the mineral matter in these spots consisted of calcium monosulfite and silica. This points to the fact that the calcium monosulfite must have been embedded in the resin since it could not have resisted oxidation during the 12 or 15 hrs. in the bleaching beater. It would then appear that the clotting is produced mechanically by cumulative cohesion due to the slow rotation of the warm pulp. Hence, more pronounced clotting will occur in the beater with pulps containing a greater number of resin-coated particles. It is probable that the trouble can be best remedied during the digestion of the chips. At the mill in which this investigation was made, the resin content of the pulp was fairly constant between 0.8 and 0.9 per cent and gave little trouble. On one occasion, however, trouble was found to occur in the bleaching beaters and no remedy could be found for it until the pulp was removed from the digesters, when the liquor was lighter in color than usual; this completely overcame the difficulty. The author believes that it is of the greatest importance to prevent as far as possible the separation of crystalline deposits in the digester, since the calcium monosulfite crystals appear to facilitate the separation of the resin particles, particularly if the wood has not been properly seasoned.—M.

stract to Prof. Allen Rogers, Pratt Institute, Brooklyn, N. Y., Chairman of the Society's Press and Publicity Committee. A copy of the abstract should be retained by the member and handed to the secretary of the special division before which the paper is to be presented in Boston, or, better, sent in advance of the meeting to R. W. Neff, 22 India Sq., Boston, Mass. Short abstracts will be printed in *Science*.

HOTELS

Members are advised to make reservations well in advance, since the meeting comes at a time when the Boston hotels are crowded. For special information write to the Chairman of the Committee on Registration, Prof. K. L. Mark, Simmons College, Boston.

FINAL PROGRAM

The final and complete program will be sent on or about September 5th to all members signifying their intention of attending the meeting, to the secretaries of sections, to the Council, and to all members making special request therefor to the Secretary's office.

AUTUMN MEETING, AMERICAN ELECTROCHEMICAL SOCIETY, PITTSBURGH, OCTOBER 3 TO 6, 1917

The provisional program for the Pittsburgh meeting of the American Electrochemical Society to be held October 3 to 6, 1917, with headquarters at the William Penn Hotel, has been announced. The final program will be distributed with the September Bulletin (Sept. 15) of the Society.

PROVISIONAL PROGRAM

WEDNESDAY, OCTOBER 3RD

To promote general acquaintance among the members previous to the Meeting, those arriving on Wednesday will be taken in automobiles from Headquarters, William Penn Hotel, to the Oakmont Country Club. An informal Dinner at the Club will be followed by a meeting of the Board of Directors.

THURSDAY, OCTOBER 4TH

Morning: Meeting at William Penn Hotel for reading and discussion of papers.
Afternoon: Optional excursions to various industrial plants in the Pittsburgh district.
Evening: Illustrated lecture, followed by an informal reception, light refreshments and dancing.

FRIDAY, OCTOBER 5TH

Morning: Papers and discussion on electrochemical products.
Afternoon: Optional excursions to the various industrial plants in the Pittsburgh district.
Evening: Subscription Dinner at the William Penn Hotel, with special entertainment features.

SATURDAY, OCTOBER 6TH

All-day excursion on special train to several industrial plants (special entertainment for ladies as it is thought this excursion would be too strenuous for them).

LOCAL COMMITTEES

The following Pittsburgh members are in charge of various local committees: General Arrangements and Finance, C. G. Schluederberg, chairman of local section; Excursion, Prof. L. C. Turnock; Entertainment, Prof. Fred. Crabtree; Publicity, Philo Kemery; Papers, R. E. Zimmerman; Membership, S. L. Goodale; and Hotel, P. M. Lincoln. Mrs. Fred. Crabtree is chairman of the local committee to care for visiting ladies.

AMERICAN INSTITUTE OF CHEMICAL ENGINEERS NINTH SEMI-ANNUAL MEETING BUFFALO, JUNE 20-22, 1917

The ninth semi-annual meeting of the American Institute of Chemical Engineers convened in Buffalo at the Hotel Statler at 9.30 A.M. F. A. Lidbury, Chairman of the Local Committee, called the meeting to order and introduced Mr. David C. Howard, 1st Vice-President of the Buffalo Chamber of Commerce, who welcomed the members of the Institute to Buffalo. Mr. Howard spoke of the importance of the chemical industries of Buffalo: within a radius of 1 mile 2,000,000 tons of pig iron are produced annually. He also urged the greater utilization of the Niagara water power. President G. W. Thompson then took the chair and responded to Mr. Howard's welcome.

The Council reported having held four meetings since the last meeting. Consideration had been given to the best means of securing cooperation of members with the National Government. A subscription of \$500 had been made to the Liberty Loan. Consideration had also been given to the best means of securing a more general adoption of the Metric system of weights and measures. During the discussion of this subject it was brought out that the chemical industries could readily adopt the Metric system but that difficulty would be met with in Mechanical Engineering and Machine Shop practice. A committee was appointed to investigate and report as to how far the general introduction of the Metric system is feasible at the present time.

The Secretary reported the issue of *Bulletin 14* and an early issuance of Vol. 9 of the Transactions.

The membership of the Institute at present is 270, consisting of one honorary member, 229 active members and 40 juniors, a total increase of 20 during the year. The deaths of E. R. Taylor and G. M. MacNider were announced.

The Treasurer reported a balance on hand of \$4170.

Dr. A. C. Langmuir, Chairman of the Membership Committee, reported the election of 13 candidates for active membership, 8 for junior membership and the transfer of 3 from junior to active membership. Five applications for active membership had been denied on account of insufficient experience in chemical engineering work.

Dr. L. H. Baekeland, Chairman of the Committee on Patents, reported that during the war no action could be taken toward improving the patent laws, with the exception of the efforts being made for temporarily suspending the patent laws of the United States for the manufacture of certain products heretofore imported from Germany.

Professor Jas. R. Withrow, Chairman of the Committee on Chemical Engineering Education, reported that the Secretary of War urged the necessity of maintaining our educational work during the war. The committee suggested that Chemical Engineering students be given instruction in some elementary subjects of military importance such as pontoon bridge building and other field work.

The Committee on Meetings reported in favor of holding the winter meeting in St. Louis early in December. By vote of the Institute this selection was confirmed.

A committee, consisting of Prof. Jas. R. Withrow, Dr. Chas. S. Palmer, Dr. Wm. P. Mason, Messrs. David Wesson and P. Kingsbury, was appointed to draft resolutions to be sent to Secretary Baker, urging that chemical engineers and chemists be permitted to remain in the industries as their work is essential to the maintenance of the production of military supplies. It was pointed out during the debate that the services of many chemists will be needed by the War Department even in the trenches. All members of the Institute were ready to offer their services to the Government and many members are actively cooperating in many capacities.

The following telegram was sent to Secretary Baker:

The American Institute of Chemical Engineers in Convention, Buffalo, N. Y., desires to emphasize the importance to the military effectiveness of the United States of Chemical Engineers and Chemists being permitted to remain in our industries as only by so doing can our military supply production be maintained and increased as required. Every member present expressed a sincere desire to be of service to his country in the most effective manner. Full resolutions will follow.

The following resolution was drawn up by the committee and sent to the President and to the Secretary of War:

We, the members of the American Institute of Chemical Engineers, in Convention assembled at Buffalo, N. Y., June 22, 1917, desire to offer you our services in any capacity in which you may see fit to call upon us in the present national emergency. We know that it is your desire to reduce to a minimum any injury to the industries of our country by the indiscriminate drafting into ordinary military service of such skilled help as

chemists and chemical engineers. Some manufacturers having, perhaps, productive units small in capacity, have not as yet been disposed to initiate claims for protection against the virtual destruction of their business either through voluntary or draft enlistment of their chemical help.

The chemical industries of the country are both directly and indirectly indispensable as a source of military supplies. A large part of modern efficiency in many industries is dependent upon adequate chemical engineering and analytical control. Skilled chemists are the result of years of training and experience in connection with chemical phenomena, and the efficiency of such chemists is similar to the efficiency of skilled naval officers, who have also had years of training and experience to develop them for their responsibilities.

We urge upon you, therefore, to avoid the errors which in the earlier stages of the war were committed by all combatant nations in weakening their industrial operations by taking technical men from the industries without due consideration as to the relative needs of those industries.

We feel it our duty to ask of you that all manufacturers and producers using chemical means of manufacture or control be required to list with designated officials for exemption consideration all employees as follows:

- A. All employees engaged in production and its direct control.
- B. All other members of the organization. These latter to be grouped as follows:
 1. Key men in the organization.
 2. Men highly desirable but not vital to the industry.
 3. All other employees of organization not engaged in production.

With the data thus at hand the Government will be able to protect itself against any stalling of industry that might jeopardize a speedy prosecution of a successful war. We do not wish to be understood as wishing in any way for exemption in such industries as are connected with luxuries merely or are in no way connected with essential military effectiveness, though serious attention must be given to the possibility of wrecking national effectiveness by the withdrawal of such key men as chemists from most of our industries.

We urge that a suitable badge or other system be devised for the social protection of men exempted for their industrial service.

We also request that the Government urge or assign to a continuation of their college studies a sufficient number of engineering and particularly chemical students, so that the Government and industrial service will not be denied this necessary yearly influx of young chemists and engineers.

We are gratified to find that the number of chemists and chemical engineers who have volunteered for admission to the Ordnance Corps and other departments where their chemical experience can be of direct benefit in military service has been in excess of the requirements. We know that this is the spirit which animates all of the chemists and chemical engineers of the country. We know that they want to be where they can be of the greatest service.

They believe that their greatest power of service is:

First, in the industries on which the success of the war directly depends.

Second, in such departments of the military service where their knowledge of noxious gases will enable them to be of help in the prevention of loss of life and in the repair and maintenance of equipment.

When they are not needed in either of the above classified departments of service, they are willing to do any kind of work and lay down their lives if need be.

A very interesting and instructive paper on "Some Machinery Employed in the Manufacture of Glue" was read by A. Lowenstein, of Chicago. Prof. Edward Bartow, of the University of Illinois, read the third paper on "Treatment of Sewage by Aeration in the Presence of Activated Sludge." Professor Bartow reported progress in filtering and drying the sludge on a commercial scale and at a low cost. Samples of the moist and dry sludge were shown. About 1100 lbs of the dry sludge were obtained per million gallons of sewage. The content of nitrogen was from 4.5 to 6.5 per cent. The cost of drying the sludge was estimated at \$3.00 to \$5.50 and the value of the dried sludge from \$7.00 to \$15.00 per ton.

Dr. Chas. S. Palmer read a paper on "Intensive Chemical Preparation" in which he urged the importance of more extended courses in Chemistry being offered in high schools and preparatory schools so that the general public would be more intelligent on chemical topics.

After luncheon, members of the Institute and their guests were given an automobile trip around the city through the many beautiful boulevards and parks. The automobiles had been furnished by members of the Engineers' Club of Buffalo, and were under the direction of Mr. David Bell, of the Pierce-Arrow Automobile Company.

The party was then driven to the plant of the Buffalo Foundry & Machine Co. At this plant a considerable number of large pieces of chemical equipment in course of construction were shown, including stills, kettles, evaporators, etc. The method of construction of each piece of apparatus was clearly shown as the pieces were not fully assembled. Each visitor was furnished with a printed pamphlet giving a description of each piece of apparatus shown. Especial interest was shown in the very large castings being made.

The party was then taken to the plant of the Larkin Co. where a great variety of interesting manufacturing operations were inspected. These were shown not only by direct inspection but also by moving pictures in the commodious theatre of the Larkin Co. After light refreshments had been served, the party returned to the hotel.

During the Wednesday evening session a paper was presented by Glenn H. Pickard on "The Manufacture of Linseed Oil." This paper dealt principally with modifications of the standard practice and their effect upon the economics and quality of the oil.

A paper on "Trade Wastes Disposal" was then read by Mr. H. P. Eddy. This paper dealt with the disposal of trade wastes in a general way. The discussion of this paper took up the disposal of tannery wastes, the destruction of the anthrax bacillus by means of chlorine, and the taste developed in waters by the introduction of chlorine.

Thursday was spent at the Canoe Club, beautifully situated on the Canadian side of Lake Erie. The party left Buffalo at 10 A.M. on the excursion steamer for Crystal Beach. A launch took the party to the Canoe Club. Immediately on arrival a session of the Institute was held in the spacious dancing hall on the pier.

Two papers were read by Prof. James R. Withrow: "The Elevation of Sulfuric Acid and Other Liquids" (by O. R. Sweeney and James R. Withrow) gave the results of some interesting experiments on using steam, for the elevation of sulfuric acid instead of compressed air, and "Conservation of Sulfuric Acid" emphasized the importance to the agricultural interests of an adequate supply of sulfuric acid for the production of fertilizers. Much dilute sulfuric acid as well as nitric acid is being allowed to go to waste in the munition industries because of the lack of concentration plants. This acid could very advantageously be used in the fertilizer industry. A very interesting discussion developed on the various means of producing sulfuric acid.

After luncheon some of the members took advantage of the good breeze and fair weather and enjoyed a sail on Lake Erie. Others spent the afternoon in technical or other discussions on the veranda of the Canoe Club or took walks along the beach. After dinner at the Club another session was held on the pier. Hugh K. Moore read a paper on "The Chemical Engineering Aspect of Renovating a Sulfate Mill." Members were very much interested in the many and difficult problems which were successfully overcome in renovating the mill and placing it on a successful operating basis. After discussion of this paper the party returned by launch to Crystal Beach and then by steamer to Buffalo.

Friday morning a business session was held at Hotel Statler. The Committee on Meetings reported in 1917 as approving a dinner or other social function during the Third Chemical Exposition in New York during the week of September 14th.

St. Louis was chosen as the place for the winter meeting, the date to be early in December. A considerable number of in-

teresting chemical and metallurgical plants could be visited in and around St. Louis.

The papers of the Symposium on Potash were then read. The paper by J. C. W. Frazer, W. W. Holland and E. Miller of the Johns Hopkins University on "A New Method for the Recovery of Salts of Potassium and Aluminum from Mineral Silicates" gave the results of experiments in which finely ground feldspar was treated with caustic soda solution at 200 to 300° C. One molecule of SiO_2 was extracted from the feldspar. The resulting product is readily acted upon by dilute acid producing a salt of potassium, the silica and aluminum remaining undissolved. On treating this residue with sulfuric acid, aluminum sulfate would be produced, the silica being filtered off. The caustic soda is regenerated by treatment with lime and can be used again. As a very pure silica is obtained by this process as well as aluminum sulfate and potash salts, it may prove profitable even after the war.

The paper on "Potash from Waste Liquors of Beet Sugar Factories" by H. E. Zitkowski was then read. This paper gave an analysis of the total amount of potash in the sugar beets produced in the United States. A considerable amount of the potash is being utilized at present as a constituent of cattle food or fertilizers in various forms. The waste waters contain both nitrogen and potash. The method at present being experimented upon consists in evaporating the waste water and incinerating to recover the potash.

The paper on "The Possibilities of Developing an American Potash Industry," by Richard K. Meade, gave a general discussion of the various methods being used and more particularly the methods by which potash is recovered as a by-product in the cement and iron and steel industry. The very interesting conclusion was reached that about two-thirds of the requirement of the American market could be supplied from this source.

A short paper on "The Potash Industry of Canada" was read by E. B. Biggar, of the *Canadian Chemical Journal*. In the course of the discussion the problem of evaporation of dilute solutions was taken up by Hugh K. Moore and the methods

in use in California for the recovery of potash from kelp were given at considerable length by H. O. Chute of Los Angeles.

After luncheon the party proceeded by automobile to Niagara Falls stopping at the Curtiss aviation field to observe aeroplane flights. At Niagara Falls the gorge ride was taken in a special car after which the party proceeded by the automobiles to Goat Island where light refreshments were served and then returned by automobile to Buffalo.

Friday evening the subscription dinner was held at the Hotel Statler. About 60 covers were laid, the dinner being a joint dinner of the Buffalo Engineering Society and the American Institute of Chemical Engineers. President G. W. Thompson acted as toastmaster. Maximilian Toch gave a good many interesting instances of important war service rendered by American chemists. At the conclusion of his remarks, he proposed a toast to President Wilson which was heartily responded to.

Professor A. W. Smith of Case School of Applied Science spoke of the war service rendered by the schools and colleges. Professor Wm. P. Mason, of Rensselaer Polytechnic Institute was introduced as the water expert who would speak on prohibition as a war measure. F. A. Lidbury was introduced as the newly elected president of the Buffalo Engineering Society, and spoke of the attempt being made in Buffalo of having but one technical society, including in its membership all branches of engineering as well as chemists and chemical engineers.

Mr. David C. Howard who had welcomed the Society to Buffalo was then called upon to say a fitting parting word. The dinner ended with the singing of The Star Spangled Banner.

Saturday morning a few of the members visited the plant of the J. P. Devine Co.

The attendance at the meeting was excellent throughout, about 100 being present at the various sessions. The entire meeting was marked by a patriotic spirit of desire to be of the greatest service to the country and Government during the present crisis.

COOPER UNION
July 11, 1917

J. C. OLSEN, Secretary

NOTES AND CORRESPONDENCE

ON THE SUBSTITUTION OF PERCHLORIC ACID FOR CHLORO-PLATINIC ACID IN THE DETERMINATION OF POTASSIUM

Editor of the Journal of Industrial and Engineering Chemistry:

Your recent editorials in *THIS JOURNAL* prompt me to suggest that the chemist, himself, may directly aid in the conservation of our platinum supply, by the substitution of perchloric acid for chloro-platinic acid in the determination of potassium.

I have made inquiries in regard to the reliability of this method and find that it is coming into general use quite rapidly. Among my informants are a number of the instructing staff of the Massachusetts Institute of Technology, and several soap and fertilizer manufacturers who are using the perchloric acid method in preference to the more expensive platinum method. This question of cost is well brought out when it is noted that the cost of chloro-platinic acid for the determination of one gram of potassium is approximately \$8.00 at the current market price, while the cost of sufficient perchloric acid for the same determination is slightly over 3 cents. Including the loss of platinum, cost of recovery, and the money tied up in a small bottle of this reagent, it is seen that the platinum method is overwhelmingly more expensive than the perchlorate method.

It should also be borne in mind that the German Fertilizer Chemists have adopted the method as official. It is to be regretted that our own soil and fertilizer methods are so slow in being revised.

Mr. P. L. Hibbard recently published the results of an investigation on the two methods in *THIS JOURNAL*, and made an error in the price of the acid. The following quotations from a chemical supply house make this evident:

"No. 1 Perchloric acid C. P. (60%)	
5 pounds.....	\$33.00
1 pound.....	7.20
1 ounce.....	0.75(a)

(a) As this is for experimental purposes, only one order for this amount will be filled."

Mr. Hibbard's conclusions are not entirely borne out by my experience in regard to the ease of manipulation and the length of time required, as I find the perchlorate method quite rapid. Clarence Scholl published an article in the *Journal of the American Chemical Society*, 36 (1914), 2085, which confirms my experience.

BATAVIA, N. Y.

EDWARD C. WALKER, JR

THE CHEMICAL COMPOSITION OF COMMERCIAL GLUCOSE AND ITS DIGESTIBILITY—A REJOINDER

Probably no paper that has appeared in recent numbers of *THIS JOURNAL* has aroused a greater amount of unfavorable discussion among a certain class of its readers than the one in the November issue of 1916, upon "The Chemical Composition of Commercial Glucose and Its Digestibility," by J. A. Wesener and G. L. Teller.

One of the first difficulties experienced in reading the paper of Wesener and Teller is that of reconciling the experimental part of their paper with the final "Summary and Conclusions." The inconsistencies between these two parts are so pronounced that the reader is forced to suspect that "Summary and Conclusions" has no connection with the rest of the paper, but is only a sort of tag which can be attached or detached at the authors' pleasure. This suspicion has, indeed, considerable outside evidence for substantiation.

The "Summary and Conclusions" of Wesener and Teller's paper was presented, exactly as printed on pages 1019 and 1020 of Vol. 8 of THIS JOURNAL, before a meeting of the Illinois State Food Standards Commission, which was held in Chicago in June, 1916. This meeting, according to the statement by its Chairman, was called by one of the large producers of commercial glucose for the purpose of revising the standards of certain foods "so that there might be a more liberal use of corn syrup, commercial glucose, in them." Wesener and Teller were two of the witnesses to appear at this hearing. For some unknown reason these authors neglected to add to their paper, when printed in THIS JOURNAL, the customary note that it had been previously presented either by summary or title. Whatever the reasons may be for this omission, the fact remains that four months before its publication in THIS JOURNAL, the "Summary and Conclusions" of Wesener and Teller's paper was printed verbatim in the *American Food Journal* (July, 1916, pp. 300 and 301).

It is curious to note that after the publication of Wesener and Teller's paper in THIS JOURNAL, "Summary and Conclusions" was again detached and once more printed in the *American Food Journal* (December, 1916, p. 623), this time with the rather naive Editorial Statement that it was reprinted through the courtesy of *The Journal of Industrial and Engineering Chemistry*. This attachable and detachable tag, through the courtesy, no doubt, of the *American Food Journal* in which it first appeared, has also been reprinted in various other trade publications.

The main thesis which Wesener and Teller attempt to establish is that when used as a food commercial glucose "pound for pound of dry weight, will furnish at least as much energy as does cane sugar." But in studying the authors' experiments to demonstrate this, the reader is first puzzled to know whether raw or refined cane sugar is meant. The dry matter of commercial glucose, according to the authors' own analysis, contains about 0.5 per cent of mineral matter and this might seem to indicate that they had in mind a raw cane sugar containing an equivalent amount of mineral impurities. The reference (p. 1011) which the authors make to the molecular equivalents of cane sugar and dextrose shows, however, that pure sucrose or refined sugar was the intended basis of comparison and this helps to explain the efforts of the authors to conjure away the mineral impurities of commercial glucose in their "Summary and Conclusions." In the experimental part of their paper (p. 1010) we find for example, 0.34 per cent of ash in the liquid glucose, while in the detachable "Summary and Conclusions" on p. 1019, this amount dwindles to "a trace" and then to "mere traces." Half a per cent of ash in the dry matter of cane sugar is regarded by refiners as something more than "mere traces." There is a device in music by which discordant tones are sometimes made to diminish in intensity until they completely vanish, but it has remained for the authors to employ the *diminuendo* as a method of chemical research.

But it is in the fallacious conclusions which the authors draw from their fermentation experiments that we are chiefly concerned. The error due to the employment of impure yeast in separating fermentable from non-fermentable carbohydrates has long been recognized. The authors state themselves that "the amount of gas ordinarily produced from 1 g. of cane sugar, when 15 g. of compressed yeast were used, varied from 1000

to 1100 cc." or in other words, a variation of some 4.5 per cent. Herzfeld found malto-dextrin to be completely fermented by yeast, whereas Brown and Morris found the dextrin and malto-dextrin of starch conversion to be unfermented by a pure culture of *Saccharomyces cerevisiae* but to be strongly attacked by *Saccharomyces ellipsoideus* and *Saccharomyces Pastorianus*.¹ The percentages of dextrin, maltose and dextrose which Wesener and Teller calculate from results obtained with ordinary bakers' yeast have absolutely no scientific value. These authors very correctly express their percentages in Table 1, as apparent percentages but in the detachable "Summary and Conclusions" the qualifying adjective *apparent* has for some reason been omitted.

Still more unconvincing is the experimental evidence by which the authors attempt to disprove the existence of isomaltose or gallisin in the unfermentable residues of commercial glucose. It has long been known that the unfermentable residues from the acid or diastatic conversion of starch could be largely hydrolyzed into dextrose by means of acids and it is somewhat strange that Wesener and Teller failed to mention the work of previous investigators along this line. If they had carefully reviewed the literature upon the subject they would have discovered why heating the unfermented residues of commercial glucose with hydrochloric acid never produces complete conversion of the products into dextrose.

The authors, for example, in their experiments with pancreatin and taka-diastase (p. 1015, Table 9), after boiling the unfermented matter of commercial glucose with 2.5 per cent hydrochloric acid, neutralizing and again fermenting, obtained a non-protein organic residue of 0.440 g. from 6 g.² of commercial glucose in case of pancreatin and 0.380 g. from 6 g. of commercial glucose in case of taka-diastase—results which are equivalent to 7.33 and 6.33 per cent, respectively, of the original glucose or, when calculated to a moisture-free basis, about 9 and 8 per cent, respectively, of the commercial glucose solids. A parallel fermentation experiment upon 5 g. of sucrose gave a final non-protein organic residue of 0.09 g. or 1.8 per cent. Wesener and Teller state that the remaining unfermented matter of their glucose experiments in their opinion "may be justly attributed to organic acids produced in one or both of the fermentations." If we take the 1.8 per cent of residue in the sucrose experiment, as the amount of organic acids, glycerol, etc., etc., formed by the action of yeast, there still remains over 5 per cent of matter³ unaccounted for. It is difficult, therefore, to understand the statement of the authors (p. 1015) "that all the products of glucose are accounted for and that there does not remain any substance which was a constituent of the glucose and which cannot by the process used be converted into substances fermentable by yeast." If Wesener and Teller had only consulted the previous work of Gatterbauer they might have spared themselves the necessity of making so unwarranted an assumption.

Gatterbauer⁴ obtained from the unfermentable residue of a sample of commercial glucose, by a method very similar and ether, a preparation of so-called *gallidic* which after fermenting away the trace of dextrin and maltose, gave a well characterized organic compound in the form of a thin layer of a diamond. The same from this preparation was hydro-

¹ For a review of these experiments see *Journal of Industrial and Engineering Chemistry*, Vol. 8, No. 1, 1917, p. 119.

² My attention has been called by a recent issue of this journal, The *Journal of Industrial and Engineering Chemistry*, Vol. 9, No. 1, 1917, p. 119, to a statement of the authors that a portion of the sample of glucose used in their fermentation experiments was from the *Journal of Industrial and Engineering Chemistry*, Vol. 8, No. 1, 1917, p. 119, and that the sample of glucose used in their fermentation experiments was from the *Journal of Industrial and Engineering Chemistry*, Vol. 8, No. 1, 1917, p. 119.

³ As a result of a recent issue of this journal, The *Journal of Industrial and Engineering Chemistry*, Vol. 9, No. 1, 1917, p. 119, it is noted that the authors have corrected a number of errors.

⁴ For a complete description of Gatterbauer's work see *Zeitschrift für Zuckerindustrie*, 1913, p. 111.

lyzed with hydrochloric acid into dextrose. The disaccharide thus corresponds in properties to the unfermentable sugar isomaltose.

Gatterbauer then attempted to hydrolyze his preparation of gallisin directly into dextrose by heating 100 cc. of a 14.7 per cent solution with 50 cc. of 0.75 per cent hydrochloric acid for three-quarters of an hour upon the water bath, but a small percentage of material failed to undergo hydrolysis. Instead of assuming, however, that all his products were accounted for, Gatterbauer next tried the effect of using stronger acid when he found that he was further away from complete hydrolysis than he was before. Reversion of the dextrose, which had been formed, had taken place, and gallisin, or isomaltose, was being regenerated. The complete hydrolysis of the unfermentable residues of starch conversion into dextrose by means of hydrochloric acid was thus shown to be impossible, for the reaction, as first pointed out by Wohl,¹ in 1890, is reversible. Ost² has also shown that with Sacchse's method of hydrolysis with 2.5 per cent hydrochloric acid, the theoretical factor of 0.90, for converting dextrose to starch, is several per cent too low on account of the formation of reversion products. Wesener and Teller, by boiling the unfermented residues of commercial glucose with 2.5 per cent hydrochloric acid, were, therefore, producing the very compound or compounds, whose existence they have attempted to explain away. The statement of these authors in their detachable "Summary and Conclusions" (p. 1020) that "the claim for the presence in glucose of unfermentable reducing bodies as reversion products brought about by the action of the acids at a high heat is untenable," is thus contradicted by their own experiments.

But the strangest perversion of the paper by Wesener and Teller upon "The Chemical Composition of Commercial Glucose and Its Digestibility" is the one contained in the final word of the title, for in their long list of experiments they have not submitted a single one which has any bearing upon digestibility. To draw conclusions, as the authors have done, from fermentation experiments as to the digestibility of commercial glucose is hardly permissible. Indeed, if we assume the combined action of amylolytic enzymes and yeasts to correspond to the process of animal digestion, the only conclusion which can be drawn from Wesener and Teller's experiments is that commercial glucose contains over 10 per cent of indigestible matter. The authors employed diastase and pancreatin to help hydrolyze the carbohydrates of commercial glucose into fermentable sugars, yet the action of such enzymes, according to the authors' own experiments, was far from complete. There always remained a considerable amount of unfermentable matter which, in the two experiments with malt diastase (p. 1013, Table 4), was 15.4 and 16.4 per cent and, in the experiments with pancreatin and taka-diastase (p. 1015, Table 9) was 15.3 and 9.5 per cent, respectively, of the original commercial glucose. In order to make this unfermentable and hence apparently indigestible matter fermentable the authors boiled the filtered solution for two and one-half hours with 2.5 per cent hydrochloric acid and then, after neutralizing, fermented again with yeast. The question naturally suggests itself, if the combined action of diastatic enzymes and yeasts be accepted as indicative of digestibility, what operation in the digestive tract of the animal corresponds to the treatment with boiling 2.5 per cent hydrochloric acid? The percentage of hydrochloric acid in the gastric juice of man is less than 0.5 per cent, while the temperature of the human stomach is over 60 centigrade degrees below the boiling point. The authors state (p. 1013) that the heating with 2.5 per cent hydrochloric acid was performed "in the usual manner, followed in determining starch." The method of Sacchse, however, is an analytical and not a physiological process, and the results obtained by this method are no more an indication

of digestibility than the conversion of cellulose into fermentable dextrose is an indication of the digestibility of sawdust.

In the final paragraph of the detachable "Summary and Conclusions," Wesener and Teller make the following statement: "The fact that commercial glucose, when it is treated with diastase and then subjected to yeast fermentation, is almost wholly converted into alcohol and carbon dioxide, goes to prove that it consists of products that are wholly assimilable." But according to the authors' experiments "commercial glucose when it is treated with diastase and then subjected to yeast fermentation" leaves an unfermentable residue of over 10 per cent. If commercial glucose from such results be considered to be "almost wholly converted" then, by a simple use of the already familiar *diminuendo*, we may, perhaps, arrive at the conclusion "that it consists of products that are wholly assimilable."

In a paper professing to deal with the digestibility of commercial glucose it is strange that no mention was made of the results obtained by feeding commercial glucose to bees. Some years ago commercial glucose was advertised extensively for the winter feeding of bees, but the experience of bee-keepers with this new substitute for cane sugar was most unfortunate. If attempts were made to coerce the bees, by withholding other supplies of food, they would feed upon the glucose, but would then sicken and die. Experiments conducted by the U. S. Department of Entomology, upon the digestibility of various sugars by bees, also showed that bees would sicken and die of dysentery if restricted to a diet of commercial glucose.

The conclusion of Wesener and Teller that when used as a food commercial glucose "pound for pound of dry weight will furnish at least as much energy as does cane sugar," is accordingly contradicted by their own experiments. The combined action of diastatic enzymes and yeast, without the outside help of boiling hydrochloric acid, was able to ferment cane sugar almost completely, yet under similar conditions was able to ferment only between 80 and 90 per cent of the dry solids of commercial glucose. What enzymes and yeast do not ferment and what honey bees reject may possibly be completely assimilated in the digestive tract of man, but most food chemists will retain their doubts upon this point until more conclusive experiments than those of Wesener and Teller are forthcoming.

THE NEW YORK SUGAR TRADE LABORATORY C. A. BROWNE
80 SOUTH ST., NEW YORK
June 8, 1917

A REPLY TO THE ABOVE "REJOINDER"

Manuscript of a rejoinder by C. A. Browne to our paper "The Chemical Composition of Commercial Glucose and Its Digestibility," which appeared in THIS JOURNAL, November, 1916, is before us for reply.

With reference to C. A. Browne's statement of our appearing before the Illinois State Food Standards Commission, June, 1916, and reading a brief on "The Chemical Composition of Commercial Glucose and Its Digestibility" we beg to state that this is correct. At that time we had finished our work, and as many witnesses appeared before the Illinois State Food Standards Commission, we confined our brief almost entirely to the conclusion of our article. The *American Food Journal* published the proceedings, for the most part, in detail. Then when our article was finally published in THIS JOURNAL, the *American Food Journal* again made it a point to review our article and publish an extract of it.

REPLY TO CRITICISMS

1—Our critic endeavors to put it forth as a fault that the body of our somewhat lengthy paper and detailed report of investigations is accompanied by a brief, comprehensive and readable summary of work done and conclusions indicated by same.

2—He criticizes and later attempts to ridicule our statement that "In this respect, glucose, pound for pound of dry weight will furnish at least as much energy as does cane sugar."

¹ Wohl, *Ber.*, 1890, 2084.

² Ost, *Chem. Ztg.*, 19, 1501.

3—He states without logical proof that certain conclusions drawn from some of our fermentation experiments are fallacious and without scientific foundation.

4—Passing by a large and very pertinent part of our work without mention, misstating other portions and setting up doubtful evidence from other sources in opposition to our findings, he attempts to lead his readers to believe that our claim for the absence from commercial glucose of a reversion product of such a nature that it cannot be utilized by the human body is without foundation.

5—Apparently unfamiliar with physiological processes and unable to understand the meaning of points which are very clearly demonstrated by our work, he contends that not a single one of our experiments had any bearing upon digestibility.

6—He recites a story about glucose and the honey bee, which is interesting but of no importance in this connection.

Going over our work critically after having laid it aside and almost forgotten it for several months, we fail to find in our summary and conclusions anything which is foreign to what we should expect to find in a summary and conclusions to an article of this kind. We would not expect the average reader of a scientific journal to follow through a lengthy article of nearly a dozen pages when the essence of the article could be condensed into about one-tenth of that space, and we certainly would lay ourselves open to severe criticism if we prepared an article of this kind and did not accompany it with a brief and readable summary. On the other hand, the entire body of the report and details of experiments described therein appear necessary to give a logical foundation for the conclusions.

The cane sugar used in all experiments described in this paper and referred to in our conclusions was a good grade of granulated sugar. Reference to other matters which have to do with this statement will be fully dealt with in a later paragraph.

Our critic states that our quantitative experiments with mixed yeast have no scientific value because different species of yeast act upon different sugars differently. We were quite familiar with the fact that not all sugars are fermented to the same extent and in the same manner by different species of saccharomyces, and referred to that in our article. This is clearly due to the fact that some species do not contain enzymes which are able to split up certain sugars into the simpler fermentable glucoses, as, for instance, maltose is not fermented by yeasts which do not contain the enzyme maltase. The compressed yeast in these experiments was such as has been developed for the use of the baking trade for the purpose of fermenting the very products with which we have to deal in our experiments. By thousands of experiments in bread making and fermentation extending over a period of many years, we have found these yeasts to be very constant in action, and they contain an abundance of all enzymes necessary to produce complete fermentation of dextrose, maltose and cane sugar. If we had used for our experiments a single species of yeasts, which might or might not have possessed all of these qualities, our results would have been open to criticism. It is quite natural that there should be some variation in the results obtained from cane sugar from day to day, for by products are known to be formed. It is no uncommon thing for the analytical chemist to find it necessary to use control experiments in the carrying out of his analytical work, and it was found in repeated tests that when there was an increased or decreased production of gas from cane sugar, there was a corresponding increase or decrease of the amount of gas produced from products resulting from the hydrolysis of starch when fermented under similar conditions.

As to whether or not the results obtained from such fermentation tests have any scientific value depends upon the purpose to which they are applied. Really we would have expected our critic to enter into a discussion of this method of analysis with some show of interest, instead of treating it as giving results which are of no scientific value, for it is one point in the

article which he is fully competent to discuss. The method of calculation has been applied to other kinds of analysis, but we believe its use in this connection with these methods of fermentation to be quite new and novel and of value as furnishing about the only practicable means of determining the amounts of these different bodies in the presence of each other.

Throughout the entire criticism we find no reference whatever to parallel experiments carried on between glucose and various starches and starch-containing food products, although these formed a considerable part of the experimental work described in our paper and the results obtained from these comparative experiments formed the basis of our point in the paper that the so-called gallisin is like similar products which are produced by the action of diastase, the result of a step in the conversion of starch to maltose. It was found in these experiments that when well-cooked starch of a half dozen varieties was fermented under the combined action of yeast and enzymes like pancreatin and taka-diastase, there was always produced a quantity of unfermentable reducing bodies, just the same as we find in commercial glucose. It was found also in such instances that the amount of reducing sugars in glucose steadily decreased until they were reduced in some instances from 8 to less than 1 per cent, calculated as dextrose, and that the unfermented, non-reducing carbohydrates of a dextrin nature were continually converted into new reducing bodies just the same as starch itself. It was found that when various starches were acted upon by 2.5 per cent hydrochloric acid at a temperature of boiling water, in comparison with glucose, under the same conditions, there was a deficiency in the theoretical amount of dextrose obtained from the starch, amounting to 2 or 3 per cent of the dry matter, and allowing for the partially hydrolyzed condition of the glucose, the same deficiency (neither more nor less) was apparent for the glucose. It is inconceivable that we should have obtained results of this kind if the glucose had contained a reverted product, having the characteristics by which gallisin is described. If our critic had read correctly the results of experiments shown in Table 9, to which he refers, he would have found it to be true, as we clearly stated in the paragraph which follows that table, that in case of the glucose organic acids were present from the preceding fermentation, which were held there by the alkali used to neutralize the solution before fermentation, and that these organic acids formed a considerable part of the organic matter still present. In the case of cane sugar no such accumulation of organic acids existed, because the cane sugar comparison was a fresh fermentation. The ash clearly shows that it did not, like the glucose liquid, contain the considerable amount of salt resulting from the neutralized mineral acid used for the hydrolysis. He would also have seen that the amount of residue shown from the glucose was from 4.8 grams and not from 6 grams of glucose as he states. Taking the total organic acidity of the liquor remaining after the first fermentation and counting the acidity produced as acetic acid, or as succinic acid, sufficient organic matter would be derived from this source to make up the excess acid that obtained in the first and second fermentations of cane sugar. It was clearly shown in the third and other experiments on glucose hydrolyzed with hydrochloric acid, as well as on the starches mentioned above, that no reducing bodies remained after fermenting the products of the hydrolysis, and, therefore, that no product such as gallisin was present that was produced.

The work of Gattermann and other authors to which the critic refers, does not seem to concern anything which disproves our findings. Gattermann's work does not seem to be by any means conclusive either as to the identity of the body or as to its formation under the conditions to which he was referring. And Westphalen, in stating the processes by which he determines that work, states that the question of gallisin is

still undecided. Gatterbauer's osazone was produced from an admittedly impure product, and Browne himself states elsewhere.¹ "The fact that maltose in presence of impurities gives an osazone of the same melting point greatly lessens the value of the osazone test for isomaltose."

It is well recognized by those who have given attention to dietetics that all sugars capable of being fermented by yeast into alcohol and carbon dioxide can be completely digested and utilized as a source of energy by the human body. It thus follows that other carbohydrates which can be converted into fermentable sugars by enzymes normally present in the human body can also be completely utilized by it as an article of food. It is a well recognized fact that starch when properly cooked and brought into a condition suitable for the action of the enzymes of the body is practically all digested. Such authoritative works as the *Encyclopædia Britannica*, in an article based as stated, upon a compilation of about one thousand actual digestion experiments, puts the digestibility of starch and sugars at 98 per cent and of carbohydrates of corn meal at 99 per cent. Our critic makes some facetious remarks about our not having reviewed the literature, but he has himself apparently overlooked a very important piece of literature on the digestibility of commercial glucose, and fails to mention the article by Sansum and Woodyatt on "The Use of Phlorhizinized Dogs to Determine the Utilizable Carbohydrates of Pure."² In this article they compared the digestibility of pure *d*-glucose with the dry matter of commercial glucose when administered to dogs which had been completely phlorhizinized, and by means of which it is possible to show the utilisability of food products administered to the animals thus treated, by measuring the total yield of sugar in the urine of the animal to which it was administered. In this paper, the authors, from a very conservative interpretation of the results of their several experiments, put the digestibility of the dry matter of commercial glucose as at least 95.48 per cent that of pure *d*-glucose.

It is our opinion on reviewing the details of their tabulated results that it would be entirely fair to accept the digestibility of one as 100 per cent that of the other, for such is clearly shown in at least 3, and possibly 4, out of 5 trials. In one of the five trials, *d*-glucose was administered subcutaneously and the results were abnormally high. This would be expected in that *d*-glucose is a natural blood sugar and, therefore, would not have the opportunity of undergoing changes in the circulation, such as would take place in the gastro-intestinal tract when it is fed by the mouth. It is, therefore, our opinion that this trial should not be included in arriving at the average of the digestibility. In all other instances the foods were administered by the mouth, and in one of these the results for commercial glucose was comparatively low, such as would indicate it to be due to some abnormal cause. Both of these abnormal results were included in the averages given by the authors. If they had been omitted, the averages for commercial glucose would have been even slightly above that for pure *d*-glucose.

Browne in his criticism makes some reference to the winter feeding of glucose to honey bees, which he endeavors to connect with the digestibility of that article. We fail to understand in what manner it has any bearing upon the question. We are not fully able to understand just why the range and nature of the digestive power of the honey bee has any important bearing upon the digestibility of food for man. We know very well that beefsteak or bread or butter or baked potatoes are not much sought after by honey bees except for the small amount of saccharine matter or moisture which might be extracted from them, and we well know that no apiculturist would think of attempting to give these to his bees to utilize for their winter food. We think it very probable that the large amount of dex-

trins in commercial glucose would not make it exactly an ideal food for the honey bee, although we know that some honeys contain a considerable quantity of dextrin. Through the kindness of the *American Bee Journal*, we have a report of some letters published in that journal on winter feeding of glucose to honey bees, and it was the opinion expressed in those letters that many of the bees which ate of the glucose became affected with dysentery. There does not appear to have been any systematic study made as to the cause of this, but it was suggested in one of the letters that the glucose contained too much acid. These letters were published in 1879 when the glucose industry was in its infancy and at that time sulfuric acid was used as a hydrolyzing agent, and sodium bisulfite was also used, and we know that should the glucose have retained any sulfur dioxide, this would have been very detrimental to the delicate digestive organs of the honey bee. At all events, the data at hand does not make it a very strong argument for any purpose, and we are very much surprised that a man who is familiar with the chemistry of sugar, commercial glucose and honey, should have attempted to make use of it in this connection.

Our statement that "In this respect, glucose pound for pound of dry weight will furnish at least as much energy as does cane sugar" was made advisably after a careful consideration of all points which to our minds were in any way involved in it. We were not unmindful of the fact that commercial glucose contains as a part of its dry substance a small quantity of protein and mineral matter. We also understood thoroughly that when cane sugar and a part of the constituents of commercial glucose undergo hydrolysis, certain molecular changes take place which make these of different caloric value when used as a source of energy for the animal economy, and because of these changes a slightly lesser amount of dry matter in the commercial glucose is over-balanced by a slightly greater amount of caloric value of energy, which because of the complex nature of the molecule (polysaccharid) have a greater concentration than does the simpler and more completely hydrolyzed *d*-glucose into which they are finally converted.

We, therefore, have made use of the composition of commercial glucose as found in our analyses in connection with the well-known caloric value of each constituent part, and from these have found the caloric value of the whole and have compared it with the caloric value of cane sugar in the manner shown below:

COMPARATIVE CALORIC VALUE OF COMMERCIAL GLUCOSE AND CANE SUGAR			
GLUCOSE CONSTITUENTS	Per cent	Caloric Value	Calories per Gram(a)
Dextrose.....	14.5	543	3743
Maltose.....	19.6	774	3950
Dextrins.....	46.3	1904	4112

TOTAL.....	80.4	3221
Calculated to Cane Sugar.....	100	4006	3955

Cane Sugar energy in per cent of Glucose energy, 98.7 per cent

(a) *Chemie der menschlichen Nahrung- und Genussmittel*, 11 Band, Seite 284.

It thus appears that from the standpoint of energy, we still have a slight margin in favor of the dry matter of commercial glucose, even after allowing for the small amounts of protein and mineral matter present.

THE COLUMBIUS LABORATORIES
31 N. STATE ST., CHICAGO
July 10, 1917

J. A. WESENER
G. I. TELLER

CEMENT MILL POTASH-CORRECTION

In the article under the above title [THIS JOURNAL, 9 (1917), 646] the following corrections should be made:

Page 647, 3rd table, first line of 3rd col., " K_2O (Total) 1.33%" should read " K_2O (Total) 11.33%."

Page 650, 1st col., last word of fourth line under center head "Effect of Soil Admixture"—"soluble" should read "insoluble."

R. J. NESTELL AND E. ANDERSON

¹ "Handbook of Sugar Analysis," first edition, first thousand, page 707.

² *Jour. Biol. Chem.*, 26, No. 1, Jan., 1916.

WASHINGTON LETTER

By PAUL WOOTON, Metropolitan Bank Building, Washington, D. C.

Just how far the pending reorganization of the Council of National Defense will affect its Committee on Chemistry headed by Dr. Wm. H. Nichols, and the Chemistry Committee of the National Research Council, of which Marston T. Bogert is chairman, is problematical. Dr. Nichols is very certain that nothing will be done which will result adversely to the efficiency of his committee.

While there has been much caustic criticism of the Council of National Defense emanating from Capitol Hill, the severe criticism heard in Washington is confined to that source. There is some talk among those friendly disposed toward the Council, of loss of efficiency due to the multiplicity of committees. Some complaint is being made by those connected with industries that all ill-advised policy of secrecy appears to be in effect. Information which should be reaching American industries is not being given out freely, it is said, while such fragmentary facts as do become known are made the basis of incorrect conclusion. This policy, which seems to pervade the entire Defense Council, is based on the fear that data useful to the enemy will become known. Zeal in this direction seems to have become almost an obsession and, as a result, much of the constructive work of many of the committees is not reaching the public, thereby making the real worth of the Council less appreciated.

The work of the chemical committees is of a nature to make necessary a greater degree of secrecy than should apply to most of the subdivisions within the Council of National Defense. Prof. Bogert stated that there was none of the activities of his committee during the past month which would admit of discussion. Dr. Nichols declared that several of the major activities of his committee are reaching such a stage that it will be possible to discuss them in the near future.

Chemists in Washington were surprised recently when an official statement was issued by the Treasury Department which said: "Experts of the Internal Revenue Bureau have discovered a process for the fermentation of a sugar solution whereby glycerine is produced in such large quantities that it can be recovered commercially." Dr. Arthur D. Adams, in charge of the laboratory of the Internal Revenue Bureau, declined to comment on the reported discovery while Treasury officials stated that details are withheld, that they may not reach Germany. Chemists here are not inclined to attach great importance to the alleged discovery. They express doubt that anything new has been found. Dr. Nichols' committee has made some investigations along this same line. In the course of this investigation, this description of molomoline, which is a type of invert sugar, was obtained: "It is suitable as a substitute for glycerine. It is a water-white liquid, but coagels into a white amorphous mass due to the precipitation of dextrose. This change does not alter its chemical properties. A second grade is manufactured, which has no precipitate and remains as a clear liquid. It has found large use in the following products: textiles, flexible fibers, patent medicines, soft drinks, tobacco, confectionery, antiplogistic pastes, tooth pastes, printers' rollers, embalming fluid, oil-proof cement, crown corks, flexible leather, book bindings, flexible glue, coated paper, stamping ink, asbestos packing, puncture-proof compounds and anti-freeze mixtures."

With the necessity becoming greater for increasing the production of toluol, it is the opinion of Dr. Nichols and his committee that this product should be stripped from illuminating gas. It is believed that this can be done practically in most of the gas plants of the country. In order that toluol may be extracted, it is necessary in many cases to obtain technical changes in the regulations governing the quality of gas. This will require the cooperation of the public utilities commissions. There is reason to believe, however, that little difficulty will be encountered in securing permission to remove the toluol from illuminating gas. Experts on this subject from the Geological Survey and the Bureau of Standards testified before the public utilities commission of Trenton at a recent hearing on the subject.

Experiments looking to the production of substitutes for platinum have flooded the chemical division of the Bureau of Standards with requests for official tests. The Bureau is willing to try out developed substitutes provided it is given full information in regard to their composition and what is claimed for them. Dr. W. F. Hillebrand, in charge of the chemical division of the Bureau of Standards, believes there is little hope for a satisfactory substitute for platinum for use in the manufacture of chemical ware unless it is composed of metals of the platinum group combined with gold. In this connection, it is of interest to know that the Carnegie Geophysical Laboratory is using

much gold ware to take the place of platinum. Since the gold will not stand high temperatures, the substitution is only partial.

Many of the chemists at the Bureau of Standards have been diverted to war problems.

In addition to the work being done by the chemical committees on the iron pyrite and manganese problems, specialists in the service of the United States Geological Survey and of the Bureau of Mines have been very busy on these problems. The most encouraging results are being obtained. Domestic supplies of both of these minerals are being developed at a faster rate than had been anticipated. In fact, the point has been reached where the country could supply its own needs if it should become imperative to do so.

Hope of obtaining any important volume of pyrites from Spain has been abandoned. While there are large reserves of practically pure sulfur at the wells in Calcasieu parish, Louisiana, and at Freeport, Texas, as has been established positively by the recent visit to those properties of P. S. Smith, of the Geological Survey, it is the desire to conserve the supplies of pure sulfur as far as possible. Since the question of transportation enters so importantly, especially at this time, into the pyrite situation, efforts are being banded toward the development of supplies as near as possible to the point of consumption. Particularly effective work has been done in this connection by the Bureau of Mines. The saving of coal brasses from the mines of the Middle West is expected to add importantly to the supply obtainable in the immediate vicinity of various sulfur-consuming industries.

To add to the encouragement caused by the rapidly increasing production of manganese from domestic sources, is an announcement by the Geological Survey of important conclusions with regard to the occurrence of manganese. With the establishment of more definite geological information as to the formations best suited to the deposition of manganese, prospecting can be carried on much more intelligently. Owing to the fact that manganese deposits usually are near the surface and require only the simplest forms of mining and treatment equipment, the production could be increased greatly in a very short time, once geologists are able to narrow prospecting down to the areas most favorable to the occurrence of the mineral.

In carrying out his desire that the Bureau of Chemistry be of the greatest possible assistance to the nation in the present emergency, Carl L. Alsberg, the chief of the Bureau, is directing intensive efforts along a number of lines. Some of the most important work being done by this Bureau may not even be mentioned, but with very active work being conducted in an effort to relieve the tin plate shortage; to make available supplies of much needed chemicals at lower prices; in obtaining preferential transportation orders covering freight movements of food containers and supplies, certain highly desired cultures of micro-organisms; in arranging for closer cooperation with the States Relation Service; in stimulating the manufacture of certain rare chemicals, in investigating the production of industrial alcohol and fat recovery from garbage disposal, the Bureau has been a particularly busy place during the last month. The fact that the Bureau has been able to take advantage of the volunteer services of a number of chemists has added materially to its capacity.

Many offers of cooperation have come to the Bureau as a result of its announcement concerning the manufacture of phthalic acid and phthalic anhydride. The announcement tells of the perfecting, on a laboratory scale, by the Bureau of Chemistry, of a new process for the manufacture of these compounds. Since the process was developed in the laboratory and has not been reproduced upon a technical scale, the cooperation of manufacturers was sought in the perfecting of these compounds on a commercial basis. The success of the technical installation and of the labor and materials are to be known by the manufacturer. The chemists of the Bureau will assist with expert advice. The right to publish the data obtained from the resulting experiment is reserved by the Bureau.

The Bureau of Chemistry, issued in the recommendation of the Committee on Conservation of Tin Plate of June 10, to the effect that certain of the restrictions on the use of tin plate could be removed. The tin plate restriction has suffered to the extent that it has removed the use of tin containers for non-perishable food may be resumed. The restriction now recommended on the use of tin containers for perishable products such as tobacco and talcum powder remains in force.

PERSONAL NOTES

Prof. Alfred H. White, head of the department of chemical engineering at the University of Michigan, recently accepted a commission as captain in the Ordnance Department. His headquarters are at Washington, D. C., and his duty will probably be to assist in the organization of the munitions production, particularly the part containing explosives, although it is understood his work will not be confined entirely to that particular field. According to later information, the investigation of the large number of gasoline "discoveries" recently brought to the attention of government officials, has been turned over to Capt. White.

The executive committee of the Michigan Gas Association, at a recent meeting in Grand Rapids, decided to discontinue their two scholarships at the University of Michigan this year as the instructor, Prof. Alfred H. White, is in the military service.

L. F. Nickell, formerly of Washington University, St. Louis, is now with the Monsanto Chemical Company, of St. Louis.

Mr. William Hoskins, of Chicago, has been appointed a member of the Western branch of the Naval Consulting Board.

Mr. L. W. Bahney has left the Sheffield Scientific School, Yale University, to accept a position as metallurgical engineer with the Scovill Manufacturing Co., Waterbury, Conn.

Mr. Burr A. Robinson has resigned as assistant secretary of the American Institute of Mining Engineers to go into industrial work, and Prof. G. A. Roush, of Lehigh University, has succeeded him as managing editor of the Institute's monthly bulletin.

The U. S. Civil Service Commission announces the open competitive examination of an *Assistant Metallurgical Chemist* (male), salary \$1000 to \$1500 a year. *Junior Gas Chemist* (male), salary \$1200 to \$1500 a year, on August 22, 1917.

Dr. Chas. S. Venable, Massachusetts Institute of Technology, 1917, has been elected associate professor of chemistry in the University of Virginia.

Dr. Duncan MacRae, Massachusetts Institute of Technology, 1917, is now a member of the research staff of the Westinghouse Company, at the laboratories in Bloomfield, N. J.

Vasco E. Nunez, formerly of Arthur D. Little, Inc., and now with the Nashua Gummed & Coated Paper Co., Nashua, N. H., has been appointed chairman of the Abstracts Committee of the Technical Association of the Pulp and Paper Industry, to succeed Prof. John D. Rue, on duty as captain in the Ordnance Officers' Reserve Corps.

The Committee on Standard Specifications for Purchase of Wood, of the Technical Association of the Pulp and Paper Industry, completed by recent appointments, is as follows: (*Chairman*) C. P. Winslow, Forest Products Laboratory; O. L. E. Weber, Watab Pulp & Paper Co., Sartell, Minn.; W. R. Wheaton, Pulpwood Co., Appleton, Wis.

Dr. J. Ehrlich is now chief chemist of the Verona Chemical Co., at North Newark, N. J.

Mr. Arthur Nash, of Chicago, has accepted a position in the development department of the E. I. du Pont de Nemours Company, and is located at Wilmington, Del.

The Board of Directors of the American Electrochemical Society invested \$2,000.00 of the Society's funds in the Liberty Bond Loan.

H. M. Deavitt, analytical and consulting chemist, with offices in the Rookery Building, 209 So. La Salle St., Chicago, has been elected a director of the Mechanics and Traders State Bank of Chicago.

The Fall meeting of the Technical Association of the Pulp and Paper Industry will take the form of a joint convention with the Canadian Technical Association, to be held at Holyoke, Mass., September 27 to 29, 1917, with headquarters at the Hotel Nonotuck. The Committee of Arrangements consists of (*Chairman*) Henry P. Carruth, of the American Writing Paper Company; George E. Williamson, Strathmore Paper Company, Mittineague; Raymond S. Hatch, Crocker-McElwain Company; W. L. Nixon, Chemical Paper Manufacturing Company; and L. M. Yoerg, Carew Manufacturing Company, South Hadley Falls. The first two days of the meeting will be occupied with the official program for the presentation and discussion of technical papers and committee reports; the third day will be reserved for unofficial visits to mills situated at a distance from Holyoke. Mr. Yoerg, of the committee, has given out the statement that those attending the Holyoke meeting will find themselves within easy distance of no less than thirty well-known paper mills.

It is announced that the executive committee of the Ramsay Memorial Fund, after prolonged and careful consideration, have resolved to aim at raising \$500,000 and to devote that sum to two objects, (1) Provision of Ramsay Research Fellowships, tenable where the necessary equipment can be found, (2) establishment of a Ramsay Memorial Laboratory of Engineering Chemistry in connection with University College, London.

The English Ramsay Memorial Fund Committee has requested Dr. Chas. Baskerville, professor of chemistry at the College of the City of New York, to act as the American representative on the Committee and to organize the American Committee. The work of the committee is to collect a fund as a memorial to the late Prof. Sir William Ramsay, the income from which is to be used for promoting chemical teaching and research. The American Ambassador at the Court of St. James, Dr. Walter H. Page, has accepted the vice-presidency of the fund. The English Committee has felt that the work of Sir William Ramsay was of such great importance, and his friendship of such wide-spread limits, that other countries should have the privilege of participating in the memorial. Dr. Baskerville is organizing the American Committee and is requesting representatives of the Universities, the Industries and Research Organizations to become members of the committee.

The president of the British Board of Trade has established a special department of the board for the temporary control of the dye industry, the object of which is to further develop that industry in Great Britain. The department will be under the direction of Sir Evan Jones, with the official title Controller of Dyes.

Dr. H. K. Benson, professor of industrial chemistry at the University of Washington, has accepted a position as research chemist with the American Nitrogen Products Co., until October 1st, when he will return to his school work. He is located at La Grande, Wash., where he will conduct research work relating to the manufacture of nitrogen products from the air by means of electricity.

The U. S. Civil Service Commission announces the appointment of Mr. H. C. Pritham as explosives chemist in charge of the technical force at the Frankford Arsenal. This selection by the Commission is from an examination of February.

F. R. Weaver, formerly of Chicago, Ill., has been detailed as ordnance officer at the Frankford Arsenal, Philadelphia.

Prof. Joseph S. Ames, of Johns Hopkins University, chairman of the commission of scientists sent to England and France by the Advisory Commission of the Council of National Defense, returned to New York City on June 26th and left directly for Baltimore. Prof. Ames' special subject was on aeronautics.

We learn from *Science* that Prof. Haller has been elected honorary president of the newly organized French Society of Industrial Chemistry.

Union College has conferred the doctorate of science on William Pitt Mason, professor of chemistry in the Sennelsaer Polytechnic Institute.

John E. Bucher, professor of chemistry at Brown University, has been given the degree of doctor of science by that university.

Bowdoin College has conferred the doctorate of science on A. H. Sabin (class of 1876), consulting chemist of the National Lead Co. and lecturer in New York University.

The Engineering Council, a department of the United Engineering Society and recently created as a medium of cooperation between the four national engineering societies, held its organization meeting on June 27th. The by-laws of the United Engineering Society prescribe: "The Council may speak authoritatively for all member societies on all public questions of a common interest or concern to engineers." The Council is composed of twenty-four members, five being appointed by each of the four founder societies and four by the United Engineering Society. At the organization meeting the following officers were elected: *President*, I. N. Hollis; *Vice-Presidents*, H. W. Buck and G. F. Swain; *Secretary*, Calvert Townley; *Executive Committee*, the four officers named, with P. N. Moore and D. S. Jacobus. The unanimous desire to help the Government prosecute the war resulted in a resolution instructing the Executive Committee to cooperate with the Government in procuring the services of engineers, and also in the appointment of a committee consisting of Messrs. H. W. Buck, A. M. Greene, Jr., and E. B. Kirby, to consider the best means of utilizing the inventive ability of members of the founder societies.

Dr. John F. Norton has resigned his position as assistant professor of chemistry of sanitation at the Massachusetts Institute of Technology, to accept a position as assistant professor of bacteriology at the University of Chicago. Dr. Norton has an S.B. degree from the Massachusetts Institute of Technology, 1906, and a Ph.D. degree from the University of Chicago, 1911. He will be at his new address after September 15.

Prof. Leverett Mears, head of the department of chemistry, Williams College, Williamstown, Mass., died on June 22, 1917.

We note from *Science* that Miss Amy Walker, Smith College, has been appointed research assistant in the chemistry of foods at the Massachusetts Institute of Technology, under the Ellen H. Richards Fund, for the year 1917-1918. Prof. A. G. Woodman will direct the work, and it is proposed to study chemical changes (with special reference to the nitrogen compounds) which take place when fish decomposes before and after heating at relatively high temperatures. This question is of particular interest in the sardine industry.

Will H. Coghill has been appointed consulting metallurgist in the cooperative work of the Oregon Bureau of Mines and Geology and the U. S. Bureau of Mines.

Henry N. Thomson has resigned as metallurgist for the United Verde Copper Co., and is engaged in consulting practice at 918 So. Kingsley Drive, Los Angeles, Cal.

INDUSTRIAL NOTES

On July 16, 1917, a conference was held at the U. S. Customs House, New York City, between representatives of the Department of Commerce, the manufacturers of fertilizers and of sulfuric acid, and the importers of pyrites, concerning ways and means of relieving the pyrites situation. The result of the conference was the appointment of a committee to cooperate with the Department of Commerce in securing from the British Government licenses for the importation of pyrites. The committee consists of Henry Howard, chairman of the executive committee of the Manufacturing Chemists' Association; Horace Bowker, of the National Fertilizer Association; and A. H. Strone, representing the importers.

The General Filtration Company, Inc., Rochester, N. Y., have issued a new *Filtros* booklet which supersedes the previous booklet. This new catalogue contains considerable detailed information on the manufacture, composition, chemical and physical properties, shapes, grades, uses and applications of *Filtros*, an artificial porous stone used for filtration purposes.

The Research Laboratory of Chicago has been recently incorporated, stock \$50,000, by W. S. Shaw, (*Manager*) H. McCormack, A. G. Wackeneuter, of Chicago, G. S. Rice, of Petosky, Mich., F. S. Howse, of Boston, and (*President*) E. C. Klipstein, of New York. This Illinois corporation will carry on research work in the development and exploitation of chemical processes and also expects to manufacture some pharmaceutical and photographic chemicals.

Dr. Alexis Carrell, in conjunction with Dr. H. D. Dakin, has evolved a comparatively new and revolutionary method for treating infected wounds, using a definite hypochlorite solution. The method for the preparation of this so-called Dakin Solution was worked out by G. Ornstein for the Electro-Bleaching Gas Co. The method consists in enclosing liquid chlorine in quantities of exactly 5 g. in glass tubes, sealed at one end, of 8 to 9 mm. outside diameter and 8 to 9 in. long, and then sealing the other end of the tube by drawing it out to a point. All of these tubes before they are allowed to go out of the laboratory are tested under increased pressure by heating them to a temperature of 75° C., which raises the pressure of the liquid chlorine from a pressure at ordinary temperatures of 80 to 90 lbs. to over 150 lbs. per sq. in. The glass tubes will stand this immense pressure although their walls are only $\frac{1}{16}$ to $\frac{1}{8}$ in. thick. The method of breaking the ampoule with liquid chlorine in the alkali solution has been recently improved by a simple device. The glass bottle in which the solution is prepared is now closed by a rubber stopper, to the bottom of which is fastened a short piece of rubber tubing by means of a short piece of glass rod. The ampoule is fastened with its butt in the open end of the rubber tubing so that the pointed end points downward, and the ampoule is suspended pendulum-like in the liquid containing the alkali solution. The Electro-Bleaching Gas Co. has recently completed arrangements with the pharmaceutical firm of Johnson & Johnson, New Brunswick, N. J., for the marketing of this new development in the liquid chlorine field.

Dr. H. C. Sherman, professor of food chemistry at Columbia University, New York City, has accompanied the Red Cross Mission to Russia in the capacity of food expert. He will probably be gone for four months. The mission is under the chairmanship of Dr. Frank Billings of Chicago.

At a meeting held at the Institute of Chemistry, London, on Friday, April 28th, the President and Council presented a silver rose bowl to Mr. Richard B. Pilcher, Registrar and Secretary, in appreciation of 25 years faithful service.

Stillwell & Gladding, Inc., announce the removal of their offices and laboratories to their new building, 95-97 Front Street (near Wall Street), New York City.

The New York City Municipal Civil Service Commission has announced an examination for junior chemists, applications for which will be received at Room 1400, Municipal Building, New York City, until August 9 at 4 p. m. For further particulars apply or write to the Municipal Civil Service Commission, at the above address.

Dr. H. D. Dakin, who, with Dr. Alexis Carrel, has charge of the military hospital being constructed and equipped by the Rockefeller Foundation on the grounds of the Rockefeller Institute of Medical Research, New York City, returned from France to New York City on June 26. Dr. Dakin went to France in April to consult with Dr. Carrel.

The Chemical Industry Exhibition Association, of Tokyo, Japan, will hold a chemical industry exposition, open also to foreign manufacturers, at that city, beginning September 20 and lasting for sixty days. The list of advisers of the exposition includes the name of Jokichi Takamine and other well-known names.

The organization of the National Aniline & Chemical Co., the great dyestuff merger, has been perfected by the election of the following officers and directors: Wm. H. Nichols, Sr., chairman of the board; J. F. Schoellkopf, president; W. Beckers, 1st vice-president; I. F. Stone, 2nd vice-president and treasurer; C. P. Hugo Schoellkopf, 3rd vice-president; Wm. T. Miller, secretary. The directors of the company include the foregoing officers, except Secretary Miller, and the following: J. F. Schoellkopf, Jr., Eugene Meyer, Jr., Chas. J. Thurnauer, Henry Wigglesworth, J. M. Goetschius, T. M. Rianhard, W. N. McIlravy, H. H. S. Handy and E. L. Pierce.

The Handbook on "Hoisting Machinery for Industrial Works," issued by the Shepard Electric Crane & Hoist Company, Montour Falls, N. Y., has just come off the press and is ready for distribution. The book contains descriptions of hoists for varied purposes, supplemented with cuts giving valuable dimensional data.

A fire, on July 9, in the aniline dye and chemical plant of the Seydel Manufacturing Co., Jersey City, N. J., caused a loss of between \$40,000 and \$50,000.

The main factory of the Montclair Chemical Works, Indianapolis, Ind., was recently destroyed by fire, estimated loss \$500,000.

A recent fire in the Midvale Chemical Company plant, Bayway, Elizabeth, N. J., was caused by a leak in an aniline still in the reduction plant. The loss is estimated at from \$50,000 to \$75,000.

A \$30,000 fire occurred on July 8 at the plant of the Federal Dyestuffs Company, Kingsport, Tenn. The fire threatened to assume large proportions, but was confined to one of the plant units.

Martin Diaz de Cossio, of Barcelona, Spain, announces the existence of an important Spanish market for all chemical products, drugs and colors, manufactured in the United States. He says that the manufacturer or exporter who will establish a Barcelona depot, enabling immediate delivery of the products wanted, will be the German who in 1914 will have the greatest chance for the confidence and the sale of his products. To facilitate this operation, Martin Diaz de Cossio will publish a monthly review of chemical products, thereby giving to American exporters and producers an idea of the Barcelona market. He also announces that he will select and recommend all aniline dyes and chemical products to be manufactured in Spain, under these commitments on the part of the value of the exportation from 25 to 60 days, according to the greater or lesser distance of shipment.

GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

BUREAU OF STANDARDS

Glasses for Protecting the Eyes from Injurious Radiations. W. W. COBLENTZ AND W. B. EMERSON. Technologic Paper 93. 14 pp. The object of the present paper is to give the general characteristics of certain newly developed glasses sometimes used for protecting the eye from radiant energy, especially from the infra-red or so-called heat rays. Because of the difficulty in reproducing the same color in different melts, no attempt is made to give specific data on the transmission for a given thickness of glass. The data given are representative of an extensive group of glasses available for protecting the eye from (1) the ultra-violet, (2) the visible, and (3) the infra-red rays.

The Standardization of Bomb Calorimeters. Circular No. 11, 3rd Edition, issued June 23, 1917.

Specification of the Transparency of Paper and Tracing Cloth. Circular No. 63, 1st Edition, issued May 17, 1917. "In response to the demands of several Government departments and of dealers in tracing cloth, the Bureau has developed and adopted a standard method for specifying the transparency of paper and tracing cloth.

"The purposes of the present circular are to (1) state definitely the form of the specification, (2) explain its significance, (3) describe the apparatus and method of test, and (4) give general information and instructions to applicants for tests in terms of this specification."

Properties of the Calcium Silicates and Calcium Aluminate Occurring in Normal Portland Cement. P. H. BATES AND A. A. KLEIN. Technologic Paper 78, 36 pp., issued June 9. Paper, 25 cents.

Temperature Measurements in Bessemer and Open-Hearth Practice. GEORGE K. BURGESS. Technologic Paper 91, 27 pp., issued May 8. Paper, 5 cents.

"It is the object of this paper to demonstrate that in so far as casting temperatures of furnaces, steel ingots, and similar operations involving the temperature of streams of iron and steel are concerned, well-known pyrometric methods may easily be applied with a relatively high degree of accuracy if certain recently determined corrections are made and precautions taken. Greater but not insurmountable difficulties will be encountered in the case of open-hearth furnace temperatures, while for those of the converter type a ready solution does not seem practicable."

Measurement and Specification of the Physical Factors which Determine the Saturation of Certain Tints of Yellow. IRWIN G. PRIEST AND CHAUNCEY G. PETERS. Technologic Paper 92, 11 pp., issued June 30. Paper, 5 cents. "Frequent and persistent demands have been made on the Bureau of Standards to draft a form of specification which would be suitable to define rigorously in law a limiting value of what, in common parlance, may be called the 'color,' the 'depth of color,' the 'strength of color,' or the 'yellowness' of butter and oleomar-

garine. More specifically stated, it is desired to define a line of demarcation between the paler tints of yellow and those of a more pronounced color.

"The purposes of this paper are:

"1—To outline the rational principles which should govern the formulation of such a specification.

"2—To present and explain the form of specification recommended by the Bureau, together with the methods and apparatus used to make the necessary measurements for testing in terms of the specification.

"An attempt will be made to present the subject in such a way as to make it intelligible to interested persons who may have little or no previous knowledge of the scientific principles or the technique involved."

Effusion Method of Determining Gas Density. JUNIUS DAVID EDWARDS. Technologic Paper 94, 28 pp. Paper, 10 cents. "Although no results of high accuracy can be expected from apparatus of the effusion type, yet it should serve well for approximate results or for work where relative values only are needed, as in control work.

"It has been shown that the apparent specific gravity determined by this method can be varied within rather wide limits by changing the conditions. However, by the observance of certain precautions in the construction and use of the apparatus, it is possible to secure results accurate to about 2 per cent. The greatest precision is obtained where the physical properties of the gas tested show the least differences from those of air. Some further increase in accuracy, and particularly in reliability, can be gained by standardizing the apparatus as recommended."

An "Average Eye" for Heterochromatic Photometry, and a Comparison of a Flicker and an Equality-of-Brightness Photometer. E. C. CRITTENDEN AND F. K. RICHTMYER. Scientific Paper 299, 27 pp., issued May 26. Paper, 5 cents.

Emissivity of Straight and Helical Filaments of Tungsten. W. W. COBLENTZ. Scientific Paper 300, 17 pp., issued June 8. Paper, 5 cents.

Wave Lengths of the Stronger Lines in the Helium Spectrum. PAUL W. MERRILL. Scientific Paper 302, 8 pp., issued June 18. Paper, 5 cents. "Wave lengths of 21 of the stronger helium lines have been accurately measured by interference methods. Nine of them were compared directly with the standard cadmium line.

"The possibility of eliminating the effect of apparent variation of interferometer thickness with wave length is noted.

"The Kayser and Runge formula for spectral series, based upon three consecutive lines, will not reproduce accurately even the next member in any one of the six helium series."

Calculation of the Constants of Planck's Radiation Equation: An Extension of the Theory of Least Squares. HARRY M. ROESER. Scientific Paper 304, 17 pp., issued June 29. Paper, 5 cents.

Luminous Radiation from a Black Body and the Mechanical Equivalent of Light. W. W. COBLENTZ AND W. B. EMERSON. Scientific Paper 305, 11 pp. Paper, 5 cents. "This paper gives some applications of the curve of visibility of radiation for the average eye (125 observers) to radiation problems.

"The most reliable data now available indicate that the value of the luminous equivalent of radiation of maximum luminous efficiency is of the order of:

1 watt = 617 lumens = 49.1 candles.

1 lumen = 0.00162 watt of luminous flux.

"Among other data this paper gives the determination of

the radiant luminous efficiency of a vacuum tungsten lamp, the value being 1.42 per cent when operated at 1.23 watts per candle."

GEOLOGICAL SURVEY

A Comparison of Paleozoic Section in Southern New Mexico. N. H. DARTON. From Shorter Contributions to General Geology, 1917, pp. 31-35. Published May 29, 1917.

Wasatch Fossils in So-Called Fort Union Beds of the Powder River Basin, Wyoming, and Their Bearing on the Stratigraphy of the Region. CARROLL H. WEGEMANN. From Shorter Contributions to General Geology, 1917, pp. 57-60. Published May 29, 1917.

Ground Water in San Simon Valley, Arizona, and New Mexico. A. T. SCHWENNESEN. With a Section on Agriculture, R. H. FORBES. From Contributions to the Hydrology of the United States, 1917, pp. 1-35. Published May 7, 1917. This was prepared in cooperation with the Arizona Agricultural Experiment Station.

Graphite. HENRY G. FERGUSON. Bulletin 666-L, 7 pp. The following table shows the imports and domestic output of crystalline graphite for the year 1916:

	Quantity (short tons)	Value
Imports(a): Ceylon.....	24,972	\$6,013,362
Other countries.....	7,188	920,369
Domestic Production.....	32,160	6,013,731
	5,466	914,748
TOTAL AVAILABLE SUPPLY.....	37,626	7,848,479
Per cent represented by Domestic Production.....	14.6	11.7

(a) From records of the Department of Commerce.

"During 1914 and 1915 the imports from Ceylon were less than normal, owing chiefly to the high freight rates and scarcity of ships. The sharp increase in the value of the Ceylon graphite imported in 1916 is due largely to the fact that because of the conditions mentioned only the higher-grade material was imported.

"Domestic flake graphite of a grade suitable for crucible use has increased greatly in price during the last two years. The prices paid at the mines for the highest-grade product, in cents a pound, have been as follows: 1911 and 1912, 6 to 7; 1913, 6 to 8; 1914, 6 1/2 to 8; 1915, 7 to 10; 1916, 10 to 16.

"Average prices of crystalline graphite of all grades, including dust as well as flake, have been as follows:

PRICES OF CRYSTALLINE GRAPHITE, 1911-1916
IN CENTS A POUND

	Ceylon	Domestic	Ceylon	Domestic
1911.....	4.3	5.3	4.8	5.5
1912.....	4.1	5.3	6.4	5.9
1913.....	4.9	5.0	12.0	8.4

"Amorphous graphite is suitable for all purposes for which graphite is used, except the manufacture of crucibles. As it does not enter to any large degree into the manufacture of munitions, the war has not greatly affected either price or production. Moreover, artificial graphite and crystalline graphite in particles too small for crucible manufacture are adapted to practically all uses to which natural amorphous graphite can be put, and the reserves of amorphous graphite are therefore less important. The uses of amorphous graphite vary greatly with the purity of the substance mined. For paint and foundry facing, a high degree of purity is not essential, but for lubricants, pencil, and electro purposes, high-grade material is necessary. The better grades of amorphous graphite are imported from Mexico and Ceylon, and the imports, like those of crystalline graphite, greatly exceed the domestic output. The sharp decrease in importation in 1916, shown in the following table, was due chiefly to the disturbed conditions in Mexico, but also to decreased imports from Ceylon, owing to high freight rates and scarcity of ships.

AMORPHOUS GRAPHITE IMPORTED AND PRODUCED IN THE
UNITED STATES IN 1916

	Quantity (short tons)	Value
Imports.....	10,837	\$345,732
Domestic Production.....	2,622	20,723
TOTAL AVAILABLE SUPPLY.....	13,458	366,455
Per cent represented by Domestic Production.....	19.5	5.7

"Graphite in large quantities is manufactured at Niagara Falls, N. Y., by the International Acheson Graphite Company, which utilizes electric power generated at the Falls. The bulk graphite produced by this company in 1915 was reported as 2,542 short tons, and in 1916 as 4,199 tons. This represents only the graphite that would come into competition with natural graphite and does not include graphitized products that do not compete with natural graphite. The material, most of which is made either from anthracite or from petroleum coke, comes from the furnace in an earthy, incoherent condition and is utilized mainly in lubricants and paints and for foundry facings, boiler-scale preventives, and battery fillers.

"Besides the graphite products that enter into competition with natural graphite, there are a large number of graphite products for which only artificial graphite is adapted. Chief among these are graphite electrodes, the demand for which has greatly increased during the last two years on account of the remarkable growth in certain electrochemical industries. The extent of this growth is indicated by the statement that during 1915 the number of electric steel furnaces in operation in this country increased 78 per cent."

Geology and Water Resources of Big Smoky, Clayton, and Alkali Spring Valleys, Nevada. OSCAR E. MEINZER. Water Supply Paper 423, 153 pp. This contains a report on numerous water and soil analyses.

Barium and Strontium. JAMES M. HILL. Bulletin 666-W, 3 pp. "Since the beginning of the war a barium chemical industry has been established in the United States to supply barium carbonate, nitrate, chloride, chlorate, hydrate, and binoxide, which were formerly imported from Germany. In 1915 this industry consumed 10 per cent of the output of domestic barite, but the consumption in 1916 was apparently somewhat larger. The barium chemicals have a wide variety of applications, perhaps the most important of which are the use of barium binoxide in the preparation of hydrogen peroxide, that of barium chloride as a water softener, and that of various salts in the manufacture of optical glass.

"The production of 108,547 short tons in 1915 was over twice as large as that of 1914, and in 1916 the output was again doubled. The value of the 1916 output was over \$1,000,000—a figure never attained before.

"Strontium salts, chiefly the nitrate, are employed to make 'red fire,' which is of wide use at this time not only for signal lights on battle fronts but for railway signals to promote the safe handling of trains at night. It is estimated that prior to 1914 about 2,800 tons of strontium nitrate were used annually in the manufacture of such devices as flares, and flares of light and fireworks. Since 1914 the demand has increased considerably.

Before the war chloride of strontium and strontium carbonate were imported from Germany, England and Italy. During 1914 and 1915 the demand was met almost entirely by manufacturers in this country. The manufacture of strontium compounds is being rapidly increased.

Apparently Ceylon produces no amorphous graphite, and the imports are increasing only by the small amount of material that is being produced there. The demand for this material is increasing rapidly.

Clay and Clay Products. DEPARTMENT OF COMMERCE, BUREAU OF MINES, TECHNICAL SERIES 1, 1917.

Notes on the Geology and Iron Ores of the Cuyuna District, Minnesota. E. C. HARDER AND A. W. JOHNSTON. Bulletin 660-A, from Contributions to Economic Geology, 1917, Part I, pp. 1-26. Published June 7. "The preliminary report, of which the present paper is an abstract, is being published by the Minnesota Geological Survey; the more complete report will be published by the United States Geological Survey."

The Rarer Metals. FRANK L. HESS. Bulletin 666-U, 13 pp. This separate covers a discussion of antimony, arsenic, bismuth, nickel, tungsten, molybdenum, vanadium and tin.

"The fact that a large production of some mineral has been made in one year does not necessarily imply that it can be repeated under the impetus of great need. In estimating the possible production of any mineral for any period, a proper weighing of the attending circumstances, the statistics of production of preceding years, and a knowledge of the deposits themselves are all necessary, and these statements probably apply more forcibly to the metals used in alloy steels than to others, for these metals occur in vastly less quantities than coal, iron, copper, or the other common metals, and the individual deposits are smaller and much less widely distributed and, unlike those of copper or iron, are in very few places concentrated from lean into richer deposits.

"Comparatively restricted markets and lack of knowledge concerning these metals themselves and of the minerals in which they occur have prevented prospecting for them until within the last few years, so that as a rule developments of such deposits are small.

"The subjects briefly discussed here with reference to their availability as war supplies are treated more fully in Mineral Resources and other publications of the United States Geological Survey, especially those for recent years."

COMMERCE REPORTS—JUNE, 1917

A detailed survey of the **petroleum** prospects of Argentina has shown four well defined oil fields besides numerous doubtful localities. Efforts are being made to increase the oil production sufficiently to meet the present critical fuel situation there. (P. 841)

Graphite has been discovered in Mysore Province, India, in what is believed to be a paying deposit. (P. 843)

Use of **saccharine** and other artificial sweetening products has been permitted in France for the period of the war. Since 1902, its use in France has been prohibited. (P. 847)

There has been a great increase in the demand for Japanese **bleaching powder**, both in Japan and abroad. (P. 854)

Estimates by the Geological Survey place the quantity of **platinum** in the United States at 1,000,000 troy ounces, and the annual requirements as 165,000 ounces. With the expected increase in the production of Colombia, Russia and the United States, and a decreased consumption in the dental and jewelry business, it is believed that the requirements of the chemical industries can be met. (P. 866)

There has been a great increase in the output of **iron ore** from the mines in Manchuria, which contain principally low-grade ore (30-40 per cent iron) with occasional masses of high-grade ore (60-70 per cent iron). An ore separation plant is to be installed for concentrating the poor ore. (P. 871)

Deposits of **wolframite** are reported from several points in Brazil. (P. 878)

A **cement** factory is being erected in Buenos Aires, with a capacity of 3000 barrels per day. (P. 882)

Imports of **camphor** crude, refined and synthetic, into the United States have far exceeded those of previous years. (P. 886)

By a **rapid tanning process** recently discovered in Australia it is claimed that sole leather can be tanned in seven days, and other skins in much less time, yielding products much stronger than normal. (P. 890)

Production of **plantation rubber** in French Indo-China has greatly increased and that of wild rubber has decreased. (P. 891)

A detailed description of the **sisal industry** in East Africa is given. (Pp. 917-25)

Grease, valued at nearly \$400,000, was recovered from the sewage of Bradford, England; this was derived from the wool scouring establishments. It is useful for leather dressing, etc. (P. 1014)

The "**British Engineering Standards Committee**," formed in 1901 and originally consisting of seven members, has grown to an organization with a main committee of 22 members, with 64 sectional committees and subcommittees including a total membership of over 500. It contains representatives of all technical and trade organizations possibly interested in engineering standardization. (P. 1040)

In a process for treating empty **tin cans** in Hornsey, England, the tin is simply burned off by waste flue gases, with no attempt at recovery of the tin. The steel scrap is then ready for delivery to the steel works. (p. 1045)

In the United States there were in 1916, 756 plants making **cottonseed oil**, and 112 plants engaged in manufacturing other **edible vegetable oils**, from peanuts, mustard seed, kapok, rape, sunflower seed, soya beans, walnuts, corn, copra, palm kernels, and olives. A great increase in the domestic cultivation of soya beans and peanuts is expected. (P. 1060)

In Sweden the consumption of **gas and electricity** at the usual rate, for both private and commercial use, has been restricted to 60 per cent of the normal with 30 per cent additional permitted at greatly increased rates. (P. 1073)

Efforts are being made in Trinidad, British West Indies, to increase the use of **banana flour** as a substitute for wheat. Flour equal to about 25 per cent of the weight of the bananas is obtained. (P. 1106)

Production of **glycerine** in Japan has greatly increased as a result of Government subsidy. (P. 1123)

In order to increase the consumption in France of **vegetable fats and oils**, it is proposed that the Academy of Medicine issue statements regarding their high nutritive value and the desirability of using them to conserve the supplies of animal fats. (P. 1139)

The most important new industry developed in Venice the past year is that of spinning glass for commercial uses. The spun glass is marketed in three forms—hanks of straight spun glass fibers, known as "glass cotton;" masses of curled fiber called "glass wool;" and sheets or pods of felted material. Its principal use at present is for **electrical insulation**. It is made of soda glass, free from lead, etc. (P. 1156)

A large modern **tannery**, with a weekly capacity of 3000 cow-hides and 100,000 sheep skins, is being erected in Hongkong. Chinese tan bark will be used. (P. 1170)

The American demand for Abyssinian civet (used as a basis of **perfumes**) has greatly increased. The civet cats are raised in large numbers in Abyssinia. (P. 1181)

SPECIAL SUPPLEMENTS ISSUED DURING THE MONTH

Netherlands	9a	Cuba—25a
STATISTICS OF EXPORTS TO THE UNITED STATES		
SWANSEA, WALES	P. 1134	AMSTERDAM—Sup. 9a
Nickel sulfate		Cinchona bark
Nickel ammonia sulfate		Cocoa butter
Copper, regulus and scale		Copal gum
Hides, sheep, salted		Diamonds
Tin plate		Drugs
CUBA—Sup. 25a		Chemicals
Asphalt		Hides
Beeswax		Kapok
Hides		Leather
Molasses		Linoleum
Copper Ore		Magnesite
Iron Ore		Essential Oils
Manganese Ore		Paint
Sugar		Potash
		Quinine
		Rags
		Rubber
		Tin

BOOK REVIEWS

Elements of Industrial Chemistry. By ALLEN ROGERS, in charge of Industrial Chemistry, Pratt Institute, Brooklyn, N. Y. An abridgement of Manual of Industrial Chemistry written by forty eminent specialists and edited by Allen Rogers. 117 illustrations. New York: D. Van Nostrand Co., 1916. 8 vols. viii + 513 pp. Price, \$3.00, net.

The express purpose of this book is to meet the needs of teachers who do not have sufficient time in their courses to use more extended treatises. This work is therefore a handy sized compilation from the author's well-known Manual which contains so many excellent chapters. "The endeavor has been, in arranging this condensation, to treat the subjects covered in a general manner only, thus eliminating as much of the detail as possible in order that the fundamental principles might be more clearly set forth."

The 49 chapters of the Manual are condensed to 27 in this volume. The subjects included are: General Processes (meaning by that engineering operations such as grinding, distillation, etc.); Water; Fuels; Sulfuric Acid; Nitric Acid; "Elements and Inorganic Compounds;" Ceramics; Pigments; Fertilizers; Illuminating Gas; Coal-Tar; Petroleum; Wood Distillation; Oils, Fats and Waxes; Lubricating Oils; Soap and Glycerine; Essential Oils; Resins and Gums; Varnish; Sugar; Starch and Glucose; Beer, Wine and Liquor; Textiles; Dyestuffs and Their Application; Paper; Explosives; Leather.

The book makes a pleasing appearance and is of handy size, though heavy. It is not bound well enough to wear as a student text. The back of the review copy is already split. Good paper, however, is used throughout and the cuts and half-tones are clean-cut and distinct. Many of these are reduced from the Manual. References to the literature would have been a welcome addition, for the students who use this text are really advanced men, the Manual being too clumsy for vigorous class use.

Any one who takes the trouble to write an industrial chemistry deserves to be absolved from all criticism. It even seems ungrateful to call attention in the best of spirit to any errors or lapses, for no teacher of chemistry, unless he has been himself a manufacturer, can understand the weight of the task entailed by such a writing. The teacher with manufacturing experience will detect at once many of the doubtful matters in all such books, though no one could have enough experience to detect all of them. It will be necessary to call attention in this review to only enough of these items to warn teachers, not broadly experienced industrially, that they must not accept implicitly every impression from industrial chemistry texts.

It is pleasant to see transportation of solids, liquids and gases added to the usually enumerated engineering operations in the chapter on "General Processes." It seems a pity, however, to appear to stress special types of evaporators which are comparatively little used and omit more current ones altogether. The "type of column still in common use," p. 23, is really quite rare, for it is of very low efficiency (especially its return cooler), and as drawn would not even separate benzol from water, as the reviewer has good reason to know from the experience of having many years ago received a column with *only a single* "down commer" pipe not sealed. In the drawing in question all "down commer" pipes are unsealed and such a column could not be operated. It would intermittently flood and blow.

One wonders at the exclusive mention of lead platinum-sulfuric concentration except "in England." Do we not also in this country have other types? Eighteen years ago the reviewer worked on one in Philadelphia that used no platinum. Charging "pot stills" for nitric acid with merely 2200 lbs. of nitrate once or

twice in 24 to 27 hrs. probably would have ruined the allied cause. Five to six thousand pounds per 8-hr. turn is the more modern achievement. Too much space is given to the Skoglund condenser and no mention made of more recent and efficient developments. These unmentioned developments in this and the sulfuric acid industry in the last five years through the use of high silicon irons and silica ware are among the great achievements of chemical engineering.

The chapter on "Elements and Inorganic Compounds" is an alphabetized dictionary into which has been condensed several chapters of the Manual. It partakes of the same fault as a similar chapter in the Manual, in that it gives astonishingly small space to that most highly organized, in a chemical engineering sense, of all our chemical industries and one of our most important as well, namely, the Solvay Soda process, and gives over twice the space, as is done in all the classics that have gone before, to the Le Blanc process which is not in operation in this country, a thing also now true of the cryolite process. This brevity in considering the Solvay process is not done to save detail to make room for more fundamental material as the preface might make one believe, for, in the same chapter, pages are literally wasted on a catalog of substances practically by mere name without any fundamental industrial principle or information attached. For example, there are such paragraphs as: "*Cæsium*. This is one of the rare elements and is of no commercial value." A similar admission is made in the case of many other substances such as barium, erbium, gadolinium, germanium, indium, neodymium, osmium, samarium, scandium, tellurium, thallium, and thulium. In addition, many more of such materials, which are as unused industrially, are not so marked and thus give the impression that they *are* so used. A large portion of this chapter, by far the largest in the book, is not industrial chemistry at all but simply general or inorganic chemistry, of the character of the paragraph "*Cerium*. This element is found in the mineral cerite and forms both cerous and ceric salts."

It seems too bad to leave out even the names of so many of the successful chlorine and NaOH cells in use all over the country, while giving a whole page to the Acker cell that is not in operation at all.

In discussing wood distillation, destructive distillation is mixed up and condensed badly with steam distillation of chipped wood for turpentine, throughout the whole paragraph on this subject. Contrary to the impression one would receive here the distillation of "packed" sawdust may some day solve the waste sawdust problem if distillation can do so at all. Electricity is a laboratory, and not a factory method of heating wood retorts. The saving of one distillation in making gray acetate by a fractionating device on the ovens is not used as stated. It has never been a success in American sized units, though much money has been needlessly wasted upon it, when such a result could have been predicted on thermal-chemical grounds. This chapter on wood distillation partakes throughout of the errors of the chapter on this subject in the Manual, which incorrectly states the hardwood practice and then gratuitously assumes that this practice will apply also to soft wood, which it does not. Then the somewhat steam distillation turpentine apparatus, and methods, are scattered through this material giving the impression that they apply to hardwood and softwood alike. Evaporating pans for acetate are not made of copper as stated. This would be a needless expense. Mechanical stirring devices are also not used and certainly not necessary to prevent sticking to the pan, if one has operatives who know how to load acetate liquor. Wood alcohol refining over iodine, metallic sodium or

P_2O_5 could hardly be classed as refinery methods. Even the lime distillation is not necessary, and the unsatisfactory $CaCl_2$ separation of acetone is probably never used. Copper stills and HCl are rarely used in America in making acetic acid from calcium acetate, but iron stills and sulfuric acid, when the product is 70–75 per cent and not 50 per cent as with HCl . The lack of smoothness in operation stated to occur when H_2SO_4 is used is not the experience of the reviewer.

These citations, some of which are obviously a matter of opinion, merely serve to indicate the difficulty and breadth of the field covered by the teacher of industrial chemistry, and what a pathetically fatal policy it is, in so many of our schools of technology, which ignores entirely the labor of keeping even partially informed in this field, and crushes the vitality of its specialist teacher of industrial chemistry by saddling upon him the distraction of elementary classes as well.

As a teachable book this volume is divided into convenient sized chapters. It is a distinct advance on its predecessors in that it is more American than they, while giving due credit to foreign processes. For a book of such a character it is remarkably free from errors.

JAMES R. WITHROW

Explosives. By ARTHUR MARSHALL. Second Edition, Vol. I, History and Manufacture. 8vo, 407 pp. and 77 illustrations. P. Blakiston's Sons & Co., Philadelphia, 1917. Two volumes, \$16.00 (not sold separately).

The first edition of this book was issued in 1915 as a volume of 624 pages. The second edition is now being issued in two volumes, the extent of the enlargement being somewhat indicated by the description above. The order of treatment of topics follows that of the first edition, wherein the author has designated his topics as "Parts" and, in his treatment of them, divided each "Part" into several chapters, but these topics are, in the new edition, preceded by an introductory chapter dealing with general characteristics, which is of the nature of a résumé of Brunswig's "Explosives;" there is intercalated between the "Parts" on the "Nitric Esters of Glycerin" and "Smokeless Powders" of the first edition, a "Part" on "Nitro-Aromatic Compounds," and the volume ends with the "Part" on "Blasting Explosives" from which the chapter on "The Choice of a High Explosive" has been dropped in order that it may be treated more fully in Volume II, which was expected to be published in June. The extent of the revision may be gauged not only by the additions noted but also by the facts that Part I, "Historical," is increased six pages; II, "Black Powder," five; III, "Acids," seven; VII, "Smokeless Powders," eleven; and VIII, "Blasting Explosives," three pages over the space devoted to the same topics in the first edition, while all of the chapters appear to have been revised.

The call for a second edition so soon after the publication of the first, coupled with the large price exacted for this work, is a gauge of the value at which it is appraised. This edition has been revised from the standpoint of the necessities developed by the Great War, and the means by which they have been satisfied. It is dedicated to David Lloyd George and adorned with an excellent photograph of the Prime Minister. In view of this, and of the frankness with which information regarding the fixation of nitrogen, the methods for the production of nitrosubstitution explosives, and the manufacture and properties of smokeless powders is set forth, one who has been placed under the seal of secrecy in piping times of peace appreciates the sound common sense of the Premier in allowing these additions and revisions to the new edition to appear. Referring in his preface to the effects of the Great War, Marshall says that, although it has completed its second year, it "has not caused the introduction of any very novel explosives, despite sensational statements of some journal-

ists. Certain aspects of the manufacture of explosives have, however, become of greater importance, and have, therefore, been treated in greater detail in this edition." Before the war, nitric acid made from air could hardly anywhere compete with that manufactured from sodium nitrate, but the blockade of Germany has altered this. Thus does history repeat herself, for in the Napoleonic wars, England cut off the supply of potassium nitrate from India to France and caused a great development of the French saltpetre industry. The blockade has also caused Germany to pay more attention to chlorate and perchlorate explosives and those made with liquid oxygen."

The author has been favored by the appearance of "Les Poudres et Explosifs" by L. Vennin and G. Chesneau, which contains a systematic account of all classes of explosives both organic and inorganic, and he has drawn freely upon this work in his descriptions of French explosives and methods. In his list of sources, while German, French and English journals and publications are cited, no mention is made of the several publications of the American Chemical Society, but he does make considerable use of the publications of the U. S. Bureau of Mines. In presenting the book he says: "I have spared no trouble to make the work as reliable and useful as possible to those engaged in making and dealing with the explosives used in this titanic struggle, and I hope that in this way I have assisted slightly, in spite of the fact that I am detained far from the principal theatres of war (at Naini Tal, India). There are, of course, some matters in connection with explosives which cannot be published."

The author has done his work well but this may not be said of printer and proof-reader, for while the book has been planned in good form and is printed on heavy glazed paper, which serves to bring out the illustrations admirably, there is much evidence of haste in broken and turned letters, irregular impressions, omissions and bad spacing. There are numerous examples on pages 273–278. A glaring example of bad proof-reading occurs in the marginal legend on page 337 where ether-alcohol appears as "etherealcohol."

CHARLES E. MUNROE

The Microscopic Examination of Steel. By HENRY FAY. 18 pp. and 55 illustrations. John Wiley & Sons, Inc., New York, 1917. Price, \$1.25 net.

It is stated in the preface of the book that this material was originally issued by the Ordnance Department, U. S. A., and represented the results of investigative work carried on at the Watertown Arsenal. It was intended for the exclusive use of inspectors. It is not to be considered as a textbook, but is meant to present a mere outline of metallographic methods illustrating typical examples.

The text matter is somewhat sketchy, but is very concisely stated. Some exception might be taken to the author's definition of troostite, and a few minor criticisms might be made, but as a whole the book would be of value in the hands of those who know how to use the material. So little has been published in listed form regarding ordnance material that it is to be regretted that the author did not cover the ground in a more detailed way and did not offer more examples.

The author touches upon the various conditions in which steel occurs (slowly cooled, rapidly cooled, annealed), upon the occurrence of non-metallic impurities, examination of the macrostructure, and upon heat treatment, giving a few examples. The methods of polishing and etching are outlined, and a short bibliography is given.

The book is well worth while for the really excellent photomicrographs which it contains, covering a fairly wide range of material and treatment.

RALPH H. SHERRY

NEW PUBLICATIONS

By IRVING DE MATTEY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- Analysis: A Laboratory Manual of Qualitative Analysis.** T. J. BRADLEY. 4to. 94 pp. Price, \$1.25. Mass. College of Pharmacy, Boston.
- Analysis: A Manual of Qualitative Chemical Analysis.** G. D. TRIMMONS. 12mo. 253 pp. Price, \$1.25. M. A. Donahue & Co., Chicago.
- Artificial Electric Lines; Their Theory, Mode of Construction and Uses.** A. E. KENNELLY. 8vo. 348 pp. Price, \$4.00. McGraw-Hill Book Co., New York.
- Chemical Discovery and Invention in the Twentieth Century.** W. A. TILDEN. 8vo. 487 pp. Price, \$3.50. E. P. Dutton & Co., New York.
- Chemical French: French Scientific Reader.** F. DANIELS. 748 pp. Price, \$1.75. Oxford University Press, New York.
- Chemistry: One Hundred Chemical Problems.** C. A. MASON. 8vo. Price, 6d. George Bell & Sons, London.
- Chemistry: A Textbook of Sanitary and Applied Chemistry.** E. H. S. BAILEY. 4th Ed. 12mo. 395 pp. Price, \$1.60. The Macmillan Co., New York.
- Chemistry of Plant and Animal Life.** HARRY SNYDER. 12mo. 388 pp. Price, \$1.50. The Macmillan Co., New York.
- Clays and Clay Products.** A. B. SEARLE. 16mo. 163 pp. Price, \$0.85. Sir Isaac Pitman & Sons, New York.
- Drying Oils, Boiled Oil and Solid and Liquid Driers.** L. E. ANDRES. 2nd Ed. 8vo. 340 pp. Price, 12s. 6d. Scott, Greenwood & Son, London.
- Dyestuffs: The Chemistry of Dyestuffs.** M. FORT and L. L. LLOYD. 8vo. 311 pp. Price, 7s. 6d. Cambridge University Press, London.
- Electric Heating.** E. A. WILCOX. 8vo. Price, 10s. 6d. E. and F. N. Spon, London.
- Engineers' Year Book for 1917.** H. R. KEMPE. 8vo. 2225 pp. Price, 20s. Crosby Lockwood & Son, London.
- Evaporating, Condensing and Cooling Apparatus.** E. HAUSBRAND. 2nd Ed. 8vo. 400 pp. Price, 12s. 6d. Scott, Greenwood & Son, London.
- Food Poisoning.** E. O. JORDAN. 12mo. 115 pp. Price, \$1.00. University of Chicago Press, Chicago.
- Gas and Fuel Analysis for Engineers.** A. H. GILL. 12mo. 145 pp. Price, \$1.25. John Wiley & Sons, New York.
- Irrigation: Use of Water in Irrigation.** S. FORTIER. 8vo. 325 pp. Price, \$2.00. McGraw-Hill Book Co., New York.
- Irrigation Works Constructed by the U. S. Government.** A. P. DAVIS. 8vo. 425 pp. Price, \$4.50. John Wiley & Sons, New York.
- Milk Production.** C. W. LARSON. 8vo. Price, 3s. 6d. Oxford University Press.
- Mining and Mine Ventilation.** J. J. WALSH. 8vo. 187 pp. Price, 8s. 6d. A. Constable & Co., London.
- Oxy-Acetylene Welding Practice.** R. J. KEHL. 8vo. 110 pp. Price, \$1.00. American Technical Society, Chicago.
- Paper: The Chemistry of Paper-Making.** R. B. GRIFFIN and A. D. LITTLE. 8vo. 517 pp. Price, \$6.00. G. E. Stechert & Co., New York.
- Paper: A History of Paper Manufacturing in the United States.** L. H. WHEISS. 8vo. 352 pp. Price, \$3.00. Lockwood Trade Journal Co., New York.
- Patents: Walker on Patents.** 5th Ed. 8vo. 1300 pp. Price, \$12.00. Baker, Voorhis & Co., New York.
- Radioactivity: La Radioactivité et les Principaux corps radioactifs.** A. MUGERET. 18mo. 202 pp. O. Doin et fils, Paris.
- Rare Earths: Introduction to the Rarer Elements.** 4th Ed. 8vo. 250 pp. John Wiley & Sons, New York.
- Resistance of Air.** G. EPPLE. 4to. 242 pp. Price, \$10.00. Houghton, Mifflin Co., Boston.
- Sanitation Practically Applied.** H. B. WOOD. 8vo. 473 pp. Price, \$4.00. John Wiley & Sons, New York.
- Tractor: The Modern Gas Tractor.** V. W. PAGE. 12mo. 503 pp. Price, \$2.00. Norman W. Hensley Publishing Co., New York.
- Turbines Applied to Marine Propulsion.** J. S. REED. 2nd Ed. 180 pp. Price, 15s. A. Constable & Co., London.
- Water Purification.** J. W. FLEMING. 8vo. 188 pp. Price, \$5.00. McGraw-Hill Book Co., New York.
- Chemical Reactions of Iron Smelting.** H. P. HOWLAND. *Iron Trade Review*, Vol. 60 (1917), No. 24, pp. 1291-1292.
- Coal Mining in China.** A. C. REED. *Scientific Monthly*, Vol. 5 (1917), No. 1, pp. 36-49.
- Coke: Recent Developments in the By-Product Coking Industry.** T. K. KURAHASHI. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 12, pp. 700-701.
- Copper: Impurities in Electrolytic Copper Refining.** LAWRENCE ADDICKS. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 12, pp. 687-692.
- Cutting Oils.** C. W. COPELAND. *Metallurgical and Chemical Engineering*, Vol. 17 (1917), No. 1, pp. 25-32.
- Disinfection of Tannery Wastes.** D. D. JACKSON and A. M. BUSWELL. *Journal of the American Leather Chemists' Association*, Vol. 12 (1917), No. 6, pp. 229-253.
- Dyestuffs: The New Dyestuff Industry.** H. G. MCKERROW. *Textile World Journal*, Vol. 52 (1917), No. 31, pp. 37-39.
- Glycerine: Analysis of Glycerine.** ERNEST LITTLE. *Journal of the American Leather Chemists' Association*, Vol. 12 (1917), No. 6, pp. 254-257.
- Heat Transmission: Testing Blankets for Heat Transmission.** G. B. HAVEN. *Textile World Journal*, Vol. 52 (1917), No. 29, pp. 25-27.
- Heat Treatment of Steel Forgings.** H. H. ASHDOWN. *American Drop Forger*, Vol. 3 (1917), No. 6, pp. 201-206.
- Iron and Steel Industry in Australia.** R. A. FIELD. *Blast Furnace and Steel Plant*, Vol. 5 (1917), No. 7, pp. 299-301.
- Lead: Laws of Distribution of Lead in Southeast Missouri Ores.** S. BAGNARA. *Engineering and Mining Journal*, Vol. 103 (1917), No. 24, pp. 1056-1058.
- Limestone of Burnt Lime for Sulfite Mills.** G. D. JENSEN. *Paper*, Vol. 20 (1917), No. 14, pp. 12-18.
- Mining: The Great Adventure.** T. A. RICKARD. *Mining and Scientific Press*, Vol. 114 (1917), No. 24, pp. 831-838.
- Molybdenum: On a Unique Occurrence of Molybdenum in Natal.** A. L. DE TOL. *Chemical News*, Vol. 115 (1917), No. 3001, pp. 287-289.
- Oils: A Study of Fuel Oils from Coal.** HAROLD MOORE. *Iron Trade Review*, Vol. 60 (1917), No. 24, pp. 1294-1296.
- Oils: Testing of Lubricating Oils.** H. K. MOORE and G. A. RICHTER. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 12, pp. 692-694.
- Ore-Testing Laboratory.** C. J. TRAUBMAN. *Engineering and Mining Journal*, Vol. 103 (1917), No. 26, pp. 1142-1144.
- Phosphoric Acid Determination in Phosphate Rock.** C. C. SEMPLE. *Engineering and Mining Journal*, Vol. 103 (1917), No. 26, pp. 1140-1141.
- Saccharin: Determination of Saccharin in Foods.** C. B. GNADINGER. *Journal of the Association of Official Agricultural Chemists*, Vol. 3 (1917), No. 1, pp. 25-32.
- Soils: American Smelting and Refining Company's Tests with Sulfur and Sulfuric Acid on Soils.** P. J. O'GARRA. *Mining and Scientific Press*, Vol. 114 (1917), No. 24, pp. 840-843.
- Spelter Statistics for 1916.** W. R. INGALLS. *Engineering and Mining Journal*, Vol. 104 (1917), No. 1, pp. 17-23.
- Steels: Mayari and Nickel Steels Compared.** S. W. PARKER. *The Iron Age*, Vol. 99 (1917), No. 23, pp. 1380-1381.
- Sulfide-Filming Plant at Magma, Arizona.** J. M. CALLOW. *Mining and Scientific Press*, Vol. 114 (1917), No. 10, pp. 317-319.
- Sulfite Pulp: Experiments in the Beating of Sulfite Pulp.** OTTO KREBS and G. C. McNEIGHAN. *Paper*, Vol. 20 (1917), No. 11, pp. 18-21.
- Sulfur as a Component of Furnace Slag.** W. G. IMHOFF. *Blast Furnace and Steel Plant*, Vol. 5 (1917), No. 8, pp. 308-311.
- Surface Combustion Used in Galvanizing.** W. L. HANCOCK. *The Iron Age*, Vol. 99 (1917), No. 14, pp. 813-815.
- Synthetic Rubber.** A. H. KEMP. *Metallurgical and Chemical Engineering*, Vol. 16 (1917), No. 9, pp. 411-418.
- Talc: Growth of the Talc Industry.** FRANKLIN PEABODY. *Engineering and Mining Journal*, Vol. 104 (1917), No. 1, pp. 11-13.
- Temperature Measurements of Steel.** G. K. JOHNSON. *The Iron Trade Review*, Vol. 60 (1917), No. 11, pp. 517-518.
- Textile Mill Organization and Costs.** GEORGE C. FLETCHER. *Textile World Journal*, Vol. 52 (1917), No. 31, pp. 3-21.
- Textiles: Conservation of Textile Products.** H. C. HARRISON. *Textile World Journal*, Vol. 52 (1917), No. 31, pp. 22-23.
- Tinctories of Various Henna Derivatives to Dyes.** WILLIAM MONTGOMERY. *Journal of the Association of Official Agricultural Chemists*, Vol. 3 (1917), No. 1, pp. 171-181.
- Tungsten and Its Ores.** FRANKLIN PEABODY. *Engineering and Mining Journal*, Vol. 104 (1917), No. 1, pp. 2-3.
- Vanadium: Influence of Vanadium on Steels.** J. A. SHERMAN. *Iron Trade Review*, Vol. 60 (1917), No. 11, pp. 519-521.

NEW JOURNALS

Color Trade Journal. EDITOR, J. MORTIMER MATTHEWS. Monthly. Price, \$5.00 per year. Color Trade Journal, Inc., 300 Fifth Ave., New York City.

RECENT JOURNAL ARTICLES

Acetylene: Specific Properties of Acetylene. G. G. POUND. *Acetylene Journal*, Vol. 19 (1917), No. 1, pp. 30-32.

Bleach Liquor Determinations. ROSE A. ANSELL. *Paper*, Vol. 20 (1917), No. 14, p. 11.

Case Hardening of Iron by Boron. PETER TCHISTCHENKO. *Iron Trade Review*, Vol. 60 (1917), No. 31, pp. 1292-1293.

MARKET REPORT—JULY, 1917

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON JULY 20

INORGANIC CHEMICALS

Acetate of Lime.....	100 Lbs.	5.25	@	5.50
Alum, lump ammonia.....	100 Lbs.	4.50	@	4.75
Aluminum Sulfate, high-grade.....	Ton	75.00	@	80.00
Ammonium Carbonate, domestic.....	Lb.	10 1/4	@	11
Ammonium Chloride, white.....	Lb.	14 1/4	@	15
Aqua Ammonia, 26°, drums.....	Lb.	8 1/4	@	8 1/2
Arsenic, white.....	Lb.	16 1/2	@	17
Barium Chloride.....	Ton	80.00	@	90.00
Barium Nitrate.....	Lb.	11	@	11 1/2
Barytes, prime white, foreign.....	Ton	30.00	@	40.00
Bleaching Powder, 35 per cent.....	100 Lbs.	1.35	@	1.50
Blue Vitriol.....	Lb.	9 1/4	@	10
Borax, crystals, in bags.....	Lb.	7 1/4	@	8 1/4
Boric Acid, powdered crystals.....	Lb.	13	@	13 1/2
Brimstone, crude, domestic.....	Long Ton	50.00	@	55.00
Bromine, technical, bulk.....	Lb.	.55	@	.60
Calcium Chloride, lump, 70 to 75% fused.....	Ton	30.00	@	32.00
Caustic Soda, 76 per cent.....	Lb.	7.15	@	7.25
Chalk, light precipitated.....	Lb.	4 1/4	@	4 1/2
China Clay, imported.....	Ton	18.00	@	30.00
Feldspar.....	Ton	8.00	@	15.00
Fuller's Earth, foreign, powdered.....	Ton	35.00	@	
Glauber's Salt, in bbls.....	100 Lbs.	.75	@	.85
Green Vitriol, bulk.....	100 Lbs.	1.00	@	1.05
Hydrochloric Acid, commercial, 18°.....	Lb.	1 1/4	@	1 1/2
Hydrochloric Acid, C. P. conc., 22°.....	Lb.	1 1/4	@	1 1/2
Iodine, resublimed.....	Lb.	3.50	@	3.55
Lead Acetate, white crystals.....	Lb.	.16	@	.16 1/2
Lead Nitrate.....	Lb.	15 1/2	@	16
Litharge, American.....	Lb.	11	@	11 1/2
Lithium Carbonate.....	Lb.	1.25	@	
Magnesium Carbonate, U. S. P.....	Lb.	.20	@	.22
Magnesite, "Calcined".....	Ton	60.00	@	65.00
Nitric Acid, 36°.....	Lb.	.7	@	.7 1/2
Nitric Acid 42°.....	Lb.	.8	@	.8 1/2
Phosphoric Acid, sp. gr. 1.710.....	Lb.	.35	@	.37
Phosphorus yellow.....	Lb.	2.25	@	2.30
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, casks.....	Lb.	.36	@	.37
Potassium Bromide (granular).....	100 Lbs.	1.00	@	1.10
Potassium Carbonate, calcined, 80 to 85%.....	Lb.	.65	@	.75
Potassium Chlorate, crystals, spot.....	Lb.	.50	@	.52
Potassium Cyanide, bulk, 98-99 per cent.....	Mixture	2.30	@	2.40
Potassium Hydroxide, 88 to 92%.....	Lb.	.84	@	.86
Potassium Iodide, bulk.....	Lb.	2.90	@	
Potassium Nitrate.....	Lb.	.30	@	.32
Potassium Permanganate, bulk.....	Lb.	4.00	@	4.25
Quicksilver, flask.....	75 lbs	112.00	@	115.00
Red Lead, American, dry.....	Lb.	.13	@	.13 1/2
Salt Cake, glass makers'.....	Ton	21.00	@	23.00
Silver Nitrate.....	Oz.	50 1/2	@	
Soapstone in bags.....	Ton	10.00	@	12.50
Soda Ash, 58%, in bags.....	100 Lbs.	2.85	@	2.90
Sodium Acetate.....	Lb.	9 1/4	@	10
Sodium Bicarbonate, domestic.....	100 Lbs.	2.35	@	2.50
Sodium Bichromate.....	Lb.	15 1/4	@	16 1/2
Sodium Chlorate.....	Lb.	23 1/4	@	24 1/2
Sodium Fluoride, commercial.....	Lb.	12 1/4	@	13 1/2
Sodium Hyposulfite.....	100 Lbs.	1.75	@	1.85
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	4.27 1/2	@	4.30
Sodium Silicate, liquid, 40° BÉ.....	100 Lbs.	1.70	@	1.75
Sodium Sulfide, 60%, crystals, in bbls.....	Lb.	.3	@	3 1/4
Sodium Bisulfite, powdered.....	Lb.	.5	@	5 1/4
Strontium Nitrate.....	Lb.	.28	@	.30
Sulfur, flowers, sublimed.....	100 Lbs.	3.05	@	3.45
Sulfur, roll.....	100 Lbs.	2.85	@	3.25
Sulfuric Acid, chamber, 66° BÉ.....	Ton	32.00	@	35.00
Sulfuric Acid, oleum (fuming).....	Ton	40.00	@	50.00
Talc, American white.....	Ton	10.00	@	12.00
Terra Alkali, American, No. 1.....	100 Lbs.	.85	@	.90
Tin Bichloride, 50°.....	100 Lbs.	19.25	@	19.50
Tin Oxide.....	Lb.	64 1/4	@	65
White Lead, American, dry.....	Lb.	11 1/4	@	12
Zinc Carbonate.....	Lb.	.23	@	.25
Zinc Chloride, commercial.....	Lb.	.16	@	.17
Zinc Oxide, American process XX.....	Lb.	.15	@	15 1/2

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	.49	@	.50
Acetic Acid, 56 per cent, in bbls.....	Lb.	.10	@	10 1/2
Acetic Acid, glacial, 99 1/4% in carboys.....	Lb.	.35	@	.37
Acetone, denatured.....	Lb.	.32 1/2	@	.33
Alcohol, denatured, 180 proof.....	Gal.	1.00	@	1.01

Alcohol, grain, 188 proof.....	Gal.	4.02	@	4.04
Alcohol, wood, 95 per cent, refined.....	Gal.	1.00	@	1.02
Amyl Acetate.....	Gal.	4.00	@	4.25
Aniline Oil.....	Lb.	.29	@	.30
Benzoic Acid, ex-toluol.....	Lb.	5.00	@	5.50
Benzol, 90 per cent.....	Gal.	.53	@	.55
Camphor, refined in bulk, bbls.....	Lb.	.84 1/2	@	.85
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	.40	@	.42
Carbon Bisulfide.....	Lb.	.6	@	6 1/2
Carbon Tetrachloride, drums, 100 gals.....	Lb.	16 1/2	@	17
Chloroform.....	Lb.	.60	@	.61
Citric Acid, domestic, crystals.....	Lb.	.72	@	.75
Cressote, beechwood.....	Lb.	1.90	@	2.00
Cresol, U. S. P.....	Gal.	1.25	@	1.30
Dextrine, corn (carloads, bags).....	100 Lbs.	6.35	@	6.40
Dextrine, imported potato.....	Lb.	.15	@	.16
Ether, U. S. P., 1900.....	Lb.	.31	@	.39
Formaldehyde, 40 per cent.....	Lb.	.17	@	.18
Glycerine, dynamite, drums included.....	Lb.	.62 1/2	@	.63
Oxalic Acid, in casks.....	Lb.	.46	@	.47
Pyrogallol Acid, resublimed bulk.....	Lb.	3.80	@	3.85
Salicylic Acid.....	Lb.	1.50	@	1.80
Starch, cassava.....	Lb.		@	
Starch, corn (carloads, bags) pearl.....	100 Lbs.	5.05	@	5.10
Starch, potato.....	Lb.	12 1/2	@	13
Starch, rice.....	Lb.	10	@	12
Flour, sago.....	Lb.	.6	@	6 1/2
Starch, wheat.....	Lb.	5 1/4	@	6 1/2
Tannic Acid, commercial.....	Lb.	.80	@	.95
Tartaric Acid, crystals.....	Lb.	.81	@	.83

OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	.62	@	.65
Black Mineral Oil, 29 gravity.....	Gal.	.13	@	13 1/2
Castor Oil, No. 3.....	Lb.	.27	@	.28
Ceresin, yellow.....	Lb.	nominal	@	
Corn Oil, crude.....	Lb.	.13	@	.14
Cottonseed Oil, crude, f. o. b. mill.....	Gal.	.94	@	.96
Cottonseed Oil, p. a. y.....	Lb.	.14	@	14 1/2
Menhaden Oil, crude (southern).....	Gal.	—	@	—
Neat's-foot Oil, 20°.....	Gal.	1.75	@	
Paraffin, crude, 118 to 120 m. p.....	Lb.	.7 1/4	@	7 1/2
Paraffin Oil, high viscosity.....	Gal.	29 1/2	@	30
Rosin, "F" Grade, 280 lbs.....	Bbl.	5.85	@	
Rosin Oil, first run.....	Gal.	.35	@	
Shellac, T. N.....	Lb.	.58	@	
Spermaceti, cask.....	Lb.	.24	@	
Sperm Oil, bleached winter, 38°.....	Gal.	nominal	@	
Spindle Oil, No. 200.....	Gal.	.24	@	.25
Stearic Acid, double-pressed.....	Lb.	.23	@	.24
Tallow, acidless.....	Gal.	1.47	@	1.50
Tar Oil, distilled.....	Gal.	.34	@	.35
Turpentine, spirits of.....	Gal.	.41	@	41 1/2

METALS

Aluminum, No. 1, ingots.....	Lb.	.55	@	.60
Antimony, ordinary.....	Lb.	15 1/2	@	16
Bismuth, N. Y.....	Lb.	3.00	@	3.10
Copper, electrolytic.....	Lb.	.27	@	.27 1/2
Copper, lake.....	Lb.	.27 1/2	@	.28
Lead, N. Y.....	Lb.	.10	@	10 1/2
Nickel, electrolytic.....	Lb.	.55	@	.56
Platinum, refined, soft.....	Oz.	105.00	@	
Silver.....	Oz.	79 1/2	@	
Tin, Straits.....	Lb.	.62 1/2	@	.62 1/2
Tungsten (W'o).....	Per Unit	22.00	@	23.00
Zinc, N. Y.....	Lb.	.8 1/2	@	.8 1/2

FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	6.70	@	6.75
Blood, dried, f. o. b. Chicago.....	Unit	5.95	@	
Bone, 4 and 50, ground raw.....	Ton	32.00	@	35.00
Calcium Cyanamid.....	Unit of Ammonia	4.00	@	
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	—	@	—
Phosphate, acid, 16 per cent.....	Ton	15.00	@	16.00
Phosphate rock, f. o. b. mine.....	Ton	1.75	@	2.00
Florida land pebble, 68 per cent.....	Ton	4.75	@	5.00
Tennessee, 78-80 per cent.....	Ton	350.00	@	365.00
Potassium "muriate," basis 80 per cent.....	Unit	—	@	—
Pyrites, furnace size, imported.....	Unit	—	@	—
Tankage, high-grade, f. o. b. Chicago.....	Unit	5.75	@	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

AT EASTON, PA.

Volume IX

SEPTEMBER 1, 1917

No. 9

Editor: CHARLES H. HERTY

Assistant Editor: LEOLA E. MARRS

Advertising Manager: G. W. NOTT

ADVISORY BOARD

H. E. BARNARD, H. K. BENSON, F. K. CAMERON, B. C. HESSE, A. D. LITTLE, A. V. H. MORY, M. C. WHITAKER

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly; single copy, 60 cents. Price per single copy to American Chemical Society members, 50 cents. Foreign postage, seventy-five cents. Canada, Cuba and Mexico excepted. Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

All communications should be sent to The Journal of Industrial and Engineering Chemistry,

Telephone: Vanderbilt 1930

35 East 41st Street, New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

Chemists Enlisted in the Army and Navy	826
Chemists and War Service	826
Aviation and the Chemist	826
Permanent Progress	827
Financial Support for the National Research Council . .	828
Platinum Conservation in France	828

NITRATE SUPPLY COMMITTEE RECOMMENDATIONS ON SYNTHETIC NITRIC ACID FOR THE GOVERNMENT WITH REPORTS ON VARIOUS METHODS

829

ORIGINAL PAPERS:

The Influence of Superimposed Alternating Current on the Electrodeposition of Nickel. S. A. Tucker and H. George Loesch	841
Purification of Sewage by Aeration in the Presence of Activated Sludge—III. Edward Bartow	845
The Analysis of Sulfated Oils. Ralph Hart	850
The Determination of Tantalum in Alloy Steels. G. L. Kelley, F. B. Myers and C. B. Illingworth	852
Notes on the Analysis of Alloys of Nickel and Zirconium. G. L. Kelley and F. B. Myers	854
A Method for Fractionating Fats and Oils. Armin Seidenberg	855
The Thermal Values of the Fats and Oils. II—The Sulfuric Acid or Maumenné Number. J. W. Marden and M. V. Dover	858
The Determination of Fat in Certain Milk Products. C. K. Francis and D. G. Morgan	861
Application of the Cryoscopic Method for Determining Added Water in Milk. J. T. Keister	862
Insoluble Phosphoric Acid in Organic Base Goods. F. O. Thomas	863

LABORATORY AND PLANT

Discontinuous Extraction Process. L. F. Hawley	866
An Investigation of the Wet Thimble Process. A. E. Wells	871
Weighting Burette for Liquids. W. Ed. Burkhead	873

ADDRESSES:

The Vapor Pressure and Volatility of Several High-Boiling Metals—A Review. John Johnston	873
THE PYROGENESIS OF HYDROCARBONS	879

CURRENT INDUSTRIAL NEWS:

Copper, Aluminum, Zinc and Iron Windings for Dynamos; Removing Rust from Iron Plates; Sulfate of Ammonia in India; Alcohol from Acetylene; Tar Varnish for Iron-Work; Prevention of Leakage through Cement; Natural Gas as a Boiler Fuel; Beet Sugar Manufacture in Japan; The French Saffron Market; The World's Centre for Paper and Pulp; The Dye Industry; Effect of Ammoniated Liquor on Concrete; Motor Spirit from Kerosene; Swedish Substitute for Benzol; Mineral Output in Canada; Gelatine; Glycerine Substitutes in Germany; Camphor Refining at Formosa; Alizarine Delphinol; Alcohol from Wood-Pulp Lyes; Chemical Manufacture in France; A New Reagent for Aldehydes; Production of Platinum; Olive Oil Production in Portugal; Experiments in Substitutes; British Board of Trade	903
---	-----

SCIENTIFIC SOCIETIES:

Calendar of Meetings; The Chemical Societies in New York City; Descriptive Index to Chemical Abstracts; Third National Exposition of Chemical Industries, Grand Central Palace, New York, Week of September 24, 1917	907
--	-----

NOTES AND CORRESPONDENCE

Two Letters on Ethyl Ether and Its Application for the Oil Industry; Recovery of Gaseous Nitric Method for Determination of Potassium in Potassium A. S.	909
WASHINGTON LETTER	910
PERSONAL NOTE	911
INDUSTRIAL NOTE	913
GOVERNMENT TECHNOLOGY	914
BOOK REVIEWS	915
NEW PUBLICATIONS	916
MARKET REPORT	917

EDITORIALS

CHEMISTS ENLISTED IN THE ARMY AND NAVY

We cannot urge with too much emphasis the importance of the following announcement:

All chemists enlisted in the Army and Navy (if they have not already done so) are requested to send their names, together with the military unit to which they are assigned, to the Secretary of the Society as soon as they have the information themselves. This is done in order that, so far as possible, the military establishment may be kept informed of chemists in its employ, in order that they may be assigned, so far as possible, to chemical service if it is in the country's interest so to assign them. Such assignment can be made only by the War and Navy Departments, and it is intended to keep them informed of the men available.

Members should remember that the Secretary of the Society has no power of assignment, and it is useless to write him asking when they will be so assigned.

It is becoming more evident every day that chemical service will be necessary, and it is expected that the War and Navy Departments will deem it wiser to assign trained men fitted for this service to the work if information can be given them on request.

Box 505

WASHINGTON, D. C.

CHAS. L. PARSONS, *Secretary*

CHEMISTS AND WAR SERVICE

We journeyed to Washington recently, not with the expectation of securing official statements as to the government attitude toward chemists, but in the belief that a brief sojourn in near-official atmosphere might enable reasonable inferences which would be of interest to chemists. These are here given for whatever they are worth.

First—It is clear that no special exemption of chemists as a class will be made.

Second—Many young chemists, from both the universities and the industries, have already volunteered.

Third—The draft is bringing many chemists into war service.

Fourth—It is heartening to know that the true value of the services of drafted chemists seems to be appreciated in government circles, and that the fullest possible use will be made of such men as chemists. It yet remains to be seen what the official attitude will be toward drafted chemists who are absolutely essential to certain industries contributing directly to government needs. For example, one firm has had eight of its research chemists drafted. This firm is manufacturing large quantities of alkaloïds necessary for hospital supplies. Is this line of manufacture to be totally disrupted? We believe not. Common sense must prevail in the adjustment of such cases and there is abundant evidence that wise solutions of these problems will be found, though in the momentary rush they may seem to be overlooked.

Fifth—The knowledge gained by the recent census of chemists, embracing fully fifteen thousand replies, has been carefully classified and is now available to the government in whatever form desired. This work, so prompt in its compilation and so thorough in its classifications is considered in Washington a model of its kind.

AVIATION AND THE CHEMIST

Like a flash this nation became convinced that it could deal an effective blow in the war against Germany by an overwhelming production of men and machines for aeronautic service on the battlefields of Europe. Reflecting this conviction Congress, with a rapidity hitherto unequalled, voted an initial sum of \$640,000,000 for this purpose. Engineers and manufacturers are coöperating to bring America's unique talent for standardized manufacture to its very highest efficiency for unlimited aeroplane output. Haste is all-important, and therefore the best of present practice will be utilized. However, the possible prolongation of the war, whose close no one can now foretell, emphasizes the necessity of intensive research. Certainly at the close of the war the world will face a new era in transportation. The advent of the aeroplane in every-day life will be at hand. Here then lies a field of research in which chemists must play a great part.

With this feeling at heart, yet possessed of little technical knowledge as to the problems involved, we interviewed recently Mr. Leon Cammen, Vice-President of the American Aeronautical Society. Without hesitation he affirmed that in the future development of the aeroplane the research chemist will be the greatest factor. Without attempting to give the full details of that interview, but with the hope of being able to impart some of the deep conviction which prompted his earnest call to the chemists, some of the problems he discussed are here presented.

In general, the materials entering into aeroplane construction are subjected to two unusual conditions: first, extreme vibration, a condition which will become more and more accentuated as greater possibilities of speed are realized; second, sudden and extreme changes of temperature due to rapid ascent or descent.

As to particulars, there is needed an ideal "dope" for impregnation of the fabric, Irish linen. To be ideal, this material should make the fabric water-proof, air-proof, fire-proof, or at least slow-burning, should give low visibility, prevent deterioration and be non-poisonous; some now in use are poisonous and the drippings seriously affect the aviators.

Another problem is the drying of all wood used in construction. Air-drying requires at least nine months; kiln-drying is not successful as the wood is thus injured by the outside being drier than the inside. Vacuum drying has been attempted, but so far without much success. An ideal impregnating medium for the wood is needed, not to prevent rotting but the disintegration resulting from rapid changes of temperature, whereby the juices of the wood freeze, expand and weaken the cells.

An ideal means is needed to prevent rusting, one which can be applied after the machine is built. Nickel-plating has not proved successful; the varnish makers

have had before them heretofore no such conditions of vibration and sudden changes of temperature. Indeed the whole subject of rusting has never been systematically studied from the standpoint of these conditions.

Much study is needed in the field of light alloys. Those with aluminum as a base disintegrate under the intense vibration and stresses in high altitudes. Why? We should know. A more thorough knowledge of magnesium alloys is desirable, both those with aluminum and those with other metals, while interesting possibilities might be developed through a thorough study of beryllium alloys. Are the properties of aluminum alloys affected by occluded gases? For such studies more refined methods are needed for the determination of the presence and amount of occluded gases.

As to lubricants, the behavior of such types as castor oil under the temperature conditions in question, calls for investigation. What is the best method for testing and what should be the standard specifications for so important a factor in aeronautics?

In connection with the ignition system a wide field of research is open for the study of spark discharge from the chemical standpoint. Better insulating material for spark plugs should be developed; at present mica and porcelain are used. This is considered the weakest feature of present-day motors.

Much of the advance in aeronautics has been empirical. Further progress can be best assured by the application of the strictest methods of scientific research. It is through this medium that such wonderful advances have been made in the steam turbine during the past decade. For the full grasp of the many problems here awaiting solution, chemists must become familiar with the principles of aviation. Success in the solution of these problems carries with it the promise of rich reward and is now invested with the halo of patriotic service.

PERMANENT PROGRESS

It is our privilege to write this editorial on a rocky cliff in Maine overlooking beautiful Lake Megunticook with its encircling mountains. On the same spot during the two previous summers, we wrote two series of editorials, each of which was connected by a slender thread of continuity, and through the courtesies of the occasion given the conventional term—presidential address. The present environment has led us to read again those addresses. While thinking of the two great gatherings of chemists soon to take place, the Annual Meeting of the American Chemical Society in Boston and the Third National Exposition of Chemical Industries in New York City, we are disposed to quote briefly from those addresses and to sketch in general outline the developments which have taken place meanwhile. Laying no claim to any special gift of prophecy or to any particular share in their accomplishment, but simply for the purpose of review.

A year ago we wrote: "The dynamic center of this movement is the American Chemical Society which now consists of 8136 members, a net growth of more than 1000 during the year just ended. This splendid growth is not only a tribute to the energetic activities of our efficient secretary, but is an evidence of increased activity in chemistry and of a quickened realization of the need of the strongest possible national organization." If the explanations of that growth were correct it should prove inspiring to the members of the Society at the Boston Meeting to know that during the past twelve months the growth of the previous year has been doubled, as shown by the following letter received from Secretary Parsons: "You will be glad to know that the mark which I have been striving for has been reached. On the morning of August 2, 1917, the membership of the American Chemical Society passed the 10,000 mark." We will not betray the confidence of the Secretary by disclosing the mark which he has set for the end of the year 1918; suffice it to say that the limit of growth has not yet been approached.

A year ago we wrote: "If we are to proceed promptly and intelligently with the development of a diversified and comprehensive chemical industry we must know the detailed character and amounts of chemical importations." Until recently the movement to secure such knowledge was characterized by much effort and a woeful lack of results. Fortunately, however, through the cooperation of the chemical industries with the government the work is now well under way, and it is safe to state that we will soon enter upon a new era in the development of our industries insofar as such development can be guided by accurate and fully itemized statistics of imports.

Two years ago, confessedly with much hesitation, we urged, for our country's welfare, the accumulation of greater supplies of sodium nitrate, pending the construction, in case of war, of plants for the adequate manufacture of nitric acid from the air. The nation has skated on very thin ice as far as concerns a marked increase in supplies of sodium nitrate, but the response of the general public to appeals for development of air-nitrogen fixation plants was immediate, as evidenced by the \$20,000,000 appropriation by Congress for the purposes not only of munitions but also of agriculture. Plans now under way for the expenditure of a part of this appropriation give ample assurance of protection to this country and will constitute a lasting testimonial to the resourcefulness of the American chemist.

Again, two years ago, we wrote, regarding the rebuilding of the troubled dyestuff industry: "We must, as a people, meet the expensive, growing, reasonable time, that pressure of protection which will offset a union of capital and enterprise will under no undue stress of undue foreign interference." Following the lead of the New York Southern textile protective tariff and as effective anti-dumping laws were urged. Both policies are now soundly the logical equivalent.

The prompt response to the need of anti-dumping legislation fully justified the confidence expressed two years ago: "I badly misjudge the temper of our people and their spirit of fair play, which is the essence of democracy, if, given opportunity to understand this situation, they do not speedily set about to correct, through their representatives in Congress, this serious defect in national legislation by the enactment of an effective 'anti-dumping' clause." No more conclusive proof could be given of the justice of the contention that a protective tariff was necessary for the upbuilding of this industry than the fact that such legislation was enacted by a Congress in which the majority party was committed to the doctrine of "Tariff for Revenue Only," and in the midst of a presidential and congressional campaign. Fortunately, assurance has been given that the one blotch which marred this legislation, a feature which operated solely for the benefit of the German manufacturers at the risk and expense of the American industry, will in due course of time be removed. The union of capital and scientific skill resulting from this legislation has effected a development which gives assurance that the American dyestuff industry has now become a permanent national asset.

Two years ago we wrote concerning the approaching First National Exposition of Chemical Industries: "This assemblage has in it great potentialities which, if realized, may have far-reaching influence in the rapid promotion of hitherto undeveloped lines of chemical industry." To those who were present at the two expositions since held, the first a marked success, the second far greater than the first, there can be no question of the powerful stimulus thereby afforded. Skeptics have been changed to enthusiasts. The third exposition will soon be held and its still greater scope is already assured. The successful chemical exposition can be considered purely an American product and its growth is merely illustrative of the growth of the American chemical industries.

A year ago we wrote: "An educational campaign is getting under way in the daily press and in periodical literature which will eventually result in the arousal of our people to a full comprehension of the value of chemistry as a national asset." The volumes of clippings received by the chairman of the Press and Publicity Committee show how prompt the response of the press has been to the efforts to bring chemistry closer home to our people. Untiring work has been done, chiefly by Chairman Allen Rogers and by Mr. Ellwood Hendrick of the Committee. As the year has advanced, the usefulness of this campaign has been continuously enhanced by the increasing number of Local Section Press and Publicity Committees, which have cooperated closely with the National Committee.

Surely any picture of chemistry as it exists in America to-day forms a joyful contrast to that of two years ago. What of the coming year? There is much to be done. Working amidst the surroundings of war, new conditions must be faced, new problems solved. The times call for broad-minded thought and the utmost effort.

The personal conferences at the two meetings this month should point the way and should prove a source of inspiration for "full speed ahead."

FINANCIAL SUPPORT FOR THE NATIONAL RESEARCH COUNCIL

At the request of the President of the United States, the National Research Council has been engaged during the past year in mobilizing the research forces of the nation. It has been an enormous task, to which many of the most brilliant workers of the country have given their undivided time. The work has gradually and logically centered at Washington, and the research forces of the country are now quickly available to any department of the government. Development has proceeded to the point where this organization can be truly considered a going machine, forming a connection between the research workers of the country-at-large and the government, and serving as a valuable coordinating influence. With the preliminary work now accomplished, its full value will be more and more nearly attained with each succeeding day.

For the continuance of the work, however, funds will be necessary. Up to the present its operations have cost the government absolutely nothing: office rent, stationery, postage, clerical assistance, etc., have been provided by private contributions, and the time of members of university staffs has been contributed by the respective institutions. For so important a body such an existence is too precarious. If the government needs war material it pays for it and a willing citizenry furnishes the funds through taxation. Are the brains of our scientific men less valuable in this crisis than coal or cotton? As an American citizen we hope that Congress before adjournment will supply adequate funds for the carrying on of the work of the National Research Council on the most intensive and extensive scale possible. We are unwilling to believe that the government of the United States is so pauperized that it must depend on "the passing of the hat" or that it is willing to continue to draw further upon the seriously impaired incomes of our universities in order that the salaries of the men engaged in this work may be met.

PLATINUM CONSERVATION IN FRANCE

The movement for conservation of platinum supplies for scientific and industrial purposes continues to spread. Secretary Parsons has received from M. A. Valeur, General Secretary of the French Chemical Society, the following extract from the minutes of the General Assembly of that Society on July 13, 1917:

"La Société chimique de France s'associe au vœu formulé par la Société chimique américaine, déconseillant l'emploi du platine dans la bijouterie et dans la joaillerie de façon que ce métal puisse être réservé exclusivement pour les usages scientifiques et industriels.

"Cette motion est adoptée à l'unanimité."

NITRATE SUPPLY COMMITTEE RECOMMENDATIONS ON SYNTHETIC NITRIC ACID FOR THE GOVERNMENT WITH REPORTS ON VARIOUS METHODS

NITROGEN FIXATION FOR AMERICA

The fixation of atmospheric nitrogen in the United States, pursuant to the Congressional appropriation for that purpose, is now assured at an early date. In the following pages there are published by permission of the Secretary of War, official documents in regard to this subject.

From the very outset the paramount idea in the minds of all connected with this work has been the need of the country for nitrogenous fertilizers by the quickest and cheapest method possible. The need of independence in nitric acid production for munitions was naturally always to the fore, but the developments of the war during the past twelve months made more and more improbable any danger of a hostile cutting off of supplies of sodium nitrate from Chile.

A great advantage of the process adopted lies in the fact that a large plant can be built near the fertilizer consumption center, thus minimizing transportation charges in the distribution of the output; at the same time numerous smaller plants can be erected, if desired, in any part of the country in connection with plants now manufacturing, or contemplating the manufacture of, explosives.

Furthermore, the product is obtained in the form of ammonia. This is the most valuable primary product for the production of fertilizer material whether it be issued in the form of ammonium sulfate or ammonium phosphate. Should it be deemed advisable to put out the fertilizer in the form of ammonium phosphate, no patents can interfere, as Section 124, "Nitrate Supply," of The National Defense Act gives the Government authority to condemn patents for this purpose. However, there is no reason at present to believe that any such condemnation will be necessary.

We beg to extend to the General Chemical Company, and particularly to Dr. Wm. H. Nichols, the Chairman of its Executive Committee, unfeigned appreciation of the patriotic spirit which led that Company to tender the nation its process for the fixation of atmospheric nitrogen, a process which promises to produce ammonia at less cost for plant or production than by the famous German Haber process. The Government may use the process without recompense; for the manufacture of fertilizers, however, a royalty is asked amounting to only a small fraction of that which would be required under other commercial processes for nitrogen fixation. Heartiest congratulations to the skilled chemical engineers of the General Chemical Company whose brilliant scientific work has triumphed over all difficulties!

Like appreciation is due the Nitrogen Products Company, and Mr. Edward E. Arnold, the President of that Company, whose process, though not to be utilized at present on a commercial basis, was tendered in the same patriotic spirit, and upon the same terms as that of the General Chemical Company.—EDITOR

A STATEMENT OF THE ACTION TAKEN AND CONTEMPLATED LOOKING TO THE FIXATION OF NITROGEN*

Pursuant to Section 124, "Nitrate Supply," of the Act of Congress approved June 3, 1916, generally known as "The National Defense Act."

DIVISION T, ORDNANCE OFFICE, WAR DEPARTMENT

August 21, 1917

The National Defense Act, in its Section 124, provided for a supply of nitrogenous materials by authorizing and empowering the President to make or cause to be made such investigation as, in his judgment, might be necessary to determine the best, cheapest, and most available means for the production of nitrates and other products for munitions of war and useful in the manufacture of fertilizers and other useful products—this by water power or any other power as might be best and cheapest—to designate for the exclusive use of the United States such water power sites as in his opinion might be necessary to construct and operate dams, etc., or other means than water power as in his judgment might be best and cheapest for the generation of power and for the production of nitrates as above; also to procure by condemnation or otherwise any lands, rights-of-way, materials, minerals, and processes, patented or otherwise. It was provided by this Act, that "the products of such plants shall be used by the President for military and naval purposes to the extent that he may deem necessary, and any surplus which he shall determine is not required shall be sold and disposed of by him under such regulations as he may prescribe."

The primary step required under these provisions of law was, therefore, an investigation to determine the best, cheapest and most available means for the production of the desired nitrogenous materials, or "nitrates."

With this purpose in view, the President of the National Academy of Sciences in cooperation with the American Chemical Society, and at the request of the Secretary of War, appointed a committee consisting of the following scientists and engineers:

ARTHUR A. NAYLER, Chairman	CHARLES H. HENCKY	THEODORE W. RICHARDS
LEO H. BAERLEND	WARREN K. LEMUS	LESLIE THOMPSON
GASO DUNN	MICHAEL I. PIERCE	WILLIAM R. WHITNEY

In addition to this committee's investigations, special agents were appointed to acquire all possible further information. These agents had access to some quite unusual sources of information and collected data, including details of results of the partial vacuum processes employed at home and abroad, which have been most trustworthy, but which represent of the nature of them, which they were obtained and the conditions under which they were given, cannot be made public.

* Published by permission of the War Department.

One of these agents was Mr. Eysten Berg, who visited Europe and submitted a report. Another of these agents was Dr. Charles L. Parsons, Chief Chemist of the Bureau of Mines, Interior Department, who, in the course of his investigations, visited the noted plants of Italy, France, England, Norway, and Sweden during the fall of 1916, and was able to give in his reports a most valuable summary and comparison of recent progress and conditions in the nitrogen-fixation industry at home and abroad, elaborated by extensive statistics of a confidential nature.

In his reports, Dr. Parsons laid special emphasis upon the rapid development in the United States of processes for the direct synthesis of ammonia from nitrogen and hydrogen, for its synthesis through the formation of cyanides as an intermediate product, and for the oxidation of ammonia to nitric acid. He called attention to the process, developed by the General Chemical Company, for the synthesis of ammonia by the direct combination of nitrogen and hydrogen at lower pressures than those previously deemed necessary and contemplated by the Haber patents, and to the facts that this process had been in successful use on a large experimental scale and that, indeed, one unit thus in use was larger than those supposed to be in use in Germany. He showed that this American company had also developed and brought to a commercial basis a method of producing the mixture of nitrogen and hydrogen required for the synthesis of ammonia at a cost lower than any theretofore attained in this country or probably even in Germany, and that this company had progressed so far that it had already made plans for a commercial plant using this process. Dr. Parsons also obtained from the General Chemical Company a tentative proposal of an agreement whereby that company would grant to the Government of the United States the use of its processes and designs for apparatus for the synthesis of ammonia and for the oxidation of ammonia to nitric acid, upon the following very liberal terms—without compensation of any kind for products to be used exclusively for munitions of war, and with a royalty upon products to be used for fertilizers.

Dr. Parsons' reports also contained a summary of recent developments in the Cyanide process and a confidential statement from the Nitrogen Products Company of their estimated costs by that process, together with an offer of unrestricted use of their patents upon such processes, without any compensation for use in the manufacture of munitions of war, and subject to a royalty of \$5.00 per ton of fixed nitrogen for use of their processes for the production of fertilizer.

He was also able to report that under a cooperative arrangement between the Bureau of Mines and the Semet-Solvay Company a small plant for the oxidation of ammonia to nitric acid had been constructed, and was progressing successfully; also that an experimental plant for the same purpose was being operated by the General Chemical Company and had developed some new features, thus showing that satisfactory progress was being made in this country toward the

solution of the difficulties involved in the construction and operation of such a plant upon a large scale.

Finally, Dr. Parsons stated his belief that the processes using large quantities of power would be in this country displaced by these newer processes which require comparatively little power, and he recommended that the Government build a moderate sized plant for production of ammonia by synthesis, and undertake active experimentation with the Cyanide process.

With the object of securing an opinion, based upon a comprehensive view of all the facts collected by the several agencies, the Secretary of War appointed the following "Committee on Nitrate Supply:"

Brig.-Gen. William Crozier, Chief of Ordnance, U. S. Army, War Department
Rear Admiral Ralph Earle, Chief of Bureau of Ordnance, Navy Department
Brig.-Gen. Wm. M. Black, Chief of Engineers, U. S. Army, War Department
Mr. F. W. Brown, Bureau of Soils, Department of Agriculture
Dr. Leo H. Baekeland, Yonkers, N. Y.

Mr. Gano Dunn, 43 Exchange Place, New York
Dr. Charles H. Herty, 35 East 41st St., New York
Dr. William F. Hillebrand, Bureau of Standards, Department of Commerce
Dr. Arthur A. Noyes, Institute of Technology, Boston, Mass.
Dr. Charles L. Parsons, Bureau of Mines, Interior Department
Dr. Willis R. Whitney, Schenectady, N. Y.

This committee gave careful consideration to all the information available, and duly weighed the several purposes stated by the language of the Act, recommending the following action:

I—That the Government negotiate with the General Chemical Company for the right to use its synthetic ammonia processes.

II—That, contingent upon satisfactory result of such negotiations, there be set aside from the \$20,000,000 appropriated, such sum, estimated as about \$3,000,000 as should be necessary to build a plant to produce by that process about 60,000 pounds of ammonia per 24-hour day; location, southwest Virginia preferably.

III—That, out of the same appropriation, \$600,000, or as much more as needed, be set aside for building a plant for producing by oxidation of ammonia about the equivalent of 24,000 pounds of 100 per cent nitric acid per 24-hour day.

IV—That the War Department proceed at the earliest practical date with the construction of the oxidation plant and contingent upon satisfactory arrangements with the General Chemical Company with the construction of the synthetic ammonia plant also.

V—That the Government negotiate with the Nitrogen Products Company with the view to a contract for the right to use that company's patents and proceed with experimentation looking toward the industrial development of the Bucher process for production of ammonia through cyanide; and that contingent upon satisfactory arrangement as above a sum not over \$200,000 be allotted out of the Nitrate Supply appropriation.

VI—That out of the \$20,000,000 Nitrate Supply appropriation \$100,000 be allotted for active investigation of processes for the industrial production of nitrogen compounds useful in the manufacture of explosives or fertilizers—this under supervision of the War Department.

VII—That in order to increase the production of ammonia and to let the government promote the installation of by-product coke ovens by directing priority in production and transportation of materials and parts.

VIII—That the decision as to more extensive installation of nitrogen fixation processes and water-power development in connection with them be postponed until the plants above recommended are in operation or until further need arises.

IX—That while the preceding recommendations include all the measures that can now judiciously be taken for the fixation of ammonia it is the opinion of the Committee that the immediate accumulation and the permanent maintenance of an ample reserve not less than 500,000 tons of Chile saltpeter is the measure most urgently necessary.

The foregoing report having met with general approval, the Secretary of War has directed the Chief of Ordnance of the Army to proceed to carry out the first six of the recommendations of the Nitrate Supply Committee and has announced that for the present the consideration of development of large water-power installations which had been begun by the Interdepartmental Board (Secretaries Baker, Lane and Houston) appointed by the President would be suspended.

The outstanding feature of this program for action is the construction of the synthetic ammonia plant using the General Chemical Company's process which was largely developed by their engineer, Mr. Frederick deJahn. As has been indicated, this process has already had trial upon a sufficient scale to demonstrate its practicability and to indicate as most probable its ability to produce ammonia at a very favorable price. In fact, in the search of the Nitrate Supply Committee for the best, cheapest and most available means for the production of nitrates and other products that would be of use in the manufacture of munitions and in the manufacture of fertilizers, this process appeared to give more promise of affording relief from dependence upon foreign nitrates for the defense of the country and more promise of a reduction in the cost of the nitrogenous constituent of fertilizer than others. Furthermore, this process is one which can be put into operation in a much less time than would be required to develop such a large water-power as would be needed for other prominent processes available. This process gives as its primary product ammonia which may be used directly as a constituent of fertilizer or which can be converted into ammonium sulfate or ammonium phosphate in the same manner as ammonia from any other source may be so converted. Processes for such conversion are known and appear to require no special development under this particular act. The cost of ammonia is expected to be quite low by this process, and will not be increased when the ammonia is used for munitions manufacture by any payments whatever for the rights to the processes, a satisfactory agreement to this effect having been made with the General Chemical Company. That same agreement provides that insofar as the General

Chemical Company's processes shall be used in the manufacture of products for fertilizers a royalty of \$5 per ton of 2,000 lbs. of fixed nitrogen in any form shall be paid. This extremely liberal arrangement will add but a very small amount to the cost of producing the nitrogenous portion of the fertilizer, amounting to a charge of something less than 25 cents per ton of the usual mixed fertilizer. From the tentative offer of the Nitrogen Products Company it is expected that there will be formally ratified a like liberal agreement for the use by the Government of that company's processes. There thus appears at this time to be no necessity for the President to exercise the rights granted by the Act for the acquisition of necessary processes by condemnation, all that it has been considered necessary to use having been freely granted upon liberal terms.

The Ordnance Department of the Army is proceeding as energetically as possible with the work entrusted to it, has made arrangements for taking over orders at cost which the General Chemical Company had placed for apparatus for a considerable size plant for their own use and thus gains considerable headway upon much of the apparatus, as well as favorable prices; the prominent engineering and construction firm, the J. G. White Engineering Corporation, has been engaged for the remaining engineering work and the actual construction; the plans for apparatus are essentially complete, and designs for all of the buildings are very nearly completed as a result of work done by the engineers of the General Chemical Company. There is thus at the present time every reason to expect that notwithstanding the extreme difficulty and expense involved in any large construction work at this time the plant will be not unduly delayed.

The construction of the oxidation plant is a less extensive work, and its commencement is being postponed for a short time in order to reap the full advantage of the important experimental work being carried on by the General Chemical Company, the Smet-Solvay Company, and the Bureau of Mines.

PROCEEDINGS OF THE NITRATE SUPPLY COMMITTEE

WASHINGTON, D. C.

May 11, 1917

The Nitrate Supply Committee constituted as follows,

Brig. Gen. William Crozier, Chief of Ordnance, U. S. Army, War Department
Rear Admiral Ralph Earle, Chief of Bureau of Ordnance, Navy Department
Brig. Gen. Wm. M. Black, Chief of Ordnance, U. S. Army, War Department
Mr. F. W. Brown, Bureau of Ordnance, Department of Agriculture
Dr. Leo H. Brackland, Yonkers, New York
Mr. Gano Dunn, 15 Exchange Place, New York
Dr. Charles H. Hart, 351 East 114th St., New York
Dr. Wm. F. Hillebrand, Bureau of Industrial Department of Commerce
Dr. Arthur A. Noyes, Institute of Technology, Boston, Mass.
Dr. Charles L. Parsons, Bureau of Mines, Interior Department
Dr. Willis R. Whitney, Schenectady, N. Y.

and appointed by the Secretary of War to attend and continue the work of a former committee which was appointed by the National Assembly of America at the request of the War Department, met at 10 o'clock A. M. at the call of General Crozier.

All of the members were present excepting General Black, who was represented on the Committee by Colonel Charles Keller of the Corps of Engineers. Colonel C. B. Wheeler, Ordnance Department, also sat with the Committee and took part in its proceedings, General Crozier presiding at the meeting but not voting. The authority for General Crozier to call the Committee together and the object of the meeting is indicated by the following letter of the Secretary of War:

WAR DEPARTMENT

WASHINGTON, April 14, 1917

BRIGADIER-GENERAL WILLIAM CROZIER,
Chief of Ordnance, U. S. Army,
Member Nitrate Supply Committee

Sir: Referring to my letter of March 9th last appointing you a member of the Nitrate Supply Committee, I desire that you shall act in calling the Committee together at appropriate times, for necessary action, and that you shall convey to it such communications as I may have to make.

The Committee should now be called together as soon as practicable for the purpose of considering the reports and recommendations concerning the process which should be adopted for the manufacture of nitrates, which reference to the possibility of harmonizing the various views and reaching a common conclusion in regard to as many of the recommendations as possible.

Respectfully,

(Signed) NEWTON D. BAKER, *Secretary of War*

After a preliminary statement by the chairman, the Committee proceeded to the matter in hand and considered previous reports and recommendations concerning the process which should be adopted for the manufacture of nitrates which included the following papers:

I—Report on nitrate supply presented to the Secretary of War by the Committee on Nitrate Supply of the National Academy of Sciences and of the National Research Council, dated January 20, 1917.

II—Preliminary report to the Ordnance Department of the War Department on the nitrogen industry with recommendations regarding the methods to be used by the United States Government in procuring the necessary nitric acid required for munitions by the War and Navy Departments by Charles L. Parsons, Chief Chemist, Bureau of Mines, Department of the Interior, January 27, 1917 (*see p. 833, this issue*).

III—Report on the nitrogen industry by Eysten Berg, C.E., dated January 15, 1917.

IV—Report on the nitrogen industry by Charles L. Parsons, Chief Chemist, Bureau of Mines, Department of the Interior, dated April 30, 1917. This latter report included an offer of the General Chemical Company granting to the Government under certain conditions the right to use its synthetic process for the production of ammonia, etc., and also an offer of the Nitrogen Products Company, granting to the Government under certain conditions the right to use the so-called Bucher process for the production of sodium cyanide and ammonia (*see p. 839, this issue*).

After a deliberate and careful consideration of all the matter and information at the disposal of the Committee, it submits the following as its action.

The Committee, appreciating the offer of the General Chemical Company, recommends:

1—That the Government enter into negotiations to acquire the rights to use the synthetic ammonia process of that company.

2—That contingent upon satisfactory arrangements with the General Chemical Company, out of the \$20,000,000 nitrate supply appropriation, such sum as may be needed, now estimated at \$3,000,000, be placed at the disposal of the War Department to be used in building a synthetic ammonia plant, employing the said process of the General Chemical Company, and of a capacity of 60,000 pounds of ammonia per 24-hour day, said plant to be located in a region where land, water, coal, and sulfuric acid are cheaply available, where good transportation facilities exist, and where the proposed new powder plant of the Government can be properly located. In the opinion of this committee all of these conditions just enumerated are best fulfilled by a location in southwest Virginia or contiguous region.

3—That out of the \$20,000,000 Nitrate Supply appropriation an amount now estimated at \$600,000, or as much as may be needed, be placed at the disposal of the War Department to be used in building a plant for the oxidation of ammonia to nitric acid and the concentration of nitric acid, of a capacity equivalent to 24,000 pounds of 100 per cent nitric acid in a 24-hour day, said plant to be located in the neighborhood of the aforesaid synthetic ammonia plant and the proposed new powder plant of the Government.

4—That the War Department proceed at the earliest practical date with the construction of the oxidation plant and contingent upon a satisfactory arrangement with the General Chemical Company, also with the Synthetic Ammonia plant, and that the Government give such priority orders as will secure from contractors prompt delivery of the materials and rapid construction of the structure and machinery needed for these plants.

The Committee appreciating the offer of the Nitrogen Products Company granting, in this country, to the Government under certain conditions the right to use the so-called Bucher process for the production of sodium cyanide and ammonia recommends:

5—That a form of contract, drawn with the advice of the legal authorities of the Government, such as to give that company no guarantee or exclusive rights in the process, or in its future development, beyond those which the company's own patents give to it, be entered into with the Nitrogen Products Company, and that experimentation looking toward the industrial development of the Bucher process for the production of ammonia be at once proceeded with. And further that, contingent upon a satisfactory arrangement with the Nitrogen Products Company, a sum not to exceed \$200,000 be allotted for this purpose out of the \$20,000,000 nitrate supply appropriation.

6—That out of the \$20,000,000 nitrate supply appropriation \$100,000 be made available for the active prosecution of investigations of processes for the in-

dustrial production of nitrogen compounds useful in the manufacture of explosives or fertilizers, and that these investigations be planned and supervised by the War Department.

7—That, in order to increase the production of ammonia and toluol, the Government promote the installation of by-product coke ovens by directing that priority be given in the production, delivery and transportation of the materials and parts needed in their construction.

8—That the decision as to more extensive installation of nitrogen fixation processes and water power development in connection with them, be postponed until the plants above recommended are in operation or until further need arises.

9—While the preceding recommendations include all the measures that can now judiciously be taken for the fixation of nitrogen and the oxidation of ammonia, it is the opinion of the Committee that the immediate accumulation and the permanent maintenance of an ample reserve, not less than 500,000 tons of Chile salt peter, is the measure most urgently necessary.

There being no further business before it, the Committee then, at 6.15 P.M., adjourned to meet at the call of the Chairman.

WILLIAM CROZIER, *Chairman*
Brigadier-General, Chief of Ordnance, U. S. A.

RALPH EARLE
Rear Admiral
Chief of Ordnance, U. S. N.

CHARLES KELLER
Colonel
Corps of Engineers, U. S. A.

F. W. BROWN
LEO H. BAEKELAND
GANO DUNN
CHARLES H. HERTY

WM. F. HILLEBRAND
ARTHUR A. NOYES
CHARLES L. PARSONS
WILLIS R. WHITNEY

PRELIMINARY REPORT TO THE ORDNANCE DEPARTMENT OF THE WAR DEPARTMENT ON THE NITROGEN INDUSTRY WITH RECOMMENDATIONS REGARDING THE METHODS TO BE USED BY THE UNITED STATES GOVERNMENT IN PROCURING THE NECESSARY NITRIC ACID REQUIRED FOR MUNITIONS BY THE WAR AND NAVY DEPARTMENTS

(All confidential data including detailed costs omitted)

By CHARLES L. PARSONS, Chief Chemist
Bureau of Mines, Department of the Interior

January 27, 1917

BRIGADIER GENERAL WILLIAM CROZIER,
Chief of Ordnance, War Department

Sir: Since giving you in a letter bearing date of June 6, 1916, my personal opinion on the nitrate situation, based at that time on an incomplete study, I have made a very careful study of the processes used throughout the world for the production of nitric acid, and, in the employ of the War Department, I have made a trip to Italy, France, England, Norway and Sweden, visiting many plants producing nitric acid. I have had conferences with leading engineers in those countries on the situation. It will require some weeks still to make my complete report, with full detailed estimates and costs, on the various processes employed as applied to American conditions, but the details of these processes are now sufficiently in hand to warrant formulating my conclusions as to the proper procedure to be followed.

The conclusions are based, by your instructions, on the maximum requirements for munitions purposes of the United States Government of:

In Time of Peace	20,000 tons of nitric acid
In Time of War	180,000 tons of nitric acid

With these quantities as a maximum and a sufficient supply of sodium nitrate in storage to meet the requirements of the Government for a period of 6 months to 1 year, no serious emergency problem confronts the Government. The increase in the output of ammonia from by-product coal since 1915, if oxidized to nitric acid, is alone more than sufficient to meet this requirement. The oxidation of ammonia, including that produced from the destructive distillation of coal, presents no serious difficulties, and the necessary plants using the emergency procedure adopted in Germany could, in case of need, be quickly installed to meet the Government requirements. Such installation would involve much cruder procedure, such as lower efficiency of oxidation and absorption of the nitrous oxides in soda lye, than would be adopted after careful experimentation and experience in the operation of the most efficient plants, but it would nevertheless furnish the country with the nitric acid required.

In my opinion the following methods include the only ones which need to be considered in the final choice of the procedure to be employed by the Government in providing a source of nitrate supply. There are many other proposed methods, modification of methods, and investigations under way, but they have proved either inapplicable when tried industrially or they have not been sufficiently tried on a practical scale to warrant the Government in considering them in this first analysis. Some of them may later be successfully developed and research on the fixation of nitrogen should be continuously carried on under Government auspices.

Following are the methods considered herein:

I—Nitric acid may be obtained directly from the air, with no raw material except that contained therein by directly burning the nitrogen and oxygen of the atmosphere by means of the electric arc.

II—Nitric acid may be obtained from the oxidation of ammonia.

The processes to be considered are:

(A) ARC PROCESS, in which nitrogen and oxygen are directly burned to nitric oxide under the influence of the electric arc.

(B) HABER PROCESS, in which nitrogen and hydrogen are directly combined to form ammonia.

(C) CYANAMID PROCESS, in which carbon and lime are first heated in an electric furnace to form calcium carbide. The carbide is then treated with pure nitrogen to form cyanamid, and, in turn, the cyanamid is hydrolyzed by steam in special autoclaves to produce ammonia.

(D) BY-PRODUCT AMMONIA, obtained as a by-product in so-called by-product coke ovens by the destructive distillation of bituminous coal.

(E) CYANIDE PROCESS, not yet commercially developed but carrying great promise of cheap combined nitrogen. This process embraces the direct combination of ammonia, carbon, and sodium to form sodium cyanide by heating together an intimate mixture of carbon, soda ash, and nitrogen in the presence of finely divided iron.

All of the processes producing ammonia involve the further oxidation of that ammonia to nitric acid. The ammonia may be oxidized by means of heated (usually in a catalytic platinum) by presenting as large a surface as possible of glowing platinum to the proper mixture of ammonia and air, under which conditions the nitrogen in the ammonia burns to nitric oxide. The methods to be considered for the oxidation of ammonia are:

(a) OSTWALD-BARTON METHOD, now used in France and England; and probably also in Germany.

(b) FRANK CARO METHOD, now used to produce 100,000 tons of concentrated nitric acid in Germany, and experimentally installed with modifications in two small plants in this country.

(c) The oxidation in solution of ammonia or dicyanamid to ammonium nitrate, as yet carried out only in an experimental installation in Sweden, and being installed in two plants now in process of erection—one near Göteborg, Sweden, and the other and larger plant near Berlin, Germany.

THE ARC PROCESS

The arc process was the first commercial process to be developed for the fixation of nitrogen. It is now installed in southern Norway, employing 250,000 kilowatts of electricity developed from the cheapest large installation of hydroelectric power in the world. This is the only large installation of the arc process, but small installations of an experimental nature have been made in other countries.

By the arc process, nitric acid is produced by the direct combination of the oxygen and the nitrogen of the air to form a dilute gaseous mixture of nitric oxides with air. The nitric oxide is converted into nitric dioxide and is absorbed in water in immense granite towers to form nitric acid. The method is one of the most inefficient known as regards production in relation to power consumed. Nevertheless, on account of the very cheap horse power available in Norway and the fact that the raw materials cost nothing and are always at hand, nitric acid can there be produced by the arc process at a cost less than by any other commercial process.

Incidental to the production of nitric acid, a large excess of heat is developed, which can be, and is in part, converted into steam, which may be, and is, used for concentrating the weak nitric acid obtained in the absorption towers to the strong acid required for munition works. The excess of steam is so large that many other methods for its application have also been devised. As the labor costs also are low, when once under way the operation goes on almost automatically. As the formation of nitric acid is direct and involves only the nitrogen and oxygen of the air and water as raw materials, no complicated processes involving intermediate products are necessary, as is more or less the case with all other processes.

In spite of these manifest advantages, however, it appears to be the general opinion of the European engineers with whom I came in contact that even with the cheap horse power enjoyed by the Norwegian plants, they might have had to discontinue their operations except for the stimulus given by the present European war. Even as it is, the Norsk Hydro Company, operating the arc plants at Notodden and Rjukan, has been obliged to install large ammonia-producing plants in order that they might convert their nitric acid to ammonium nitrate and thus render it transportable to markets where it was needed.

The cost of horse power used for the production of nitric acid in Norway is less than \$5.00 per horse-power year. The best estimates in my possession indicate that with horse power at \$10 per horse-power year, the cost of finished strong nitric acid at the plant would be as cheap as by any other process now in operation. However, the low cost of producing nitric acid by the arc process is outweighed by so many other disadvantages that, in my opinion, the process is entirely inapplicable to the uses of the United States Government, and this opinion appears to be shared by all who have given careful thought to the subject. The cost of installing the Arc process is high and it involves the use of an amount of horse power that seemingly is not available on the American continent within reach of the points where the nitric acid would have to be used.

Nitric acid is not economically transportable. As strong nitric acid it can be transported only if tank cars made of

aluminum can be obtained, and aluminum is a metal that, for this purpose, has many disadvantages besides cost. The nitric acid might be transported mixed with sulfuric acid in iron tank cars, but this involves the erection of large sulfuric acid factories near to the nitric acid plant and a large addition in freight rates. Freight rates on such nitric acid as is transported are very high and must always remain high on account of the dangers involved.

Nitric acid does not readily lend itself to the production of fertilizer material, although it may be neutralized with lime to form calcium nitrate or with ammonia to form ammonium nitrate—both of which may be transported and either of which might be used as a fertilizer. However, calcium nitrate and ammonium nitrate are not applicable to the manufacture of the mixed fertilizers that are demanded by the American farmers.

The great difficulty that has faced the Norwegian plants from the beginning, namely, a market for their products, would in peace times be a serious obstacle to the operation of a large arc plant in the United States. An arc plant at its best involves the use of 2.33 horse-power years per ton of weak nitric acid. This means that a water power development of at least 50,000 horse power would be necessary for the peace requirements of the Government, and a development of 440,000 horse power would be required for war purposes. These figures are minimum figures on the basis of the relatively high efficiency reached in Norway. No installation should be considered by the Government of less than 75,000 horse power for peace requirements or 550,000 horse power for war requirements. If the Arc process is to be used it would also be advisable to arrange for the production of explosives at the point where the arc plant was located. This would of course involve the transportation of all other raw materials needed, such as benzol, toluol, alcohol, acetone, glycerine, sulfuric acid, cotton, and other materials too numerous to mention, to the plant and the transportation of the finished explosives therefrom to the place of consumption. As these materials are highly combustible and for the most part carry high freight rates, it has been found necessary the world over to locate the plants intended for the production of munitions near to the point where the munitions are likely to be consumed.

An arc plant of sufficient size to meet the requirements of the Government in time of war would probably have to remain idle for the main part during times of peace, owing to the difficulty of disposing of the nitric acid that the plant would produce if in operation. On account of the large amount of horse power required and the consequent extent of the necessary plant and tower absorption capacity, the cost of installing an arc plant to meet the war time requirements of the Government would be several times the total appropriation made for the purpose by Congress.

ADVANTAGES

- 1—Cheapest cost of nitric acid¹ if power can be obtained at \$10 per horse-power year or less, and if the power is efficiently utilized in a large plant run continuously to capacity.
- 2—Large amount of waste heat available for producing steam for the concentration of nitric acid and for other purposes.
- 3—Free raw material.
- 4—Direct production of nitric acid without intermediate products.
- 5—Small amount of labor involved.

DISADVANTAGES

- 1—Large amount of horse power required per ton of nitric acid—at least 500,000 horse power for the Government requirements.

¹ This does not mean that it is the cheapest form of combined nitrogen for fertilizer purposes.

2—Greater dilution of nitric acid when first produced—30 to 35 per cent acid as against 50 to 55 per cent acid by other processes.

3—Large cost of installation both for horse power and for plant—probably four times the present Government appropriation to meet the Government's war-time requirements.

4—Three-fourths of plant probably idle in time of peace, with consequent large idle investment involved.

5—Nontransportability of the nitric acid produced.

6—Difficulties of disposing of the nitric acid not needed for munitions.

HABER PROCESS

The Haber process is the chief process now used in Germany for the production of ammonia. Ammonia may be oxidized to nitric acid. The process has grown very rapidly in the last three years. It was first commercially installed in Germany in 1913 with a plant capacity of 30,000 tons of ammonium sulfate. Seemingly, it actually produced in that year some 20,000 tons of ammonium sulfate. This grew to 60,000 tons in 1914; 150,000 tons in 1915; and 300,000 tons in 1916, and it is authoritatively stated that with new works now under construction by the Badische Company, the 1917 output of ammonia by the Haber process will be equivalent to over 500,000 tons of ammonium sulfate.

The Badische Company, which owns the Haber plants and process, has developed the industry without government aid other than the sale of its product, and appears to be very certain as to the ability of this process to compete, when the war is over, with all other processes for the fixation of nitrogen and also with Chile salt-peter in the fertilizer markets. On the other hand, the cyanamid industry in Germany has been developed during the war with the aid of government subsidies. The Badische Company had developed in Germany an arc process known as the Schoenherr process which is a close competitor of the Birkeland-Eyde process developed in Norway. The Badische Company and the Norsk Hydro Company pooled their interests and the Schoenherr process was installed, together with the Birkeland-Eyde process, at Rjukan, Norway. The two are now working together side by side in Rjukan, and are owned by the Norsk Hydro Company—the Badische Company having sold their interests in the arc process as soon as they had developed the Haber process.

By the Haber process, nitrogen from the air and hydrogen obtained from water are directly combined to form ammonia under the influence of finely divided iron. The production and purification of hydrogen made either by the reducing action of coal or iron upon steam involves one of the chief items of cost in the Haber process. The fact that the combination of nitrogen and hydrogen takes place at temperatures above 500° C., and at pressures of 125 to 150 atmospheres involves some danger and many other technical difficulties which have, however, seemingly been overcome in Germany. The technical control of the Haber process is of such great importance and requires so high a degree of training and skill that it is reported if the Badische people were to lose their present technical staff of experts, familiar with the process, many months would be required to train another staff capable of applying the process in practice.

The Haber process is not at present in use outside of Germany on account of the lack of detailed information regarding plant construction and operation and also owing to the very large royalty demanded by the Badische Company for its use by other concerns. It is, however, more than probable that the Badische Company will itself install and develop the process outside of Germany when the war is ended.

Trustworthy information regarding the costs of production of ammonia by the Haber process indicates that pure anhydrous

ammonia can be produced in liquid condition for a cost slightly less than 4 cents per pound. It is improbable that any arrangement could be made for the United States Government to use the Haber process pending the conclusion of the European war. It is probable that when the war is ended, the Haber process will be installed or will be available for installation in the United States. It is the cheapest process for the production of synthetic ammonia. It is independent of cheap power—the power being a small fraction of its cost. If desirable, it could be readily installed in moderate sized units in connection with ammonia oxidizing plants at any munitions plant.

ADVANTAGES

- 1—Cheap ammonia.
- 2—Ammonia in water-free liquid condition ready for immediate oxidation without purification.
- 3—Availability of raw material (air, water, and coal).
- 4—Possibility of erecting comparatively small plants wherever needed.
- 5—Easy availability of product for transportation and for fertilizer.

DISADVANTAGES

- 1—Inability to procure technical details, use of method, and trained technical force without the assistance of the Badische Company, except as the result of many months and probably years of experimentation. This is largely owing to the difficult engineering problems involved in the use of pressures as high as 150 atmospheres and temperatures of 500° to 600° C.
- 2—High repair and renewal costs.
- 3—Undoubtedly high royalty that would be demanded if the Government were to install and operate this process itself. Inability to come to terms with the Badische Company as to the use of its patents is reported to have been the sole reason for the non-adoption of this method by two large American corporations and one Norwegian corporation.
- 4—Patents and processes controlled in America by one corporation.

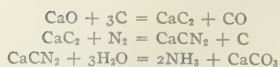
CYANAMID PROCESS

The Cyanamid process has been developed in many parts of Europe, but in the Western Hemisphere only at Niagara Falls, Ontario, Canada. It requires cheap power for its successful operation and has obtained its greatest development owing to the fact that it requires only about one-fifth the horse power per ton of fixed nitrogen per year that is required by the arc process. In other words, from a definite horse power installation the Cyanamid process produces about five times the amount of combined nitrogen that is produced by means of the arc process.

The raw materials required are coal for lime burning, anthracite coal or coke for the production of calcium carbide, limestone essentially free from magnesia, fluorspar, and nitrogen obtained from liquid air. The process involves:

First, the production of calcium carbide in a large electric furnace from lime and coke or anthracite coal.

Second, the fine grinding of this calcium carbide out of contact with air, and the heating of a portion of the ground mass to a red heat to start the absorption of the nitrogen which is then added, as long as it is taken up by the carbide, to form cyanamid. The cyanamid is in turn ground and given a special treatment to remove acetylene gas in order to avoid explosion later. The cyanamid, mixed with sodium carbonate and lime, is then treated with steam in large autoclaves to convert the nitrogen of the cyanamid into ammonia gas. The process will thus be seen to involve a number of steps and to be somewhat complicated.



The cost of ammonia from cyanamid, with power at \$8 per horse-power year in a plant to be constructed by the Government, would cost 1 to 2 cents per pound more than by the Haber process. On the other hand, royalties for using the Cyanamid process would undoubtedly be less. The technical problems involved are understood by many engineers both in this country and abroad, the manufacture of calcium carbide and cyanamid being established in many plants, and the basic patents having only some 4 years more to run. Particularly favorable conditions exist for its installation in certain sections of the South. If a hydroelectric plant is to be installed by the United States Government, and the electrical power so developed must be used for the fixation of nitrogen, the cyanamid process has advantages over all other processes now developed and should be adopted as the best means of utilizing hydroelectric power for the fixation of nitrogen.

In Germany in 1913 there were produced 30,000 tons of cyanamid. The growth has not been so rapid as in the case of the Haber process although the process has been subsidized by the German Government to assist in its development. However, the 1917 German production will be not far from 400,000 tons. The cyanamid interests in Germany have also endeavored to induce the German Government to establish a nitrogen monopoly which will insure the continuation of the cyanamid industry in Germany in competition with the Haber process and ammonium sulfate from coke ovens after the war. The German nitrate monopoly has not been established by the Reichstag chiefly owing to the opposition of the owners of the Haber patents.

Ground cyanamid is a very dusty, disagreeable product and in order to be used for fertilizer has to be treated with oil or by a special granulating process that controls the dust and enables the material to be more successfully used as a fertilizer. Cyanamid should be and probably is an excellent fertilizer if applied directly to the soil. It has not, however, found favor with American fertilizer manufacturers and is not well suited as an addition to the mixed fertilizer demanded by American farmers. It is, however, successfully used in Europe where much cheaper labor enables the farmer to spread his fertilizer, if desirable, one constituent at a time. To meet the Government's requirements of 20,000 tons and 180,000 tons of nitric acid, through the medium of cyanamid, would require the continuous use of 11,000 horse power and 99,000 horse power, respectively.

If cyanamid is to be converted into the most popular form of fertilizer material, namely, ammonium sulfate, it would cost approximately 1 cent per pound to convert the nitrogen present into the form of ammonia before it could be absorbed to form sulfate. It is the necessity of converting the combined nitrogen into ammonia, if the cyanamid process is used as a source of nitric acid, that makes up a considerable portion of the difference in cost between cyanamid ammonia and Haber ammonia.

ADVANTAGES

- 1—Most available method if hydroelectric power is to be used.
- 2—Moderate horse power requirements.
- 3—Ready transportability.
- 4—Product salable in time of peace for fertilizer.

DISADVANTAGES

- 1—Number of operations and plant installations required to produce nitric acid, *viz.*, carbide, cyanamid, ammonia from cyanamid, ammonia oxidation, and nitric acid concentration.
- 2—Patents and processes controlled in America by one corporation.

- 3—Process an extremely dusty and disagreeable one, involving unpleasant conditions, if not hardships, on the labor.
- 4—Large labor factor involved.
- 5—Comparatively high cost.

BY PRODUCT AMMONIA

The nitrogen stored up through the medium of plant life of past ages as a constituent of bituminous coal is in part recovered as ammonia when bituminous coal is converted in by-product ovens into coke. This source of ammonia is to-day the chief source of combined nitrogen in all countries, including Germany. Ammonia produced by the destructive distillation of coal when pure is the same as any other ammonia and can be readily oxidized to nitric acid.

The recovery and utilization of ammonia in by-product coal has been recognized by economists for decades to be one of the most important developments for conserving the wealth of the nation. In Germany two-fifths of the coal used is carbonized in by-product coke ovens, and all of the coke produced is produced in plants fitted for the recovery of by-products including ammonia. In this country less than one-tenth of the bituminous coal burned is coked in by-product ovens. Of the coke produced in America, over one-half is still produced in bee-hive ovens in which the gas, ammonia, and all other by-products are ruthlessly destroyed. There has been nevertheless a rapid increase in the installation and operation of by-product ovens and an increase in ammonia production that would not have been thought possible 2 years ago. By the end of the present year, we will be producing at least 115,000 tons of ammonia per annum—an equivalent of 450,000 tons of ammonium sulfate. Six thousand tons of this ammonia in time of peace, or 55,000 tons in time of war, would meet the Nation's requirements of nitric acid for military purposes, as estimated by the War Department. The growth of our ammonia production from by-product coke has been extremely rapid and is still on the increase. More than fifty million dollars worth of by-product coke ovens have been contracted for within the past 12 or 13 months and are now completed or in process of erection.

The installation of the by-product coke process means a larger supply not only of ammonia but also of benzol, toluol, phenol, naphthalene, and other products absolutely essential for munitions purposes and required in time of peace for our present and future dyestuffs industry. Benzol, toluol, and phenol are only secondary in importance to an ample supply of nitric acid for war purposes.

The use of the by-product coke process also means the production of large quantities of gas for power purposes. Indeed, if the destructive distillation of coal is conducted in special producer-gas ovens the output of ammonia can be increased five- to six-fold, and power comparable with cheap hydroelectric power can be obtained at the same time. This method is now utilized in Germany on an immense scale for producing cheap power and increased ammonia output.

That bituminous coal used should be treated in by-product ovens is recognized the world over. It is becoming increasingly practicable to do this, and the consumption of coke for domestic purposes as well as for the production of iron and steel is rapidly increasing. The general use of coke instead of coal throughout the country would do away with the smoke nuisance and all of its concomitant loss to property. It would produce, besides other by-products, approximately 1,000,000 tons of ammonia in this country alone. The day is far off before this highly desirable result will be reached, but it should none the less be striven for. Already legislation abroad requires the use of coke instead of bituminous coal for certain industrial purposes. By-product coke ovens, however, cannot be installed by the United States Government for the purpose of producing ammonia.

The ammonia should be simply a by-product incidental to the production of coke for industrial purposes. Under war conditions, however, the output of ammonia from by-product coke ovens could, by Government regulation, be greatly increased. This has been accomplished in Germany, the by-product coke ovens furnishing Germany to-day with over one-third of the nitrogen consumed in that country. Germany has had an increase from 100,000 tons to 154,000 tons of nitrogen from this source since the war began. The possibilities for an increase in America are much greater than in Germany.

Ammonia from by-product ovens has to be purified before it can be oxidized for nitric acid. The cost of purification is, however, very small and, where purification apparatus is installed at the original ammonia absorption plant, adds but a small fraction of a cent a pound to the cost of crude ammonia liquor.

The use of by-product ammonia for the production of nitric acid for munitions purposes has the great advantage that it is already available and that the plants, being situated in numerous parts of the country, could furnish ammonia to several small oxidizing plants. Accordingly, the country's source of munitions supply would not be at any one place and subject to capture and destruction.

The use of by-product ammonia has the great disadvantage that the present selling price of ammonia from by-product coke is high and, unless considerable price concessions could be obtained by the Government, it could not afford to utilize this source of raw material for nitric acid. The actual cost of pure ammonia, considered as a by-product from the coking of bituminous coal, is much less than by any other method now producing this substance.

CYANIDE PROCESS

The Cyanide process is not yet a commercial success and for that reason alone perhaps should not be included here. It has, however, such possibilities that I feel called upon to discuss it.

From a chemist's standpoint the process is to-day a success. There is no difficulty whatever in the chemical reactions. When sodium carbonate, ground coke, or carbon in any form in contact with finely divided iron are heated to redness and nitrogen or even air passed through the mass, nitrogen in quantity is fixed as sodium cyanide. The reaction takes place readily. No power factor of any consequence is involved and it appears certain that if the mechanical difficulties are solved, nitrogen will be fixed in this form cheaper than by any other known synthetic process.

There are also large quantities of waste nitrogen available in connection with the sodium carbonate plants of the country where the sodium carbonate required would also be available, and there are large amounts of nitrogen that could be obtained without cost in a sufficiently pure condition at the wood-pulp plants using the sulfite process.

When the sodium cyanide is once formed it can be readily converted into ammonia as is the case with cyanamid, but the process has the advantage that in the conversion the sodium carbonate can be recovered to be used over again. The iron can also be repeatedly used in the process. Small installations are now working successfully in the country but the mechanical difficulties of production on a large scale are yet to be solved. Four large American corporations are engaged on the problem with ample funds for its solution.

The process has the further advantage that it would also make cheaply available cyanide which is so greatly needed by our mining industries.

NITRIC ACID FROM AMMONIA

All processes for the synthetic production of nitric acid, except the Arc process, involve the oxidation of ammonia. The processes commercially in use involve the direct oxidation of ammonia gas in the presence of air in contact with metallic platinum

In Germany, according to the latest published figures, approximately 100,000 tons of nitric acid are annually produced through the Frank Caro process, which involves passing mixtures of ammonia and air through electrically heated platinum nets of 80 to 100 mesh. The platinum is heated to a dull red heat and serves as a catalytic agent under whose influence the ammonia, instead of burning to nitrogen and water, as normally would be the case, causes the nitrogen to form nitric oxide.

In the Kaiser process, also used in Germany, the air is heated before its mixture with the ammonia, and under these conditions it is claimed that no electric heating of the platinum net is necessary. The Kaiser process does not appear to have reached any large commercial development.

The Landis process installed in a small experimental plant at Warners, N. J., passes the gas downward through the net instead of upward, as is customary in the Frank Caro process, and, according to the Landis patents, cools the gases before they are allowed to come in contact with the net instead of heating them as is done in the Kaiser process. The platinum net process is also understood to be installed in a small plant in Long Island City and is being installed in Syracuse, N. Y., by the Semet-Solvay Company in coöperation with the Bureau of Mines.

The Ostwald-Barton process first developed at Villevord, Belgium, and brought there to a commercial success at the time of the opening of the war, is now installed in two large plants—one at Angouleme, France, and the other at Dagenham, England.

The principle of the process is essentially that originally patented by Ostwald, but the catalyzer is distinctly different from that used by him although it consists of metallic platinum. The details of the preparation of this catalyzer are kept secret, but it is known to have a very small cross-section and is placed at the end of a 60-mm. tube so that the products of combustion passing through the tube heat the mixed ammonia and air by radiation as they approach the catalyzer. By this means no external heat is necessary. The reaction when once started continues without interruption for weeks. It is simply necessary, by means of blowers, to force the mixture of ammonia and air through the catalyzer.

The present commercial efficiency and output by the Ostwald-Barton process is higher than by any other concerning which exact figures have been obtained. It is higher than the published figures for the Frank Caro process, but as figures for that process have been published only on a minimum basis, it is impossible to state whether as high an efficiency of conversion and capacity of catalyzer has been reached by that process as by the Ostwald-Barton.

The processes for the oxidation of ammonia are seemingly free from any complicated patent situation. The Europeans engaged in ammonia oxidation admit freely that they have no important patent rights to sell, but they claim that they have plans, specifications, and details of processes, the purchase of which would be cheaper than the necessary experimentation to work out the details.

By the oxidation of ammonia, nitric oxide gases are obtained of much higher concentration than those produced by the Arc process. Accordingly, much less tower space is necessary for their absorption and much stronger acids can be directly obtained by concentration. Although in the Arc process the concentration of 50 to 55 per cent nitric acid is strong and is required, in the oxidation process an acid of 20 to 25 per cent strength is easily obtained directly from the towers and the concentration thereof is accordingly a simpler matter.

OXIDATION OF AMMONIA IN SOLUTION

A method has been developed in Sweden, details of which are unknown, for the oxidation of ammonia or cyanamid direct to ammonium nitrate in solution. The ammonium nitrate can

then be easily concentrated by evaporation and can be converted to nitric acid if desired. The process seems worthy of very careful consideration and will be in commercial operation this coming summer—a plant being now in process of erection near Gothenburg, Sweden. A second and much larger plant is also being erected near Berlin, Germany.

As cyanamid is not necessarily converted into ammonia, as any form of ammonia, such as Haber or coal-tar ammonia, can be directly used, and as no heating of any kind is required, it is claimed that this process will produce ammonium nitrate much cheaper than any other. It is particularly important because nitrate itself is becoming one of the most important of all explosives, and the many complicated reactions necessary for its manufacture would be avoided if this process becomes a commercial success, as the engineers engaged in its exploitation confidently expect. The fact that the German engineers have seen fit to install a large plant near Berlin speaks well for the probability of its successful application.

THE NITROGEN SITUATION

Without going into full details of the nitrogen situation in this preliminary report, a short summary of some of its most important features appears to be desirable. The subject will be treated at greater length and with definite data in the final report.

The present conditions are, of course, abnormal. Importations of sodium nitrate into Germany have been entirely cut off, and Germany consumed a large fraction of the output of the Chile mines before the war. The importations of sodium nitrate into the United States have doubled, owing to the tremendous amount of munitions being manufactured for export. The importations of sodium nitrate into the allied countries have also greatly increased, owing to war demands. The production of synthetic nitrogen in Germany and the increase in the production of by-product nitrogen in Germany have much more than offset the lack of Chilean importations. The following summary of conditions in Germany, taken from the *Frankfurter Handelsblatt* of May 29, 1916, is significant.

GERMAN CONSUMPTION OF NITROGEN, 1915, IN METRIC TONS			
Sulfate of Ammonia.....	460,000 tons eq.	92,000 metric tons	Nitrogen
Norwegian Nitrate of Lime.....	35,000 tons eq.	4,500 metric tons	Nitrogen
Cyanamid.....	30,000 tons eq.	6,000 metric tons	Nitrogen
Ammonia—Haber Process....	20,000 tons eq.	4,000 metric tons	Nitrogen
TOTAL.....	545,000 tons eq.	106,500 metric tons	Nitrogen
plus Nitrate of Soda.....	750,000 tons eq.	116,000 metric tons	Nitrogen
Grand Total.....	1,295,000 tons eq.	222,500 metric tons	Nitrogen
Grand Total in tons of 2000 lbs.....	249,000		

GERMAN PRODUCTION OF NITROGEN, 1917, IN METRIC TONS			
Sulfate of Ammonia.....	700,000 tons eq.	140,000 metric tons	Nitrogen
Norwegian Nitrate of Lime.....	35,000 tons eq.	4,500 metric tons	Nitrogen
Cyanamid.....	400,000 tons eq.	80,000 metric tons	Nitrogen
Ammonia—Haber Process....	500,000 tons eq.	100,000 metric tons	Nitrogen
TOTAL.....	1,635,000 tons eq.	320,000 metric tons	Nitrogen
Total in tons of 2000 lbs.....	327,000		
Nitrate of Soda.....	None		

In spite of having more than half of her nitrogen supplies cut off by the war, Germany has greatly increased her nitrogen output, increasing her own production of nitrate resources from 116,000 short tons to 352,000 short tons of nitrogen. This has been made necessary not simply or chiefly for war munitions but largely for agricultural needs, Germany's population being dependent now on its own food supplies which in turn are greatly increased by nitrogenous fertilizer.

Conditions in the United States in case of a war which cuts us off from foreign countries would be far different. We are a food-exporting country and the larger part of our fertilizer is used on the cotton crop, the growth and exportation of which would be greatly curtailed. A comparatively small part of our fertilizer requirements are used on food crops, and being a food- and cotton-exporting nation our nitrogen requirements for agricultural purposes would largely decrease instead of increase.

Even in the case of the present war, which has increased foodstuffs exportation but decreased cotton production, the fertilizer consumption of the country has decreased rather than increased. This would be much more the case if our people were cut off entirely from food and cotton exportation.

In view of the fact that Germany has invested millions of dollars in synthetic nitrogen plants which will continue to produce synthetic nitrogen after the war; that Germany is producing more than twice the amount of combined nitrogen that she formerly imported in the form of Chilean saltpeter; that accordingly the German market for Chilean saltpeter will be essentially non-existent after the war; that the present large American and allied consumption for munitions will cease; and that during the war the American production of ammonia from by-product coke ovens has increased to a point in excess of our apparent normal consumption, it seems certain that the price of combined nitrogen for industrial and agricultural purposes must greatly decrease when the war is over. This, I think, is recognized and expected by all of those engaged in the production of combined nitrogen.

In view of the facts above enumerated, it is evident at once that the peace time requirements of the Government for nitric acid could be supplied from coal-tar ammonia with little effect on the market for the material and practically no effect on the country's nitrogen resources. It seems equally certain that in the case of such a war by-product ammonia could furnish 180,000 tons of nitric acid per year for at least one or two years without seriously affecting the Nation's agriculture. This is particularly important when it is remembered that over 60 per cent of the nitrogenous material used in fertilizer, consisting of organic nitrogen from cottonseed meal, tankage, dried blood, etc., would not be decreased at all but would rather be increased through the cutting off of exports of cottonseed meal.

Furthermore, it is well known that several of our largest corporations are engaged in active plans for installing synthetic nitrogen plants of various kinds to meet their own industrial requirements and that in all probability the Haber process will enter into active industrial competition for our ammonia markets in American plants as soon as the war is over. Plants for the oxidation of ammonia can be quickly erected in crude form as they were erected and utilized in Germany, should the need arise.

I accordingly feel that no serious emergency problem confronts the United States that could not be met with reasonable celerity in time of war, and that our first problem, after securing a reasonable reserve of Chilean saltpeter, is to familiarize ourselves with the most efficient method for the oxidation of ammonia and to train the necessary men to construct and operate ammonia oxidation plants.

COST OF NITRIC ACID

The cost of nitric acid, *per se*, whether as weak nitric acid or as concentrated nitric acid, is lowest by the arc process with hydro-electric power delivered to the furnace at a cost of \$10 per horsepower year, or less. The difficulties of its transportation, the large amount of power required, and other economic reasons, as already explained, make the arc process inapplicable to American conditions.

The cost of nitric acid obtained by the oxidation of pure ammonia is independent of the source of the ammonia and must therefore depend upon the cost of ammonia gas in the gas holders ready to be passed to the oxidizing apparatus.

COST OF AMMONIA

The cost of ammonia has at the present time no relation to its selling price. The actual cost of collecting, absorbing, and purifying ammonia from the gases developed by the destructive distillation of bituminous coal—in other words, the cost of ammonia considered as a by-product is less than by any other

process. The selling price of by-product ammonia is entirely a question of competition with other nitrogenous products and has been fixed in the past almost wholly by the market price of sodium nitrate with which it enters into competition. Even should ammonia be placed on the market by the Haber process at a price as low as 4 cents per pound, by-product ammonia will still be sold in competition therewith at a profit to the producer. Its cost price is largely a matter of bookkeeping. Its selling price will in the future as in the past depend upon the competition of other sources of combined nitrogen. The Haber process can produce and is producing ammonia synthetically cheaper than any other synthetic process now industrially applied. The Cyanamid process stands next in order.

If mechanical difficulties now confronting the cyanide process are solved, it will produce ammonia cheaper than either the Haber or the Cyanamid process and in close competition with the actual costs of saving by-product ammonia. The details of costs by all of the above methods will be considered in the final report.

SUMMARY OF CONCLUSIONS

(See final conclusions in supplementary report)

I—The Government should obtain its nitric acid by the oxidation of ammonia. It should begin the erection of an ammonia-oxidation plant of moderate capacity at an early date in order to train men and obtain experience in the most efficient method of procedure.

II—The Government should proceed slowly in the matter of the erection of plants for the production of ammonia, as developments in the cyanide process and the availability of the Haber process may render valueless within a short time any large expenditure for the production of cyanamid. This is doubly true in view of the fact that present appropriations are not nearly sufficient to install water power and erect the nitrogen fixation plants necessary to meet the Government Requirements as estimated by the Ordnance Department.

The adoption of the above procedure involves:

- 1—Purchase by the Government of a reserve supply of sodium nitrate of at least 200,000 tons.
- 2—The purchase of ammonia on the open market.
- 3—The reservation of a supply of platinum.

As platinum is an essential for the oxidation of ammonia and of the utmost importance in the production of sulfuric acid and other supplies required for munitions; as there are no platinum reserves in the United States save a small amount obtained in the electrolytic purification of copper, gold, and silver ores; and as platinum is one of the precious metals with a value above that of gold, I especially recommend that legislation be asked which will conserve the platinum obtained each year by the United States mints, putting it in the vaults if necessary and issuing treasury notes against it as in the case of gold. Platinum would then be available for immediate use in case of need for the production of nitric acid by the oxidation of ammonia and for the production of sulfuric acid so important in case of war. This platinum would be available without cost to the Government and could, if desired, be used as a reserve for circulation, because even if applied to the purposes above mentioned there would be comparatively little actual loss of the metal itself.

4—The construction of a hydroelectric plant only if the Arc or Cyanamid process is to be used. The oxidation of ammonia requires very little power and the Haber, Cyanide, and By-product Ammonia processes are all independent of cheap power cost. The development of water power, however, cannot but be of benefit to the country even if it is not used for the fixation of nitrogen.

I seriously doubt whether hydroelectric power will be necessary or desirable three years from now for the most efficient process of fixing nitrogen, and accordingly I deem it unwise to install such hydroelectric power at great cost with the sole

purpose of producing nitrogen. If, however, such water power can be utilized by the Government in the production of certain ferro alloys absolutely essential for ordnance and other munitions; can be sold to commercial companies who will take upon themselves the financial risk involved in the erection of plants for nitrogen fixation, under guarantee of cheap ammonia to the Government; or can be sold during peace times to companies requiring power for purposes which would allow instant requisition of the power by the Government in time of war without handicapping the supplies of other needed war material, the development of such hydroelectric power would be highly desirable.

REPORT ON THE NITROGEN INDUSTRY

By CHARLES L. PARSONS, Chief Chemist
Bureau of Mines, Department of the Interior
April 30, 1917

BRIGADIER-GENERAL WILLIAM CROZIER,

Chief of Ordnance, War Department

Sir: In my preliminary report of January 27, I recommended:

I—That the Government should obtain its nitric acid by the oxidation of ammonia and should shortly begin the erection of an ammonia oxidation plant of moderate capacity to train men and to obtain experience in the most efficient method of procedure.

II—That the Government should proceed slowly in the matter of the erection of plants for the production of ammonia, as "development in the Cyanide process and the availability of the Haber process may render valueless within a short time any large expenditure for the production of cyanamid."

In connection with these recommendations, I further recommended that the Government purchase a reserve supply of sodium nitrate of at least 200,000 tons, and that arrangements be made for the reservation of a supply of platinum. These last two recommendations have already been adopted and are progressing toward fulfillment.

A small plant for the oxidation of ammonia erected at Syracuse, N. Y., is progressing successfully; another experimental oxidation plant at Laurel Hill, L. I., has developed other new features. At Syracuse, two new forms of apparatus for the oxidation of ammonia are now being tried out—one of which, if successful, will do away entirely with the use of platinum in the production of nitric acid. Whether or not this will be accomplished is doubtful, but desirable. The main point is that the preliminary arrangement for the plant for the oxidation of ammonia is progressing rapidly and satisfactorily.

At the time my preliminary report was written, I felt even more confidently than I was willing to express that the Haber process and Cyanide process would be shortly available for the use of this country and would largely, if not entirely, displace the Arc and Cyanamid processes, which require large electrical development and a correspondingly large expenditure.

Development has been rapid during the last two months. A Synthetic Ammonia process and a Cyanide process have now reached a state of development where I am prepared to recommend definite action by the Government.

GENERAL CHEMICAL COMPANY PROCESS

During the past four years, the General Chemical Company, working on the basis that it should be possible to develop conditions under which the synthetic production of ammonia by the direct combination of nitrogen and hydrogen, should take place at lower pressure than those deemed necessary by the Haber process, has achieved success. The process has been demonstrated in operation on a large experimental scale with several small

units for ammonia production and one unit larger than those supposed to be used in Germany.

The General Chemical Company has also developed and brought to a commercial basis the production of a mixture of nitrogen and hydrogen from coke, air, and water which will yield hydrogen at a cost lower than heretofore obtained in this country and probably lower than that obtained in Germany.

Complete engineering plans have been prepared and bids obtained on the main items of construction so that the erection of a plant for the synthetic production of ammonia can be proceeded with without delay. The company itself would have already had a plant in operation save for the present high construction costs and other difficulties incident to operations at the present time.

The General Chemical Company feels that, so far as its own relations to the nitrogen industry are concerned, sound business policy would call for delay in the construction of a plant until the war is over. Many of the difficulties facing the General Chemical Company, however, do not apply to the Government, such as inability to secure the raw material and quick mechanical construction.

For some months I have known that the General Chemical Company was working on this Synthetic Ammonia process but only recently has it been possible to obtain detailed information. The outbreak of the war convinced the officials of the General Chemical Company, headed by Dr. William H. Nichols, Chairman of the Board of Directors, that they should place at the disposal of the Government the results of their investigations. Accordingly, when the Bureau of Mines requested information regarding the present status of their operations, a preliminary conference was arranged in Washington on April 4. As a result of the information then obtained, arrangements were made for a meeting in your office with representatives of the General Chemical Company on April 14.

After this conference, Dr. Nichols offered the free use of the process devised by the General Chemical Company to the Government and the full help of the General Chemical Company in installing and operating the process. Arrangements were made for a visit to the experimental plant of the General Chemical Company and for a further conference in New York.

On April 20, Col. C. B. Wheeler, Col. C. C. Keller, Dr. A. A. Noyes, and myself visited the plant and saw it in operation. On the same day a meeting was held at the office of the General Chemical Company at which the plans for the proposed plant were exhibited and a proposed agreement between the General Chemical Company and the Government handed to me for delivery to you. The original of this offer is now in your hands and a copy is attached hereto. Estimates on construction and on operation were also submitted.

These estimates are presented in detail under the promise, however, that they would be carefully guarded. Detailed estimates are attached both for a plant of 60,000 pounds of ammonia per day and for a smaller plant of 15,000 pounds per day.

It is estimated—I believe conservatively—that even under present conditions a 30 ton per day plant can be built for an expenditure of \$3,000,000 and can be operated at a cost of not to exceed 4 cents per pound of ammonia produced, allowing \$5.00 per ton of product for repairs and 12½ per cent of the cost of the plant for interest and depreciation. It is believed that the charges for repairs, interest, and depreciation are excessive, as, together, they comprise more than 50 per cent of the total cost of the ammonia production. In the estimates \$3.00 per ton of product is allowed for general expenses and overhead charges.

It is estimated that a smaller plant of at least 7½ tons per

day capacity can be built at the present time for approximately \$1,100,000, including land and buildings. Such a plant would yield 2,700 tons of ammonia per year—equivalent to 8,700 tons of 96 per cent nitric acid, assuming 85 per cent recovery. Such a plant would require about 500 horse power.

After examining the process in some detail and giving great weight to the standing of the General Chemical Company and to the statements of its officers and engineers—than whom there are none better fitted to judge of the situation—I recommend the following:

That an initial plant to produce 60,000 pounds of ammonia per day be immediately constructed.

To this end I recommend:

1—That the War Department set aside the sum of \$3,500,000.

2—That an agreement with the General Chemical Company be consummated whereby the process be accepted by the Government for its own use, together with the services of the requisite engineers already trained by the General Chemical Company for use in construction and

3—That an agreement be reached whereby a definite or at least a maximum royalty per ton of fixed nitrogen produced be paid to the General Chemical Company if sold for non-government use.

4—That this initial plant be constructed at some point to be selected by the War Department in southwest Virginia, or adjoining territory in West Virginia, reasonably near to the sulfur, sulfuric acid, and coal supplies of that region and so situated near to plenty of good water that an ammonia oxidation plant and a powder plant may later be erected near-by.

CYANIDE PROCESS

The Cyanide process, too, has greatly developed in the last few months as anticipated in my preliminary report.

Since that report appeared, the scientific details of the process have been published by Prof. J. E. Bucher in the *JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY*, 9 (1917), 233. The president of the Nitrogen Products Company, Mr. Edward E. Arnold, who 6 months ago declined to go on record as to the future of the process, now unequivocally states that he considers the process a certain commercial success and a probable competitor with any other process for the production of fixed nitrogen. A copy of his letter to me in reply to my request for information as to the present state of the process is attached hereto.

The Nitrogen Products Company is operating two experimental plants by the Cyanide process—one at Saltville, Va., in a coal-fired furnace and one at Niagara Falls in an electric furnace. Col. Wheeler of the Ordnance Department and Dr. J. K. Clement (on my behalf for the Bureau of Mines) visited the Saltville plant on April 6. Col. C. B. Wheeler, Col. C. C. Keller, Dr. A. A. Noyes, and myself visited the plant at Niagara in company with Mr. Arnold on Saturday, April 21.

Estimates of the cost of fixed nitrogen by the Cyanide process presented for the use of the Committee by the Nitrogen Products Company are attached. At my request, Mr. Arnold, president of the company, also submitted a proposal for the use of the Cyanide process by the Government. The offer made by the Nitrogen Products Company is essentially the same as that made by the General Chemical Company.

The process is offered free to the Government for its own use to any extent, both in time of peace and in time of war.

After careful examination of this process, I am not convinced that it has yet reached a point where plant installation should begin, as I believe a few months experimentation will add greatly to the efficiency of the furnace proposed.

It is my belief, however, that the process will become an important factor in the world's nitrogen market; that it may become a strong competitor even of other processes on account of

the simplicity of its operations and the low cost of plant construction; and that a furnace which I believe I see in embryo can be developed which will be much more efficient than either of those now used.

The process is so promising that I recommend:

1—That active experimentation on a large scale be conducted.

2—That a sum not to exceed \$200,000 be set aside for this purpose.

With this amount available I feel confident that this process can be put upon a commercial basis; that it will become a real competitor in the production of ammonia for nitric acid and of nitrogenous material for fertilizer.

I believe this investigation should begin without delay and that as soon as practicable a small experimental plant be erected at Saltville, Va., where a large supply of nitrogen, soda, and coal is available. The present plant of the Nitrogen Products Company can probably be utilized in connection therewith.

SUMMARY OF RECOMMENDATIONS

I—That \$3,500,000 be made available to build an initial plant which will produce 60,000 pounds of ammonia per day by the synthetic ammonia process, as offered by the General Chemical Company.

II—That the offer of the General Chemical Company be accepted with some subsidiary arrangement whereby a maximum royalty per ton of nitrogen, when the product is to be used for commercial purposes, shall be inserted.

III—That the construction of the initial plant be started at once at some point to be selected by the War Department in southwest Virginia or adjoining territory in West Virginia, reasonably near to the sulfur, sulfuric acid, and coal supplies of that region. The plant should be so situated that it is near

to plenty of good water and that the land is available for the later erection of an ammonia oxidation and nitric acid concentration plant. It should be so located that a powder plant may be later erected near-by.

IV—That a sum not to exceed \$200,000 be set aside for active experimentation on a large scale on the Cyanide process.

V—That experimentation on the Cyanide process be conducted at Saltville, Va., where nitrogen, soda, and coal are available and where the present plant of the Nitrogen Products Company may be studied and utilized.

ESTIMATES ON CONSTRUCTION AND OPERATING COSTS

In order that the recommendations made above may be considered in comparison with the older processes now operating on a large scale, I beg to submit herewith a table summarizing confidential data obtained from books of many companies bearing upon the cost of nitrogen production.

DATA PER TON OF NITROGEN—BY THE ARC, CYANAMID, HABER AND GENERAL CHEMICAL COMPANY PROCESSES

	ARC	CYANAMID	HABER	GEN. CHEM. ¹
Product.....	35% HNO ₃	NH ₃	NH ₃	NH ₃
Power required.....	10.5	2.2	0.2	0.2
Investment.....	\$1410(a)	\$440(a)	\$540	\$300
Operating costs ²	170	150(b)	119	97
Product.....	96% HNO ₃	96% HNO ₃	96% HNO ₃	96% HNO ₃
Power.....	10.8	2.3	0.3	0.3
Investment ³	\$1530	\$670	\$870	\$840
Operating costs ⁴	220	270	239	217

¹ Estimates on General Chemical Co. process are based on present war time construction costs. All others on normal prices.

² Amortization for cyanamid as charged by operating companies. Amortization for Haber 20% of plant cost for repairs, interest, depreciation, Amortization for Arc and Modified Haber 12 1/2% interest and depreciation. \$5.00 per ton of product for repairs.

³ Except for Arc process, includes ammonia plant as given A, power additional \$10, oxidation and absorption \$140; concentration \$40; steam plant, \$40.

⁴ Except for Arc process, includes ammonia costs as given; oxidation \$50; concentration \$70. No allowance made for unoxidized ammonia.

(a) Power plant investment reckoned at \$100 per horse power.

(b) Cyanamid production \$122, ammonia from cyanamid \$28, total \$150.

ORIGINAL PAPERS

THE INFLUENCE OF SUPERIMPOSED ALTERNATING CURRENT ON THE ELECTRODEPOSITION OF NICKEL

By S. A. TUCKER AND H. GEORGE LOHSE

Received June 2, 1917

The electrolyte generally used for nickel-plating is a solution of nickel ammonium sulfate, neutral or slightly acid with a weak acid such as boric, tartaric or citric; it may also contain alkali salts of these acids. Nickel deposits formed in nickel ammonium sulfate electrolytes are harder, smoother and more durable than those from chloride electrolytes.¹

Since the solubility of nickel ammonium sulfate (soluble in 12 parts of water at 20° C. and in 5 parts water at 50° C.) limits the concentration of nickel in the electrolyte and prevents the use of high current density, rapid plating solutions have been introduced which, on account of their greater concentration of nickel salt, can be worked at a higher current density. The solution of O. P. Watts,² consisting of 12 parts of nickel sulfate, 1 part nickel chloride and 1 part of boric acid, can be worked at a density of 200 to 300 amp. per sq. ft. at 70° C. Hogaboom, in the discussion of this paper, says that what is known as white nickel deposit cannot be obtained in hot solu-

tions, as the white in the deep parts has a tendency to turn yellow, and that fast nickel-plating is not entirely satisfactory, since the solution becomes alkaline so rapidly that it gives a dull deposit. As soon as the solution becomes alkaline, the deposit becomes dull, while if the solution is on the acid side, the deposit is usually brittle and does not adhere.

The use of nickel ammonium sulfate as the electrolyte necessitates the use of impure anodes, for anodes of pure nickel do not corrode properly but become passive, causing changes in the composition of the bath and the addition of nickel in the form of a soluble nickel salt to bring up the concentration of nickel in the depleted bath.

O. W. Brown³ has shown that in nickel ammonium sulfate electrolyte, electrolytic nickel anodes dissolve very poorly and rolled anodes are no better than electrolytic anodes; cast anodes dissolve with higher current efficiency, and impure cast anodes dissolve with poorer efficiency than rolled anodes. It is to be noted that the presence of copper in a nickel anode, rather than being a detriment, seems to be advantageous in allowing a higher anode current density to be used.

To cause good anode corrosion, commercial nickel anodes may contain from 10 and farther. Cathode

¹ E. F. Kern and F. F. Eubank, *School of Mines Quarterly*, No. 4, 29, 144

² *Trans. Am. Electrochem. Soc.* 29 (1916), 393.

³ *Trans. Am. Electrochem. Soc.* 4 (1903), 80.

and Gammage¹ analyzed commercial anodes from two different sources and found 7.57 and 7.52 per cent iron in them with 92 per cent nickel; the metal deposited from these anodes contained from 0.07 to 0.75 per cent iron. Mathers² gives the following composition of commercial anodes: Ni 95, Sn 2.5, Fe 1.0, impurities 1.5 per cent.

The objections to the use of commercial cast nickel anodes have been well summarized by Mathers. In the ordinary nickel bath, iron is deposited on the cathode along with nickel and part of it is oxidized by the air to a basic salt which goes into the sludge. Ammonium citrate prevents sludge formation. The analysis of dried sludge (using ferro-nickel anodes) gave 39 per cent Fe_2O_3 and 8 per cent sulfate. If the cathode reaches into this sludge, the finished plate has a frosted appearance similar to a deposit on improperly cleaned work. Many commercial deposits contain 3 per cent or more of iron, when the anodes contain 6 to 8 per cent Fe.³ The rest of the iron goes into the sludge. Ammonium citrate keeps all the iron in solution and, therefore, gives a deposit containing approximately as much iron as was in the anode; e. g., from an anode with 6.49 per cent iron a deposit containing 6.23 per cent iron was obtained when citrate was in the bath, and when no citrate was present the deposit contained only 3.31 per cent. The presence of iron in the deposit is one of the chief causes of the dark or bluish color.

Obviously the use of pure nickel anodes is desirable, provided they could be made to corrode properly. With pure anodes better color of deposit is obtained, greater range of conditions without dark or bad deposition is possible and the composition of the bath is more easily maintained constant. Baths using pure nickel anodes and a chloride such as nickel chloride to secure anode corrosion has been tried out and advocated.⁴

It was thought by the authors of this paper that pure nickel anodes could be made to corrode properly in ammonium sulfate solution without the addition of other chemicals by superimposing an alternating current on the direct current during electrolysis.

The corrosion of nickel anodes in nickel ammonium sulfate solution was studied: (1) when D. C. alone, (2) when both D. C. and A. C., (3) when A. C. alone passed through the solution. The current efficiencies at anode and cathode were determined in each case by the loss in weight of anode and the gain in weight of cathode, respectively, a copper coulombmeter in the circuit measuring the coulombs used.

The nickel anodes used were: roughened cast nickel, smooth cast nickel, rolled nickel, and electrolytic nickel (courtesy of International Nickel Company). Analysis of the commercial case anodes showed the following composition: nickel 91.87, iron 6.10, and carbon 1.63 per cent. The rolled nickel, tested qualitatively, showed the presence of a small amount of

carbon and iron. The electrolytic nickel contained 99.8 per cent nickel. The effective anode area was 5 to 6 sq. in.

Copper cathodes were used (5 sq. in. effective area): these were cleaned in nitric acid, washed in hot and then cold water, dipped in alcohol and dried over a flame, cooled and weighed. After the completion of a run the cathodes and the anodes were washed in hot and then cold water, dipped in alcohol, dried over a flame, cooled and weighed.

A neutral solution of C. P. nickel ammonium sulfate, 75 g. per liter, was used as the electrolyte. A fresh sample of electrolyte was used in each experiment. The electrodes were suspended in the bath 1 in. apart.

I—DIRECT CURRENT ALONE

The cells (300 to 350 cc. capacity) containing the different anodes were connected in series in a circuit containing an ammeter, copper coulombmeter, and variable resistance. The anode and cathode efficiencies at different current densities were determined. The results are given in Table I.

TABLE I—RESULTS WITH DIRECT CURRENT ALONE
Current Densities given in Amperes per sq. ft.
Time of Run, 1 hour. Efficiencies in Percentages

NICKEL ANODE	Run No.	CURRENT DENSITY		EFFICIENCY		CHARACTER OF DEPOSIT
		Anode	Cathode	Anode	Cathode	
Roughened Cast....	1	5.76	3.60	102.43	98.92	Good
	2	11.50	9.60	94.76	99.38	Good
	3	17.10	14.30	82.50	95.04	Slightly burned
	4	19.00	19.00	86.00	97.45	Burned
Smooth Cast.....	1	5.76	3.60	57.51	95.61	Good
	2	11.50	9.60	62.23	91.55	Good
	3	17.10	14.30	42.30	83.98	Good
	4	19.00	19.00	53.70	79.67	Slightly burned
Rolled.....	1	3.60	3.60	5.01	87.30	Good
	2	7.80	9.60	1.76	76.70	Good
	3	10.80	14.30	3.55	69.70	Good
	4	19.00	19.00	1.38	75.00	Good
Electrolytic:						
Sand-blasted....	1	8.90	8.90	27.40	92.90	Good
	2	16.40	16.40	8.92	70.30	Good
Smooth-ground..	1	8.90	8.90	50.60	99.60	Good
	2	16.40	16.40	26.50	69.20	Good

ROUGHENED CAST NICKEL ANODE—This anode was roughened in nitric acid (1:1) and washed in hot and then cold water. At 5.76 amp. per sq. ft. the corrosion is 102.43 per cent: the excess over 100 per cent is due to the mechanical separation of anode particles during the corrosion. At 17.1 amp. per sq. ft. the anode efficiency dropped to 82.50 per cent and at 19 amp. per sq. ft. rose to 86.00 per cent; this increase in efficiency of Run 4 over Run 3 may be attributed to mechanical disintegration of the anode, since corrosion of nickel anode decreases with increase of current density. Considerable sludge formed during each run.

SMOOTH CAST NICKEL ANODE—This anode was ground smooth on a carborundum wheel. The slight increase in anode efficiency in Run 2 over Run 1 is due perhaps to increased surface caused by previous corrosion in Run 1. The anode was re-smoothed on a carborundum wheel and Run 3 was made, resulting in anode corrosion of 42.30 per cent. In Run 4, the efficiency rose again. Sludge formed in each run.

ROLLED NICKEL ANODE—In Run 1 the rolled nickel had a smooth surface. At the low D. C. of 3.6 amp. per sq. ft. the corrosion was very poor, only 5.01

¹ *J. Am. Chem. Soc.*, **29** (1907), 1268.

² *Trans. Am. Electrochem. Soc.*, **29** (1916), 383.

³ Bancroft, *Ibid.*, **9** (1906), 217.

⁴ See Mathers, *Loc. cit.*; Bancroft, *Loc. cit.*; L. D. Hammond, *Trans. Am. Electrochem. Soc.*, September, 1916.

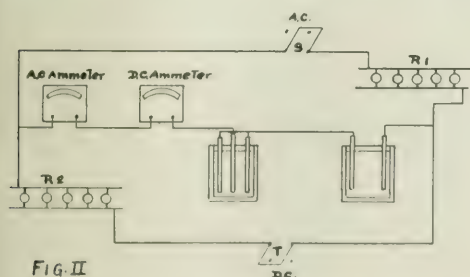
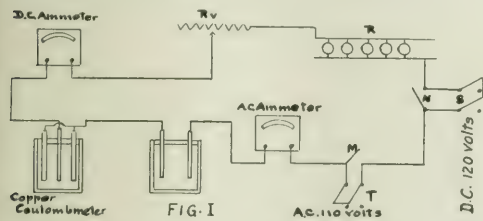
per cent. In Run 2 the anode efficiency decreased. The anode was then dipped in nitric acid (1:1), washed with hot and then cold water, and used in Run 3, this treatment causing the anode efficiency to rise. In Run 4 the efficiency dropped again. The solution after each run was clear and acid to litmus paper. It is to be noticed that the effect of using rolled anodes is to decrease the cathode current efficiency.

ELECTROLYTIC NICKEL ANODE—The corrosion of electrolytic nickel when sand-blasted and when ground smooth was studied under the influence of the continuous current. After each run the anodes were brown, the solutions clear, and the deposits good. Rapid gassing occurred at both anodes, more so in Run 2 than in Run 1. There was slight gassing at the cathodes in Run 1, which increased considerably in Run 2.

Curiously, the sand-blasted anode gave much lower efficiency than the smooth anode, which is contrary to what one would expect, since the sand-blasted anode exposes actually a greater surface than the smooth anode.

II—EFFECT OF SUPERPOSITION OF A. C. ON D. C.

The apparatus arrangement shown in Fig. I was used at first. The A. C. used throughout was taken from a 110 volt lighting main of 60 cycles per second.



In the diagram only the A. C. flows through the circuit when switches *T* and *N* are closed and *M* and *S* are open. When *M* and *S* are closed and *T* and *N* open, only D. C. flows. With *S* and *T* closed and *M* and *N* open, both A. C. and D. C. flow through the circuit.

Any change in resistance obtained by means of *R* and *Rv* affects the value of both the D. C. and the A. C. at the same time. Thus the alternating current and therefore the A. C. voltage drop across each cell could be increased by decreasing the resistance in

the circuit only to a certain extent, beyond which the value of the D. C. would rise to a current density unsuitable for nickel-plating.

After a few runs were made with this arrangement, it was abandoned and the flexible set up shown in Fig. II was used, the A. C. and the D. C. being connected in multiple. By this arrangement the alternating current could be regulated by resistance *R*₁, without affecting the direct current. By means of resistance *R*₂ the continuous current of proper density was obtained. The voltage across the cells was taken (1) with a D. C. voltmeter when both A. C. and D. C. were flowing; (2) with the D. C. voltmeter when D. C. alone flowed in the circuit; and (3) with an A. C. voltmeter when the A. C. alone flowed.

The voltage readings are but indicative and not accurate, due to variations caused by anode impurities, anode idiosyncrasies and changes in distance between electrodes.

The current density of the continuous current in all the runs was kept at or about 8.70 amp. per sq. ft. while the density of the alternating current was varied. The results are given in Table II.

TABLE II—Results with Alternating Current Superposed on Direct Current

Current Densities Given in Amperes per sq. ft. Time of Run, 1 hr., except those marked * which were 2 hrs.							
NICKEL ANODE	Run No.	CURRENT DENSITY		VOLTS		PER CENT EFFICIENCY	
		D.C.	A.C.	A.C. & D.C.	D.C. (a)	A.C.	Cathode
<i>Roughened Cast</i>							
	1	8.70	7.35	2.52	2.57	1.17	108.20 105.00
	2	8.10	8.70	2.49	2.60	1.22	112.00 102.60
	3	8.70	14.40	2.25	2.40	1.25	107.40 102.50
	4	8.70	20.80	2.33	2.72	1.55	111.20 101.50
	5	14.40	44.64	2.30	2.90	3.10	123.30 100.20
	6	14.40	66.25	0.95	1.50	4.00	121.00 102.70
<i>Smooth Cast...</i>							
	1	9.95	7.33	1.50	1.70	0.50	84.33 96.73
	2	9.50	7.85	1.50	1.65	0.55	91.50 93.00
	3	8.70	14.40	2.40	2.60	1.25	99.80 102.90
	4	8.70	28.80	2.40	2.50	1.85	101.20 98.00
	5	14.40	44.64	2.60	3.05	3.10	103.30 101.00
	6	14.40	66.25	1.00	1.50	4.00	118.00 100.50
<i>Rolled.....</i>							
	1	9.95	7.33	2.95	3.05	0.75	2.83 76.00
	2	10.30	8.78	3.10	3.20	0.85	3.59 75.50
	3	12.00	17.30	3.10	3.20	1.30	9.05 88.20
	4	8.70	20.80	2.70	3.11	1.60	22.10 84.00
	5	8.70	24.50	2.65	3.00	1.60	38.30 98.70
	6	8.70	28.80	2.30	2.90	2.10	94.50 97.20
	7	8.70	28.80	2.20	2.92	1.97	98.00 100.70
	8	14.40	44.64	2.50	3.15	2.90	101.20 100.80
	9	14.40	66.25	1.00	3.10	4.00	105.40 101.00
	10	8.70	41.80	1.72	2.85	2.52	100.50 101.50
<i>Electrolytic:</i>							
<i>Sand-blasted....</i>							
	1	8.93	52.4	1.50	2.85	3.10	104.50 99.60
	2*	8.93	50.4	0.90	1.40	4.10	109.60
<i>Smooth-ground</i>							
	1	8.93	52.4	1.67	2.72	2.60	105.00 99.40
	2*	8.93	50.4	0.80	1.20	2.60	110.80

ROUGHENED CAST NICKEL ANODE—A comparison of the results with this anode and those in Table I shows plainly that the A. C. superimposed on the D. C. causes increased corrosion which is more pronounced the higher the density of the A. C. and hence the higher the A. C. voltage across the cell. In all the runs there was slight gassing at both electrodes. Considerable sludge formed during a run.

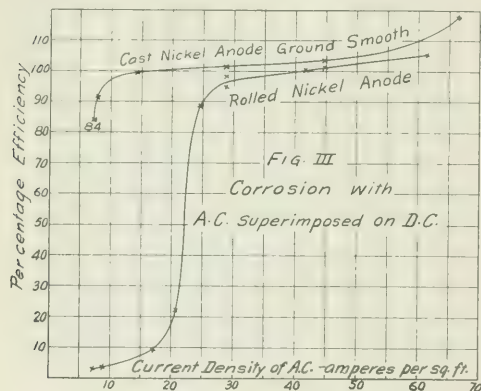
SMOOTH CAST NICKEL ANODE—Here the increase in corrosion of the anode due to superimposing A. C. on D. C. is marked. With D. C. alone (see Table I) at a density of 11.40 amp. per sq. ft. the corrosion was 68.24 per cent. With both A. C. and D. C. the corrosion rises quite rapidly with increase of the density of the A. C. till at 66.25 amp. per sq. ft. the corrosion is 118.30 per cent. The surface of the anode, however, becomes rougher after each run and adds its effect also. There was slight gassing at both electrodes during each run, and the greater the cor-

TABLE III.—RESULTS WITH ALTERNATING CURRENT ALONE
A. 1.30 amperes and 1 hour

CURRENT DENSITY amperes per sq. ft.	CELL 1		CELL 2		CELL 3		CELL 1		CELL 2		CELL 3	
	Electrolytic Nickel Rough	Electrolytic Nickel Smooth	Rolled Nickel	Copper	Coulombmeter		Electrolytic Nickel Rough	Electrolytic Nickel Smooth	Rolled Nickel	Copper	Coulombmeter	
	37.4	37.4	37.4	37.4	22.5 sq. in.	37 sq. in.	7.2	7.2	7.2	7.2	22.5 sq. in.	37 sq. in.
Volts across Cell.....	2.1-2.2	2.1-2.2	2.1	2.1	61.0270	76.5214	0.4-0.5	0.4-0.5	0.4-0.5	0.4-0.5	61.0127	76.4935
Weight in Grams: Before.....	69.3116	78.5935	28.2048	33.1970	61.0127	76.4935	69.2923	78.5865	28.2047	33.1838	61.0072	76.4775
After.....	69.2923	78.5865	28.2047	33.1838	0.0132	0.0143	69.2897	78.5842	28.2029	33.1819	0.0018	0.0019
Loss in Weight (Grams)....	0.0193	0.0070	0.0121	0.0132	0.0143	0.0279	0.0026	0.0023	0.0018	0.0019	0.0055	0.0160
Efficiency, per cent.....	1.37	0.496	0.887	0.935	0.931	1.815						
Per amp. hr. Cu = 1.182		1.182 × 1.30 = 1.636	per 1.3 amp. hr.								Per amp. hr. Cu = 1.182	
Per amp. hr. Ni = 1.085		1.085 × 1.30 = 1.411	per 1.3 amp. hr.								Per amp. hr. Ni = 1.085	

sion, the greater was the amount of sludge which formed. In Fig. III anode efficiency is plotted against density of the A. C.

ROLLED ANODE—The corrosion of the anode is slightly increased at low densities of the A. C. Then the corrosion rises rapidly as the density increases from 17.30 amp. per sq. ft. The solution after each run was clear and the deposit was good. There was slight gassing at both electrodes during the runs in which the anode corrosion was high. With low anode corrosion there was rapid gassing at the anode and little or no gassing at the cathode. The percentage corrosion against the density of the A. C. is plotted in Fig. III.



The rolled anode after continued corrosion presented a rougher surface. The following run was made after the above runs, which shows that the nature of the electrode surface had changed:

Time	Cur. Dens.	Volts	Anode Eff.	Cath. Eff.
1 hr.....	16.40	3.55		95.80%

According to previous runs (Table I) the anode efficiency was only 3.55 per cent at 10.80 amp. per sq. ft. and 1.38 per cent at 19 amp. per sq. ft.

After this run the rolled anode was tried out in the following experiment:

Time	CURRENT DENSITY	VOLTS	D. C.	A. C.	ANODE
Hrs.	D. C.	A. C.	A. C. & D. C.	Volts	EFFICIENCY
2	8.93	50.40	0.80	1.50	3.00 117.80

According to a previous run (Table II) at an A. C. density of 66.25 amp. per sq. ft. the anode corrosion was 105.40 per cent. The nature of the anode sur-

face is therefore an important factor in the corrosion of the anode.

After this last run the rolled anode presented a blackish brown surface which was to a greater or less degree the case in all the runs made with D. C. alone and with A. C. superimposed on D. C. This statement is applicable to all the nickel anodes used.

ELECTROLYTIC NICKEL ANODE—Here, as in all the other cases, the effect of the A. C. on the D. C. was to increase the anode corrosion greatly. The voltage as read by a D. C. voltmeter when A. C. and D. C. are flowing was less than that when D. C. alone passed. The corrosion of the smooth anode was slightly greater than that of the sand-blasted anode, but not markedly so. In either case the corrosion was over 100 per cent.

In Run 2, at a slightly less A. C. density than in Run 1, the corrosion of both anodes is several per cent greater than in Run 1, showing that the surface of the anodes had changed somewhat during Run 1.

III—ALTERNATING CURRENT ALONE

It was thought best to study any changes that might be brought about by the use of alternating current alone. The results are shown in Table III.

In Cell 1, containing the electrolytic anodes, there was slight gassing throughout the run at the roughened electrode. There was no gassing at the smooth electrode, a few bubbles forming on the surface. In Cell 2, containing the rolled nickel, slight gassing occurred throughout the run at both electrodes.

In the copper coulombmeter no visible action was observed. The electrodes, however, lost weight, the efficiency of corrosion of one of them being 0.93 per cent, while the efficiency of the other, which exposed about twice the area of the first, was 1.81 per cent.

The rolled nickel anodes lost about the same amount, viz., 0.86 per cent and 0.94 per cent, respectively.

The rough electrolytic nickel lost more than any of the nickel electrodes, its efficiency being 1.37 per cent, while the smooth electrolytic nickel gave the lowest efficiency of 0.50 per cent.

The results obtained with a lower current density, Table IIIB, show a decreasing corrosive effect upon the electrodes.

CONCLUSIONS

I—With the direct current alone, corrosion at the anode decreases with increase of current density.

II—A. C. superimposed on D. C. greatly increases the anode corrosion with all varieties of anode and this effect increases with the A. C. current density.

III—The increased corrosion at the anode raises the current efficiency at the cathode, particularly with rolled nickel anodes.

IV—Corrosion in general with direct current or with superimposed A. C. is markedly affected by the mechanical nature of the metal.

V—Alternating current alone has but slight corrosive effect at the anode.

ELECTROCHEMICAL LABORATORY, HAVEMEYER HALL,
COLUMBIA UNIVERSITY, NEW YORK CITY

PURIFICATION OF SEWAGE BY AERATION IN THE PRESENCE OF ACTIVATED SLUDGE—III¹

By EDWARD BARTOW

The results obtained in experiments on the purification of sewage by aeration in the presence of activated sludge at the Sewage Experiment Station of the Illinois State Water Survey at the University of Illinois, have been given in previous articles in *THIS JOURNAL*.² The removal of ammonia, and the development of nitrate nitrogen have been discussed. The process has been shown to be essentially bacteriological. By analysis of the sludge, and by cultures of wheat, the sludge has been shown to be valuable as a fertilizer. Experiments in concrete tanks operating on the fill-and-draw plan have shown that sludge can be built up rapidly without seeding from other sludges. During the building-up process the increase of the nitrogen and phosphorus content of the sludge is very rapid. The necessity for oxygen has been shown by the increase of carbon dioxide and the decrease of oxygen in the effluent air. Since the previous articles were written, a large amount of experimental work has been done in many plants in this country and in England. It would be impossible to mention them all in an article of this length, so that we shall confine ourselves almost entirely to the work done at the Sewage Experiment Station of the Illinois State Water Survey at the University of Illinois.

CONSTRUCTION AND OPERATION OF CONTINUOUS-FLOW PLANT

The continuous-flow plant which was put in operation during the summer of 1916 was expected to handle 200,000 gallons of sewage and sludge per day and was built in a septic tank designed by Prof. A. N. Talbot in 1897 for the City of Champaign. The tank was reconstructed for the activated-sludge process. The plant contains a screen chamber and pumping pit, a grit chamber, an aerating chamber, a settling chamber, a blower room and a laboratory containing sludge-drying apparatus (see Fig. 1). A sludge-drying bed and a pond into which the effluent from the process may be discharged are also provided. The sewage is drawn from the main outlet sewer from the City of Champaign. The daily flow is estimated to be from 1,000,000 to 1,500,000 gallons, though in wet weather, owing to seepage into the sewers, the amount of flow is greatly increased. The manhole nearest the septic tank was modified to serve as a screen chamber and

suction pit for the pumps. A screen with vertical bars spaced with $\frac{3}{4}$ -in. openings prevents coarse material from reaching the pumps. A grit chamber 34 ft. long with 2 compartments, each one foot wide, was provided to catch the heavy material. This was later discarded, owing to modifications in the plant which will be described later. The sewage flows from the grit chamber into the aeration chamber, a rectangular concrete tank 17 X 36 $\frac{1}{2}$ ft. in plan and 9 $\frac{1}{2}$ ft. deep. A greater depth would have been desirable, but using an old tank, it was impossible easily to obtain it. The aeration chamber, after allowances are made for baffling and sloping bottom, has a capacity of 36,000 gallons. It is divided longitudinally by 3 baffles into 4 compartments through which the sewage flows a distance of about 140 ft. The lower part of each compartment has sides sloping toward the central part to a channel $\frac{1}{2}$ in. wide and 4 in. deep, and extending the length of the compartment. Above the channel, Filtros plates are supported on T-bars embedded in concrete. The channel below the Filtros plates was divided into sections for six Filtros plates each, with the expectation that each set of plates would be separated from all the others and that the supply of air to each set could be regulated by an air pipe and valve. It was, however, found impossible to regulate independently the air for each set of plates.

The aeration chamber was calculated to treat 144,000 gallons of sewage and sludge daily, if aerated during a period of 6 hrs., 170,000 gallons if aerated 5 hrs., and 216,000 gallons if aerated 4 hrs. From 70,000 to 85,000 gallons of sludge were pumped back into the aeration chamber, for each 100,000 gallons of sewage added. The calculation for the capacity of the chamber was, therefore, reasonably accurate. From the aeration chamber, the mixed sewage and sludge passes to a settling chamber 6 X 10 $\frac{1}{2}$ ft. in plan and 11 ft. deep, at its lowest point, having a capacity of 3,700 gallons. If the sewage and sludge flowed through all parts of the settling chamber it would have a retention period of 24, 31 and 37 minutes, with a flow through the aeration chamber of 4, 5 and 6 hrs., respectively. In order to assist the settling of the sludge the liquid passes down into the center and up around the edge of a hollow frustrum of a pyramid and overflows into drains which entirely surround the settling chamber.

From the settling chamber the effluent flows over a weir and is either returned to the sewer or discharged into a pond, formed by two dams thrown across the abandoned bed of a stream. This pond covers about 0.4 of an acre and has a maximum depth of 2 ft.

The sludge is withdrawn from the settling chamber by an air lift and can be discharged at the point where the raw sewage enters the aeration chamber or be diverted for experimental purposes to be discharged into the sewer. Air is supplied for aeration and for the air lift by a rotary positive pressure blower, having a rated capacity of 100 cu. ft. per minute, driven by a 15-H. P. electric motor. The air is filtered through chemically treated fine glass filter material, and is measured through a Venturi meter.

The plant was operated from May 18 to June 11,

¹ Read at the Buffalo Meeting of the American Institute of Chemical Engineers, June 20, 1917.

² *THIS JOURNAL*, 7 (1915), 418; 8 (1916), 15, 17, and 516.

1916, when it was shut down to repair leaks due to faulty concrete work. Much care should be taken in order to make the concrete air-tight, or cast-iron or metal frames as used at Milwaukee and Cleveland should be used. The plant was again put in operation on July 11, and operated continuously until October 22. The amount of sewage added during weekly periods varied from 61,000 to 177,600 gallons per day. Approximately 2 cu. ft. of air per gallon of sewage was necessary to obtain stable effluents. Undoubtedly better results could be obtained with increased settling capacity, and a steeper slope from the vertical sides to the extreme bottom of the chamber. The actual period of flow through the settling chamber as determined by tests with fluorescein and with salt when the rate of pumping was 133,900 gallons per day, was found to be 20 minutes instead of 34 minutes as calculated. A large chamber, or two chambers possibly, with an arrangement for aeration between them, would undoubtedly increase the capacity of the plant.

For further experiments the plant was modified by cutting out the grit chamber and inserting a short box, into which the sewage was pumped. The box is 4 ft. 9 in. \times 11 in. in plan and 10 in. deep and has a V-shaped weir at the end for measuring the sewage. One-quarter of the aeration chamber was cut off from the remainder for a sludge-aerating tank. This decreased the length of flow in the aeration chamber to 105 ft. The plant was again started January 17, 1917, and has been in operation continuously until the present time, June 12, 1917.

COMPARISON OF METHODS OF AIR DIFFUSION

An important feature of the activated-sludge process is the method of air diffusion. In the original experiments air was introduced into the sewage in bottles through small glass tubes. The relatively large bubbles delivered by this method made it appear feasible that better air diffusion to break up the air stream into smaller bubbles might be productive of increased efficiency, and thus become an important feature in reducing the cost of the process. In the first continuous system experiments conducted at Manchester by Ardern and Lockett,¹ a series of perforated pipes placed at 4 in. intervals and fixed at a depth of 12 in. below the surface was used. In subsequent experiments Ardern and Lockett used porous tile similar to those used by Fowler and Mumford in connection with other work on the clarification of sewage by means of specific organisms. Ardern and Lockett reported that a comparison of the results with those obtained with pipe diffusers showed advantages in favor of porous tile. This was demonstrated in three sets of experiments using (1) an excessive amount of air on a strong sewage, (2) an average amount of air on a dilute sewage, and (3) a minimum amount of air on a dilute sewage. At Salford² a roughing filter was converted into an activated-sludge tank and the air pipes of the filter were used for diffusers. The outlets, 1 in. in diameter, were placed 8 in. apart on the top

and sides of the pipes. Effluents within the requirements of local conditions were obtained. Fowler³ described an arrangement devised originally by Jones and Atwood, which consists of a series of nozzles, one in each square yard of the aeration tank. The scheme was not satisfactory because deposits of sludge formed around each nozzle. In this country, Filtros plates were first used for air diffusion in a small tank in the laboratory of the Illinois State Water Survey, and have since been used rather generally in America.

Much has been written and various opinions expressed regarding kinds of air diffusers. Hammond,⁴ in April 1916, after visiting five working plants, stated that air distribution troubles had been rather general and that he believed that pipe grids were more satisfactory than porous diffusers. Hammond states that the use of porous diffusers has been largely from theoretical rather than practical reasons.

Hatton,⁵ after various experiments, reports that Filtros plates were the most satisfactory medium he has found for air diffusion, but that they should be of uniform porosity, should be properly installed, and all oil and dust should be excluded from the air passing through them. Wooden-block diffusers give good diffusion with least frictional loss. The bubbles are smaller than those obtained by Filtros plates. The experiments, however, are insufficient to warrant their adoption for working-scale installations. Furthermore, the deterioration is apparently rapid.

Pearse and Richardson, in a recent report⁶ on the activated-sludge process for handling Packingtown trade waste, state: "At the present time Filtros plates offer the most satisfactory air distribution. Although the cost of maintenance may be somewhat higher than the perforated-pipe grids, we believe the distribution is better and the size of air bubbles is much smaller with consequent increase of efficiency. The basswood plates, now being tested in Milwaukee, produce a remarkably fine air bubble, insuring a considerable reduction in the use of air. The life of basswood plates is at present very uncertain because of possible decay."

The statements by various authorities concerning the use of diffusers were so decidedly at variance that we were led to make some comparisons of different diffusers in service under identical conditions. The four reinforced concrete tanks used in former experiments and described in a previous paper⁷ were remodelled and each fitted with a different air diffuser (see Fig. II). The tanks operate on the fill-and-draw system and are 3 ft. 2 in. square and 8 ft. deep. At each filling 350 gallons of sewage were added.

One tank (4) was fitted with a system of perforated pipes having perforations one-twenty-fifth of an inch in diameter placed 2 in. apart and staggered at an angle of 45° from the top of the pipes. There were about 40 holes in the pipes or 4 to each square foot of surface

¹ *J. Inst. San. Engrs.*, March and April, 1916.

² *Eng. News*, 75 (1916), 798-801.

³ *Eng. and Contr.*, 45 (1916), 104-8.

⁴ "The Activated-Sludge Process for Handling Packingtown Trades Wastes," Sanitary District of Chicago, 1917.

⁵ *Loc. cit.*

⁶ *J. Soc. Chem. Ind.*, 33 (1914), 523-39, 1122-4.

⁷ *Surveyor*, 46 (1914), 681-2; *J. Soc. Chem. Ind.*, 33 (1914), 1124-30.

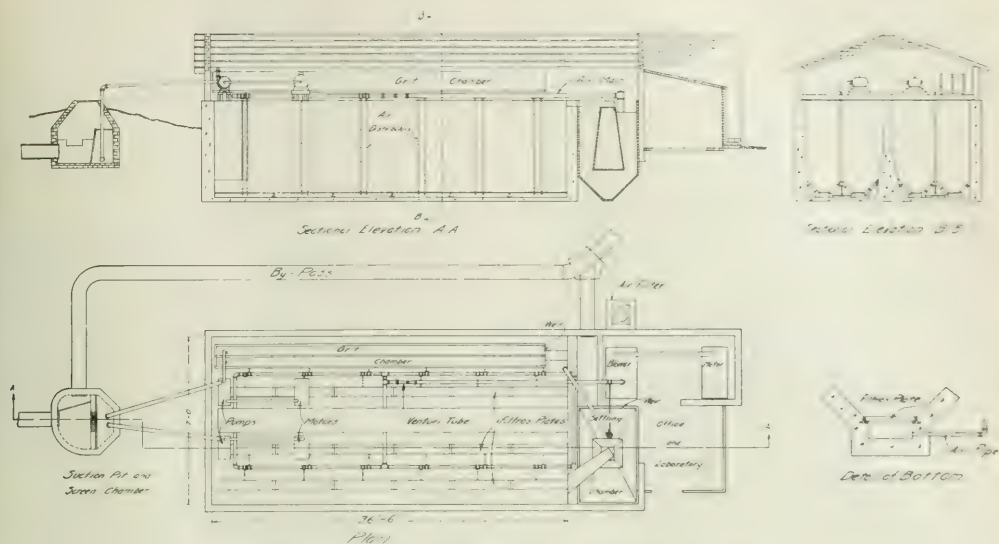


FIG. 1. ILLINOIS STATE WATER SURVEY SEWAGE EXPERIMENT STATION

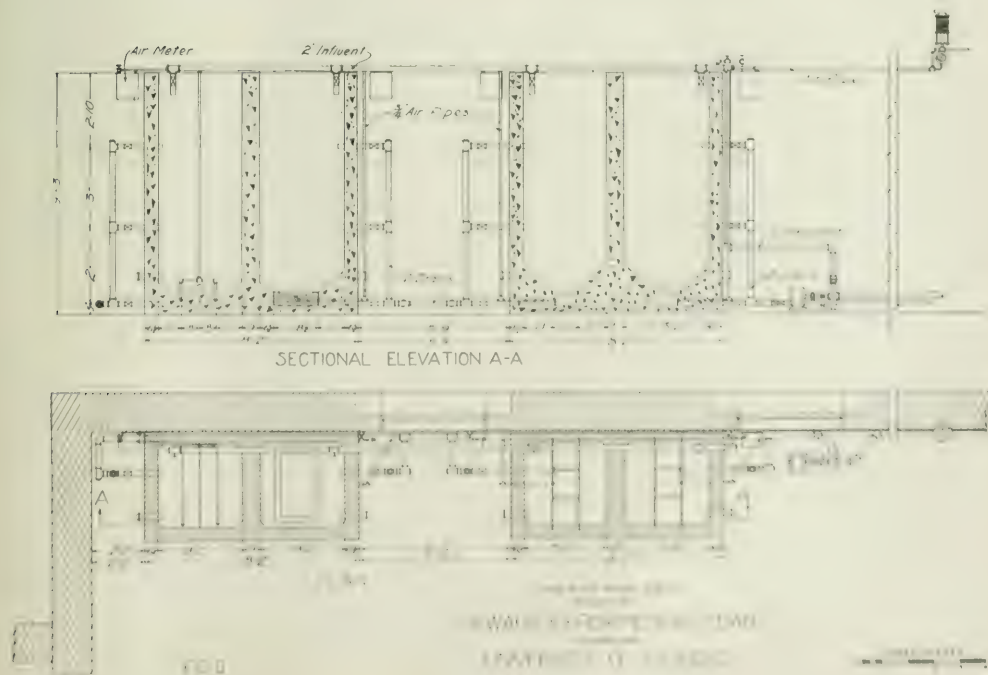


TABLE I. SUMMARY OF RESULTS (PARTS PER MILLION) OBTAINED IN THE COMPARISON OF EFFICIENCY OF METHODS OF AERATION MEASURED IN TERMS OF AMMONIA NITROGEN, NITRATE AND NITRITE NITROGEN, OXYGEN CONSUMED, TURBIDITY AND THE ACCUMULATION OF SLUDGE

Period	AMMONIA NITROGEN				NITRATE AND NITRITE NITROGEN				OXYGEN CONSUMED				TURBIDITY				PER CENT SLUDGE			
	Sew.		Effluents		Sew.		Effluents		Sew.		Effluents		Sew.		Effluents		Sew.		Effluents	
1917	age	A	B	C	D	age	A	B	C	D	age	A	B	C	D	age	A	B	C	D
Mar. 27 to Apr. 1.....	21	17	18	17	0.9	1	2	4.0	3.9	3.9	28	26	19	20	22	282	48	39	46	46
Apr. 1 to 6.....	17	17	16	16	16	4.7	3.9	4.7	6.1	6.3	46	21	18	15	14	317	9	6	6	6
Apr. 6 to 12.....	16	11	9	8	9	8.1	4.9	4.5	5.9	7.2	50	26	24	19	26	190	9	5	5	5
Apr. 12 to 17.....	26	30	29	0	0	3	0.4	0.3	6.8	10.2	85	32	26	25	16	248	7	5	5	5
Apr. 17 to 22.....	21	21	21	0	0	1.2	0.3	0.0	15.0	16.9	306	5	5	5	5
Apr. 22 to 27.....	25	24	33	0	0	1.0	0.2	0.1	25.8	26.0	309	5	5	5	5
Apr. 27 to 30.....	22	30	20	0	0	4.5	0.3	0.0	23.8	24.7	268	5	5	5	5
Average Reduction.....	21	20	19	6	6	2.5	1.7	1.9	12.6	13.6	52	21	22	20	19	274	13	10	11	11
or Percentages.....	5	10	71	71	60	58	62	63	...	95	96	96	96	...
Results April 12-30 after Activated Sludge was Formed																				
Average Reduction.....	24	24	28	0	0	1.7	0.3	0.1	17.8	19.4	55	32	26	25	16	283	5	5	5	5
or Percentages.....	0	4	100	100	41	53	54	70	...	98	98	98	98	...

A, tank with perforated pipes; B, wooden blocks; C, fine Filtros plates; D coarse Filtros plates.

area. The bottom of the tank is sloped from the center and sides at an angle of 45° , thus forming two V-shaped channels of equal size, 1 ft. in depth, running entirely across the tank.

The bottom of the second tank (B) was hopped from all four sides and a concrete container for wooden-block air diffusers was placed in the bottom of the hopper. The container was patterned after one designed by Nordell¹ and used at Milwaukee in the Nordell aerating tank. The container is a one-piece casting 2 ft. 8 in. long, 1 ft. $8\frac{9}{16}$ in. broad, and 5 in. thick with a receptacle for the blocks 1 ft. $3\frac{9}{16}$ in. by 2 ft. 3 in. in plan, $\frac{3}{4}$ in. deep at the edge, and $1\frac{1}{4}$ in. deep at the center. The wooden blocks rest upon a series of thirteen ridges, $1\frac{1}{2}$ in. wide and $\frac{1}{4}$ in. high that run across the receptacle, leaving a $\frac{1}{4}$ in. space underneath for the air to circulate. The surface of the container was cast on a curve so that the tendency of the wooden blocks on swelling would be to wedge themselves more firmly into position. The basswood blocks used in our experiments were very kindly furnished us by T. Chalkley Hatton. They were $\frac{1}{2}$ in. thick, 6 in. long and $2\frac{1}{8}$ in. wide. At first difficulty was experienced in keeping the blocks in position because of the excessive swelling that took place when they were placed under water and also because they became soft and spongy. Many of the blocks became so curved and twisted that they were discarded. It was found necessary to place strips of heavy galvanized iron on edge between each row of blocks for reinforcement and to close up certain joints with oakum.

Filtros plates of different porosity, kindly furnished by the General Filtration Co., were placed in two of the tanks (C and D). Three plates were used in each tank, covering one-third of the area and forming the bottom of a trough with sides sloping at an angle of 45° . The plates of the third tank (C) were marked "fine," because on the basis of dry rating these plates passed 5.8 cu. ft. of air per minute per square foot under a water pressure of 2 inches. When saturated with water and passing 2 cu. ft. of air per minute they showed a resistance on a water gauge of 11.4 to 11.8 in. The fourth tank (D) was equipped with plates marked "coarse" which, on the same basis, passed 12 cu. ft. of air per minute per sq. ft. When passing 2 cu. ft. of air per minute these plates registered a resistance of 8.8 to 9.6 in. of water pressure.

The tanks were operated during three periods of

15, 20, and 35 days, respectively. Each of the tanks was operated in three aeration periods daily of 510, 300, and 270 min. with a 2-hour allowance between the periods for settling, emptying and filling. The same amount of air as measured by ordinary gas meters was added to each tank. All conditions were maintained as nearly identical as possible. The sewage was pumped from the main sewer just outside the city limits of Champaign and accordingly was fresh. It was a fairly strong, domestic sewage with no trade wastes. No activated sludge was added to the tanks at the beginning of any of the series of tests.

Samples of sewage were taken as the sewage was being pumped into the tanks and samples of effluents were collected at the close of each aeration period after the sludge had been allowed to settle for 30 minutes. The methods of analysis were those given in the 1917 edition of "Standard Methods for the Examination of Water and Sewage of the American Public Health Association."

The third series of tests, which lasted 35 days, was the most satisfactory (see Table I). There was no sludge present at the beginning and, owing to the length of the test, at times some of the excess of the accumulated sludge was wasted. No accurate comparison of the sludge accumulation at the end of the series can be made. The maximum amount of sludge was reached last in the tank with perforated pipes. Removal of turbidity and oxygen-consuming capacity was practically the same in all tanks. Measured in terms of removal of ammonia nitrogen and in production of nitrate nitrogen the tanks with Filtros plates were decidedly superior. Ammonia nitrogen was entirely removed in the tanks with Filtros plates after 17 days. Owing to rains, nitrate nitrogen was present in the raw sewage during the early part of the series and continued to increase in the tanks containing Filtros plates, reaching about 25 p. p. m. Practically all of the nitrate nitrogen disappeared from the other tanks. The poor results from the tank with wooden blocks were probably caused by the development of a hole in the tank, which prevented the formation of finely divided bubbles. The stability to methylene blue was tested on and after the eleventh day and all effluents from the tanks containing Filtros plates were stable for 10 days at 20°C . Most of the effluents from the other tanks were unstable. Nearly 30,000 gallons of sewage were treated in each tank with 3.2 cu. ft. of free air per gallon. The sludges in

¹ Annual Report of Sewerage Commission of Milwaukee (1916).

the tanks with Filtros plates settled better and after removal at the end of the series, had specific gravities of 1.013 and 1.022, compared with 1.006 for the sludges from the other tanks.

The results obtained from these comparative tests indicate the superiority of Filtros plates as air diffusers over perforated pipes, such as were used in our tests under the conditions maintained. The wooden blocks were difficult to handle though this was caused in part by the faulty design of our containers. Even in the time they were used, there was evidence of considerable deterioration. From the results obtained we could distinguish little, if any, difference between the coarse and fine grades of Filtros plates. With air free from dust and oil there should be little trouble experienced from clogging of plates.

DEWATERING OF ACTIVATED SLUDGE

Satisfactory purification of sewage has been obtained by us and by many others, but before the method can be considered an unqualified success a practical and economical method of drying the sludge must be found. Various methods have been tried by different investigators, but we have at the risk of duplication experimented with many of these methods. Although drying on sand-beds had been tried at Cleveland, and we had ourselves tried it, we thought wise to repeat the experiments on better constructed beds than were used in our previous work. The experiments were not successful. Owing to the large amount of moisture in the sludge, 98 to 99 per cent, the solid matter obtainable from a foot depth of sludge would be only from one-quarter to one-half an inch, according to the residual moisture content. It was also difficult to separate the sludge and sand. The fertilizer obtained was more or less impure and of decreased value. The sand beds used were one-hundredth of an acre in area and divided into five compartments. Underdrains were overlain with 10 in. of coarse gravel and 8 inches of sand. The beds were provided with a canvas cover supported on a framework so that they could be protected during storms. One compartment was allowed to dry after a single filling, another after two fillings, and another after three fillings. In no case were the results sufficiently satisfactory to warrant the use of sand beds for the drying of the sludge and the production of a commercial fertilizer.

Experiments with a filter press with leaves 8 1/4 in. square operating on a fairly concentrated sludge were also unsatisfactory. It has thus far been impossible for us to obtain a cake of good consistency. Further experiments are to be tried with the hope that better results can be obtained.

Through the courtesy of the Koering Cyaniding Company, of Detroit, a rotary filter was placed at our disposal. This style of filter is used satisfactorily in filtering slimes in extracting gold and silver by the cyaniding process. The apparatus consists of a cylinder of Filtros plates supported on a perforated steel cylinder out side of which, at a distance of about one inch, is a solid steel outer shell. The material to be filtered is forced into the interior of the cylinder of

Filtros plates, the cylinder is revolved and a cake of sludge is built up on the inside of the plates. The liquid filters through the plates into the space between the cylinders. Air pressure can be exerted from the interior to dry the cake, and from the exterior to loosen it. The plates can be cleaned by back-flushing with water. The first trial with a comparatively heavy and not very fresh sludge did not give satisfactory results. The quick-opening door could not stand the pressure. Another trial will be given as soon as the door can be replaced.

Mohlman¹ reported experiments with two small centrifuges, one of the low-speed basket type and the other of the high-speed bottle type. The basket of the low-speed machine was 8 in. in diameter and 6 in. deep. The periphery was perforated with numerous holes 1/16 in. in diameter. When the holes were covered with a strip of muslin cloth, approximately one gallon of 98 per cent moisture sludge was put into the centrifuge and after 15 minutes, 700 g. of 91 per cent moisture sludge were obtained. The high-speed bottle-type machine reduced the moisture from 98 to 92 per cent in 3 minutes. Mohlman stated that in order to be economical there should be an automatic arrangement for removing the cake. The most successful apparatus of this type is the Schafer-ter Meer centrifuge described by Hammond.² This machine is said to be very efficient but was too expensive for us to obtain for experimental work.

At Cleveland, Pratt and Gascoigne³ used a laundry centrifuge with a 26 in. basket, lined with a 1/4 in. wire mesh inside of which was a canvas bag. In the best run, when the basket revolved at about 1200 r. p. m., 60 gallons of 97.5 per cent moisture sludge was added in about 25 minutes and in 2 hours the moisture content was reduced to 84 per cent. The time required would seem to make this process impracticable.

Working on the assumption that the principle used in drying of china clays or that used in the cream separator might be applicable, a modified basket-type centrifuge and a modified cream separator were tried. The holes of an 8-in. basket-type centrifuge were covered with a strip of rubber packing. The best results were obtained with 1500 r. p. m., which was the limiting speed of the machine. This would seem to indicate that the process would give efficient results if carried on at an increased speed, but would yield an effluent that must be returned with the sewage to the aeration chamber. A series of tests was made with a cream separator, the bowl of which was modified, by removing the inner disks and discharging the clarified liquid about an inch from the center of the bowl at the top. The sludge added at the top dropped to the bottom of the bowl, and the liquid was thrown out over the rim. Sludge cakes containing from 88 to 80 per cent moisture were obtained by the cream separator in 6 to 8 minutes, which encouraged us to obtain a small machine for further experiments.

A specially designed centrifuge was purchased from

¹ *Trans. American Soc. Heating, Vent. & Air-Cond.*

² *Eng. News* 78 (1914) 879.

³ *Proc.* 76 (1916) 1224.

the Tolhurst Machine Works, of Troy, New York. This machine is 12 in. in diameter, 9½ in. high and at a speed of 1800 r. p. m. exerts a centrifugal force of 550 lbs. According to its concentration, from 10 to 25 gallons of the sludge are added and 10 lbs. of cake obtained. The sludge cake contains about 88 per cent moisture. The space underneath the rim contains 0.158 cu. ft. Owing to the small size of the machine and to the fact that the material must be scraped out, the time of cleaning is longer than would be required for a larger machine with an opening in the bottom, so that a large machine could undoubtedly have been filled and emptied more rapidly than the small laboratory machine. We have found it entirely possible to fill and empty the small machine 4 times in one hour. Calculating that the same rate could be used with a 40-in. machine having 46 times the capacity, we could obtain in each filling 460 lbs. of sludge of 88 per cent moisture, equivalent to 55 pounds of dry material. One 40-in. machine would, therefore, deliver the equivalent of 2200 lbs. of dry material in a working day of 10 hrs. On the supposition that one-half ton of dry material will be obtained from 1,000,000 gallons of sewage, one machine would dewater the sludge from 2,000,000 gallons of sewage per day. The cost of the 40-in. machine at present is only \$750 and the power to run it is small enough to make the process appear practical for preparing sludge cake for a dryer.

The actual cost of dewatering will depend upon the amount of water that can be removed by the centrifuge, the size of dryer and the amount of coal required for removing the residual water. A drying test using 220 lbs. of 88 per cent sludge cake made by the John P. Devine Co. indicates that the dewatering process can be made practical.

The author desires to acknowledge his indebtedness to the members of the staff of the Illinois State Water Survey, and especially to J. F. Schnellbach, F. L. Mickle, W. D. Hatfield, and E. Greenfield for their interest and assistance in carrying out the experimental work.

STATE WATER SURVEY
UNIVERSITY OF ILLINOIS, URBANA

THE ANALYSIS OF SULFATED OILS

By RALPH HART

Received July 19, 1917

INTRODUCTION

The present methods for the analysis of Turkey-red oils have proven to be inadequate for the routine work of this laboratory where several such analyses have to be made every day. The determinations of importance in such products are the percentages of total fat and of combined sulfuric anhydride. The methods usually employed for total fat are (1) to extract with ether, or (2) to decompose with acid and to measure the volume of the oil which separates. Both methods were found unsuitable for our purposes; besides other reasons, the former was too tedious, and the latter consumed too much time.

The present method for the determination of combined sulfuric anhydride requires two gravimetric

analyses, and, because of its length, its application for factory control is limited. It was noted, however, that this determination afforded an excellent means of judging and controlling the manufacture of sulfated products, as is illustrated by the following case. A commercial Turkey-red oil, which was at first passed as satisfactory, was found on analysis to contain 40 per cent less bound SO_3 than it should have. As a result, the oil was retested in a practical way, and found to be faulty in many respects. The cause of the trouble was later traced to hot weather, which caused the temperature of the unwashed sulfated oil to rise during the night.

To insure uniformity in shipments, this laboratory has made it a practice to estimate the amount of fat bound as soap, and the amount present as free fatty acids; the former was determined by titrating a water solution of the sample with H_2SO_4 in presence of methyl orange, and the latter by titrating the alcoholic solution with NaOH in presence of phenolphthalein. It occurred to the writer that it might be possible to saponify completely the rest of the fat by ordinary means. A few experiments proved that such was the case, and this fact was utilized to develop a new method for the determination of fat. A short method for combined SO_3 and ammonia was also worked out at the same time.

By our new procedure, we are able to determine, within a reasonable length of time, not only total fat and sulfuric anhydride, but also ammonia and caustic soda. Furthermore, this method makes it possible to estimate from the data obtained for the other tests the amount of fat present as soap, as free fatty acids and as esters, lactones, etc.; the only additional test required is for free fatty acids, which is determined as mentioned above.

PRESENT METHOD FOR FAT

The technical procedure¹ for the determination of fat in Turkey-red oils, Monopole oils, Sulfo Textol oils, etc., is to decompose with acid a sample contained in a special flask having a long neck graduated in cc., and to boil the contents until the oil is clear. The latter is then brought within the graduation on the flask by pouring in a saturated salt solution. The per cent fat is then calculated from the volume of the oil and its specific gravity which is assumed to be 0.945 at room temperature.

This method presents many difficulties; for example, during the heating, the oil which spreads on the surface of the water prevents the latter from boiling freely, and, unless the flask is vigorously and constantly agitated, the contents are likely to spout out. Holde¹ says: "A disadvantage of the method is the fact that the layers do not completely separate, the deviation in results being as much as 1 per cent." Another source of error is that the contraction of the contents in the flask on cooling leaves behind a film of oil which is not taken into account. Finally, it has lately been almost impossible to obtain a flask of this type that will not break on heating.

A modified method is to heat the contents of the

¹ "Examination of Hydrocarbon Oils," D. Holde, 1915 edition, pp. 409 and 410. English translation by E. Mueller.

flask on the steam bath over night, or until the oil is clear. Hot salt solution is then added and the flask is immersed in the steam bath for an hour, or until the oil column becomes clear. The last procedure, if carefully carried out, gives fairly good results and was used to check our data.

NEW METHOD FOR FAT

For our purpose, we may consider that commercial Turkey-red oil consists of the following substances: (a) ammonia or soda salts of the acids $\text{HOC}_{17}\text{H}_{32}\text{CO}_2\text{H}$, $\text{HOSO}_3\text{C}_{17}\text{H}_{32}\text{CO}_2\text{H}$, and polymerized acids; (b) unchanged castor oil, lactones, etc. Benedict and Ulzer¹ state that sulfo-ricinoleic acid is not decomposed on boiling in alkaline or neutral solutions, but is easily decomposed into ricinoleic and sulfuric acid by boiling with dilute mineral acids.

The determination of fat, as developed in this laboratory, is carried out in two steps: (1) a solution of the oil is titrated with $N/2 \text{ H}_2\text{SO}_4$, in presence of methyl orange, and the alkalinity is calculated in mgs. KOH per g. of sample; (2) in another sample the saponification value of the unsaponified oil is determined in the usual manner. The sum of the two results divided by the acid number of the original castor oil fatty acids gives the per cent fat.

In case of samples whose acid numbers are not known, the average value of 190 is assumed. The acid numbers of castor oil fatty acids, as calculated from the saponification values given by Lewkowitsch,² lie between 186 and 194, or an average of 190. In assuming this figure, therefore, the maximum error is about 2 per cent of the fat, and since most commercial Turkey-red oils contain about 50 per cent fat, the average maximum error due to this assumption is around 1 per cent.

The success of this method depends obviously upon the complete saponification of the oil, and upon the accuracy with which the alkali bound as soap can be determined. The saponification is carried out in the usual manner by heating with $N/2$ alcoholic NaOH, save that the heating is prolonged to 45 minutes. Check analyses are easily obtained.

The alkalinity necessary for the fat calculation must be that which corresponds to the soda (or potash) soap only and not to the ammonium soap, as the latter acts like fatty acids during the saponification, and consequently the fat corresponding to the ammonium soap is allowed for in the saponification value. To this end, the solution is heated with a measured amount of standardized NaOH, boiled to expel ammonia, and then titrated with $N/2 \text{ H}_2\text{SO}_4$ in presence of methyl orange. With a little experience, the endpoint offers no difficulty, and check analyses corresponding to 0.2 per cent fat are easily obtained.

Even where no ammonia is present, it is best to proceed in this manner, in preference to titrating the original solution directly, that is, without the addition of alkali. The boiling with excess alkali serves as a blank on the saponification test, and avoids errors due

to the partial saponification of the sulfo group, which occasionally occurs with some Turkey-red oils.

In case the sulfated oil was entirely neutralized with ammonia, a negative alkalinity will be obtained after expelling the NH_3 , *i. e.*, the alkalinity will be less than the amount of alkali added. This is due to the fact that the NH_3 in the ammonium salt of sulfo-ricinoleic acid is displaced by NaOH on boiling; this displacement, which is quantitative, also occurs during saponification, and evidently must be subtracted from the saponification value. Such products can still be analyzed by this method with good results, as shown in the table on page 852 by Sample 1, which was entirely neutralized with ammonia.

The reliability of the fat determination, calculated from the alkalinity and saponification values, may be judged by comparing the percentage of fat thus determined (Col. III) with the fat found by the flask method (Col. II). Col. IV gives the per cent yield in fat as obtained in large commercial batches, the fat being determined according to the new method. The average yield was 95.7 per cent, which compares very favorably with the theoretical yield of 96 per cent.

AMMONIA

To determine ammonia, two samples are analyzed for alkalinity; in one, the alkalinity is determined as described above, and in the second, it is similarly determined except that the boiling with caustic soda is omitted. The difference between these two determinations is evidently due to the ammonia, and may be used to calculate it. This is much simpler than the usual method of distilling with excess NaOH, and absorbing the ammonia in standardized acid. The results obtained by this method were very good, and are tabulated in Cols. VI and VII; where ammonia is reported as present, known amounts were added either to commercial batches or to laboratory samples.

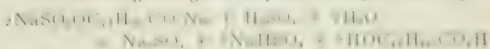
PRESENT METHOD FOR SO_2

Sulfo-ricinoleic acid on boiling with dilute mineral acids, as already mentioned, decomposes, giving as one of the products, free sulfuric acid. The usual method for determining combined SO_2 is to boil the oil with hydrochloric acid. The fatty matter is then extracted with ether and the total SO_2 is determined in the water layer as BaSO_4 . In another sample the SO_2 bound to alkali is determined by washing the oil dissolved in ether with concentrated salt solution, and analyzing the latter for H_2SO_4 . The difference between these two gravimetric analyses gives the combined SO_2 . The following is a much simpler method:

NEW METHOD FOR SO_2

The oil is treated with a measured amount of standard H_2SO_4 , boiled until the boiling solution is complete, and finally neutralized with standardized alkali in presence of methyl orange.

The following changes take place during the boiling:



After heating, the original acidity of the solution (measured as methyl orange) is altered, and increased by the formation of Glauber's salt, and is increased by the NaHSO_4 .

¹ "Analyse der Fette," Benedict and Ulzer, p. 348.

² "Chemical Technology and Analysis of Oils, Fats and Waxes," Lewkowitsch, p. 611.

Sample No.	I Appearance of Water Solution	II PER CENT FAT		IV Per Cent Yield	V Acid Value of Fatty Acids	VI PER CENT NH ₃ Added	VII New Method	VIII PER CENT BOUND SO ₂ Gravimetric New Method		IX New Method
		Method	Method					Method	Method	
1 (b)	Opalescent (e)	73.5	73.7	95.3	188	1.81	1.81	5.78	5.63	
2	Opalescent (e)	77.0	77.1	96.0	188	None	...			
3	White Emulsion	73.8	74.2	95.7	188	None	...	4.12	4.09	
4	White Emulsion	78.5	78.3	96.3	188	None	...			
5 (e)	Clear Soluble	36.6	36.0	95.4	188	0.730	0.733	2.04	1.87	
6 (e)	Clear Soluble	32.6	32.1	95.5	188	0.375	0.385	1.75	1.64	
7 (d)	Opalescent (e)	82.5	83.0	..	188	None	...			
8	Opalescent (e)	60.1	59.0	..	Assumed 190	...	0.364			
9	Opalescent (e)	68.5	69.0	..	Assumed 190	...	None			
10	Clear Soluble	40.4	40.1	..	Assumed 190	...	None			

(a) Average yield 95.7%; theory 96.0%. (b) Neutralized entirely with ammonia. (c) Neutralized partly with ammonia. (d) Sulfated castor oil soap. (e) Changes to white emulsion on standing or on warming.

The net change in acidity, which is given by the titration, is equal to the difference between the total alkalinity due to the soap and the acidity due to the NaHSO₄. The total alkalinity of the original sample is obtained as above. Hence, the acidity corresponding to NaHSO₄ or combined SO₂, can be calculated. It is to be noted that 80 parts SO₂ is equivalent, in this case, to 56.1 parts of KOH. Cols. VIII and IX give the results obtained by the gravimetric method and our present method, respectively.

PROCEDURE

Below is given in detail the analysis of a Turkey-red oil which was partially neutralized with ammonia. The solutions required are: standardized $N/2$ H₂SO₄, $N/2$ NaOH, and approximately $N/2$ alcoholic NaOH. All titrations were made in presence of methyl orange, unless otherwise indicated.

TOTAL ALKALINITY—Ten grams were weighed into a 250 cc. Erlenmeyer flask, balanced on a scale sensitive to 5 mg. (all weighings were made in this manner), 150 cc. water added, and titrated with $N/2$ H₂SO₄. The titer of the acid was 27.02 mg. KOH, and the titration required 17.2 cc.

$$\text{Total alkalinity} = \frac{17.2 \times 27.02}{10} = 46.5 \text{ mg. KOH per g.}$$

ALKALINITY AFTER NH₃ WAS VOLATILIZED—Eight grams were dissolved in 100 cc. water in a 500 cc. beaker, 25 cc. $N/2$ NaOH added, and gently boiled until litmus paper no longer indicated ammonia (about one-half hour). Water was added and the alkali titrated with $N/2$ H₂SO₄. The titer of the caustic was 27.30 mg. KOH, the acid 27.02, and it took 31.85 cc. of the latter for the titration.

Alkalinity without ammonia

$$= \frac{31.85 \times 27.02 - 25 \times 27.30}{8} = 22.3 \text{ mg. KOH}$$

Should the sample contain a high percentage of fat (shown by the high viscosity and also by the fact that such samples give with warm water white emulsions) double the amount of caustic soda should be used.

From the above data, the ammonia was calculated as follows:

$$\text{Ammonia} = 46.5 - 22.3 = 24.2 \text{ mg. KOH, or, } 0.733 \text{ per cent NH}_3.$$

SAPONIFICATION VALUE—Eight grams were weighed into a 250 cc. Erlenmeyer flask provided with a long glass tube to serve as a reflux condenser, and 25 cc. $N/2$ alcoholic NaOH added. The flask was heated on a steam bath for 45 minutes, neutral alcohol added, and excess NaOH titrated with $N/2$ acid in presence of phenolphthalein. The blank took 23.4 cc. of acid, the titration required 9.95 cc., and the titer was 27.02.

$$\text{Saponification value} = \frac{(23.4 - 9.95) 27.02}{8} = 45.4 \text{ mg. KOH}$$

The alcoholic caustic should be filtered to remove carbonate. The titration should be carried out immediately after saponification, as otherwise the absorption of CO₂ from the air makes the end-point

indistinct. Double the amount of caustic should be used for concentrated samples.

The acid value of the castor oil fatty acid being known (188) the fat was calculated as follows:

$$\text{Fat} = \frac{22.3 + 45.4}{188} = 36.0 \text{ per cent}$$

COMBINED SULFURIC ANHYDRIDE—Eight grams were gently boiled for one hour with 25 cc. of standardized H₂SO₄ solution in a 300 cc. Erlenmeyer flask, provided with a condenser as for saponification. The flask was frequently shaken. Before disconnecting, the condenser was washed out with water by a spray from a wash bottle. The sample was then titrated with caustic soda. The end-point was best observed by adding excess alkali and finishing the titration with acid. It took 21.15 cc. of the alkali to neutralize the excess acid; the titer of the alkali was 24.48 and of the acid 31.4 (in the calculation, it should be kept in mind that the acid is partly neutralized by the alkali in the oil, which, in this case, is equivalent to 46.5 mg. KOH).

$$\text{Combined SO}_2 = \left(\frac{21.15 \times 24.48 - 25 \times 31.4}{8} + 46.5 \right) \frac{80}{56.1} = 1.87 \text{ per cent}$$

CONCLUSIONS

I—Turkey-red oils and similar products are completely or nearly completely saponified by $N/2$ alcoholic NaOH.

II—Alkali bound as soap can be determined by titrating its solution with acid in presence of methyl orange.

III—It is feasible to calculate the combined SO₂ from the increase in acidity due to the splitting of the sulfo group.

IV—Based on these fundamentals a rapid method has been developed whereby sulfated oils can be analyzed for fat, ammonia and caustic soda bound as soap, and for sulfuric anhydride in the form of sulfo-ricinoleic acid.

Acknowledgments are due to Dr. F. Sonneborn and to Dr. F. W. Breth of this laboratory, for valuable suggestions and corrections.

LABORATORY L. SONNEBORN SONS, INC.
NEW YORK CITY

THE DETERMINATION OF TANTALUM IN ALLOY STEELS

By G. L. KELLEY, F. B. MYERS AND C. E. ILLINGWORTH

Received June 21, 1917

The number of methods so far published for the determination of tantalum in steels is small. Most of these deal with the determination of the element in a carbon steel and do not indicate methods available for use with steels of a more complex character. The methods outlined below may be used for the determination of tantalum in steels containing nickel, cobalt, aluminum, chromium, vanadium and tungsten in addition to other elements usually present in steel. Titanium interferes.

PROCEDURE IN THE ABSENCE OF TUNGSTEN

The weight of the sample should be 1 g. for 2 to 5 per cent tantalum steels, 2 g. for those containing 0.5 to 2 per cent and up to 10 g. for lower percentages. The sample is best dissolved in 1:1 hydrochloric acid with heat, and evaporated to dryness. The residue is treated with hot dilute HCl, boiled for a few minutes, and the solution filtered. Both the filtrate and the residue on the filter paper are to be saved. The filtrate is next evaporated to small volume, during which process the iron is oxidized by the addition of a small amount of nitric acid to the boiling solution. When the bulk has been reduced to a point where the solution has a syrupy consistency, 50 cc. of concentrated hydrochloric acid are added and the evaporation repeated. On cooling, the iron may be extracted from the solution with ether. The aqueous layer is then boiled to remove dissolved ether and treated with a slight excess of ammonia to precipitate the tantalum. If more than traces of chromium and vanadium are present, after extraction with ether, the solution should be evaporated with 15 cc. of sulfuric acid (sp. gr. 1.58) until fumes appear. It is then carefully diluted with hot water to a volume of 300 cc., and 20 cc. of a solution of silver nitrate (1 g. in 1 liter) and 3 g. of ammonium persulfate added, after which it is further boiled. This oxidizes the chromium and vanadium to chromate and vanadate, in which state they do not interfere with the determination. Ammonia in slight excess is then added as above and the solution boiled again. The precipitate in any case will contain all of the tantalum and aluminum which was in solution, together with variable, but generally small amounts of chromium, vanadium and manganese. The solution is filtered and the precipitate after washing is combined with the insoluble residue collected in the first filtration. The precipitates are ignited in a platinum crucible at a moderate temperature in order to avoid making the subsequent solution of aluminum and chromium difficult. Two to five grams of fused potassium acid sulfate were then added and the whole fused several minutes at a moderate temperature. The fused mass is then leached with hot 1:1 hydrochloric acid and filtered. SiO_2 and Ta_2O_5 are collected on the filter paper. This residue is now ready for ignition in a weighed platinum crucible. The residue in the crucible is treated with a few drops of concentrated H_2SO_4 and 2 to 5 cc. of hydrofluoric acid to remove silica. After evaporating the sulfuric acid and igniting, the residue is weighed as Ta_2O_5 . The factor is 0.82.

PROCEDURE WHEN TUNGSTEN IS PRESENT

The size of the sample is as described above. Solution is made in 1:1 hydrochloric acid which is oxidized while hot by the dropwise addition of nitric acid. The solution is then diluted with 4 volumes of water and boiled for several minutes. The tungstic oxide is then filtered out and washed thoroughly with water containing a little hydrochloric acid. The wash waters and filtrates are combined and evaporated until the solution has a syrupy consistency. Fifty cc. of concentrated HCl are then added and the evaporation re-

peated. At this point the ferric iron is extracted with ether and the aqueous layer saved. During the preceding evaporation there will usually be no separation of either SiO_2 or Ta_2O_5 , but if such a separation does occur the precipitate should be filtered out and treated like the tungstic oxide precipitate.

The precipitate of tungstic oxide should be washed into a beaker, and water and ammonia added to dissolve the tungstic compounds. The residue which may contain Ta and traces of Fe, W, Cr, etc., is collected on a filter paper and saved.

The aqueous layer left after the ether extraction is boiled to remove the ether, 15 cc. of sulfuric acid (sp. gr. 1.58) added, and the solution evaporated until fumes appear. The object is to remove chlorides. The solution is next carefully diluted to a volume of 300 cc. with hot water and 20 cc. of a solution of silver nitrate (1 g. in 1 l.) and 3 g. of ammonium persulfate added. Boiling one or two minutes oxidizes Cr, V and Mn. Ammonia then precipitates an impure hydrated tantalic oxide as described above, leaving most of the chromium and vanadium in solution. After boiling a few minutes, it is allowed to settle, and filtered. This precipitate is combined with the insoluble residue left after dissolving the tungstic oxide in ammonia. The procedure from this point is exactly as described under the procedure in the absence of tungsten except that the residue of Ta_2O_5 and SiO_2 obtained by leaching the bisulfate fusion with hydrochloric acid may in this case contain a little tungstic oxide. Therefore, after washing it with acid and water, it should be covered with a dilute solution of ammonia and finally washed with water. Ignition followed by treatment with hydrofluoric and sulfuric acids gives Ta_2O_5 .

It is to be noted that the precipitate obtained in the manner described above contains Cb_2O_3 if this is present. At this writing, it is not generally of interest to know separately the percentages of Ta and Cb present in a sample of steel, but where such information is desirable separation must be made by the known methods by work on the residue described in this paper as Ta_2O_5 .

EXPERIMENTAL

A sample of ferro-tantalum was analyzed by the method given by Arnold and Ibbotson. A portion of this sample which contained 3.5 per cent of Al besides about 70 per cent of Ta, was covered with hydrofluoric acid in a platinum dish and nitric acid added drop by drop. When the alloy was completely dissolved the solution was evaporated to perhaps half of its former volume. At this point 20 cc. of sulfuric acid (sp. gr. 1.58) were added and the solution again evaporated slightly. This gave a solution which remained clear several days on diluting with water. By calculation based upon the weight of the ferro-alloy taken, the strength of the solution was found to be such that 25 cc. contained 0.011 g. of tantalum. To test our method 2.5 cc. portions of this solution were added to 2 g. portions of plain carbon, nickel-chromium and high-speed steels, the latter containing 4 per cent of chromium, 2 per cent of vanadium,

and 14 per cent of tungsten. Acid to dissolve the steel was then added and the analyses made as described above. The analytical results which we obtained in testing our method are given in the table below:

DETERMINATION OF TANTALUM IN THE PRESENCE OF CERTAIN OF THE CONSTITUENTS OF ALLOY STEELS

50 and 100 cc. portions of ferro-tantalum solution added to 2 g. samples of steel

KIND OF STEEL	PER CENT TANTALUM	
	No. Added	Found
Plain Carbon.....	1 1.05	1.06
	2 2.10	2.05
Chromium-Nickel Steel.....	1 1.05	1.03
	2 2.10	2.10
Chromium-Vanadium-Tungsten Steel.....	1 1.05	1.00
	2 1.05	1.09
	3 2.10	2.05
	4 2.10	2.27

RESEARCH DEPARTMENT, MIDVALE STEEL COMPANY
PHILADELPHIA

NOTES ON THE ANALYSIS OF ALLOYS OF NICKEL AND ZIRCONIUM

By G. L. KELLEY AND F. B. MYERS

Received June 14, 1917

It recently became necessary in this laboratory to develop a convenient works-laboratory method for the analysis of an alloy of the following approximate composition:

Carbon.....	0.1 to 0.5 per cent	Aluminum....	0.5 to 10.0 per cent
Nickel.....	70.0 to 90.0 per cent	Zirconium....	2.0 to 18.0 per cent
Iron.....	2.0 to 6.0 per cent	Tungsten....	0.5 to 10.0 per cent
Silicon.....	2.0 to 8.0 per cent	Manganese....	0.1 to 0.3 per cent

An outline of the method used is given in this paper.

Dissolve one gram of the material, preferably of a fineness to pass a 40 mesh sieve, in 40 cc. of hydrochloric acid to which 20 cc. of nitric acid have been added; then evaporate the solution with 20 cc. of sulfuric acid (sp. gr. 1.58) until SO_3 fumes appear. On diluting with water the salts dissolve. Filtering separates nearly all of the tungsten as WO_3 and the silicon as SiO_2 , the zirconium appearing almost entirely in the filtrate.

Ignite the precipitate in a weighed platinum crucible. The first weight gives the weight of SiO_2 , WO_3 and impurities. Then treat the residue with hydrofluoric and sulfuric acids to remove SiO_2 , which is determined by the loss in weight; fuse the residue which now remains with sodium carbonate, leach with water and filter. The residue from leaching is generally very small and should be ignited in the original crucible and its weight subtracted from the weight of the crucible contents after the removal of SiO_2 ; this gives the weight of WO_3 . If extreme care is to be used in the determination of the tungsten, this residue should be fused with KHSO_4 , leached in dilute HCl and precipitated with ammonia. Under these circumstances iron, aluminum and zirconium are precipitated free from sodium compounds which may contaminate the first residue. Upon ignition a corrected residue is obtained to be subtracted from the weight of impure WO_3 . When such care is not necessary the residue may be fused with KHSO_4 and leached with the filtrate from the WO_3 precipitate.

By following the procedure as outlined above, the filtrate from the WO_3 contains in solution all of the iron, nickel, aluminum and zirconium. The solution should be made up to a convenient volume, such as 200 cc., and one-half taken for the iron determination.

To determine the iron, make the solution alkaline with ammonia and boil or heat near the boiling point for a short time; filter and wash the precipitate. Transfer the bulk of the precipitate to a beaker and wash the paper by running through it a small amount of dilute sulfuric acid. Add enough sulfuric acid to the beaker to dissolve the precipitate and an excess equivalent to 10 cc. of acid (sp. gr. 1.58). Then pass the solution through a Jones reductor and determine the iron by titration with KMnO_4 .

To the other half of the solution add ammonia in excess, and remove the nickel by electrolysis. The presence of this small amount of iron and aluminum does not seem to interfere, but in doubtful cases, the nickel may be dissolved in hydrochloric acid, evaporated with sulfuric acid, diluted and the iron and aluminum precipitated with ammonia; any iron and aluminum found in this way should be dissolved in a small amount of acid and added to the original electrolyte which now contains all of the iron, aluminum and zirconium. The ammoniacal solution of nickel is now free from the elements just named and is available for analysis by electrolysis or by the precipitation of its nickel content with dimethylglyoxime. In the event of using the latter procedure, one-tenth of the solution is sufficient for the purpose.

Boil the solution containing Al, Fe and Zr until nearly all of the ammonia has been driven off; then allow it to settle and filter, washing the precipitate with water. The precipitate contains Al, Fe and Zr. After transferring the precipitate to a beaker, dissolve in a minimum quantity of hydrochloric acid; then add solid KOH in excess to precipitate iron and zirconium, and leave aluminum in solution. Boil the mixture for one minute, allow to settle and filter, washing the precipitate with water. The filtrate contains the aluminum; make this solution acid with HCl and then barely ammoniacal; boil a few minutes, filter and wash. Then dissolve the precipitate in HCl and add 7 to 10 cc. of sulfuric acid (sp. gr. 1.58); evaporate the solution until fumes appear; cool, dilute and filter to remove SiO_2 . Again add ammonia in slight excess and after brief boiling remove the $\text{Al}(\text{OH})_3$ by filtration; ignite and weigh as Al_2O_3 .

Dissolve the precipitate of iron and zirconium hydroxides which was separated from the aluminum in HCl (1:1) and re-precipitate with ammonia while boiling. The ignited precipitate contains Fe_2O_3 and ZrO_2 . Convert the iron found by titration into Fe_2O_3 and subtract its weight from the weight of Fe_2O_3 and ZrO_2 . This gives the weight of ZrO_2 .

If manganese is to be determined, weigh 1.5 g. of the material instead of 1 g.; then determine manganese in one-third of the filtrate from the tungstic oxide. For this purpose add ammonia and ammonium persulfate to the solution before boiling. Wash and dissolve the precipitate in nitric acid with the addition of a little sodium sulfite or hydrogen peroxide to aid solution. The manganese is then ready for oxidation by sodium bismuthate and determination by the various known methods.

RESEARCH DEPARTMENT
MIDVALE STEEL COMPANY, PHILADELPHIA

A METHOD FOR FRACTIONATING FATS AND OILS

By ARMIN SEIDENBERG

Received June 30, 1917

Only a limited number of the glycerides of fats and oils have so far been isolated and in the case of no fat or oil have all its glycerides been identified. The importance of securing a more complete knowledge of the glycerides of the fats and oils is, however, very great both in a strictly scientific sense as well as in effecting a more adequate identification of the various members of this class of substances. Owing to our lack of this knowledge the identification of individual fats or oils must depend on a number of empirical constants which, for any one substance, often vary within very wide limits. While it is thus ordinarily possible to identify a pure fat, the detection of even comparatively large amounts of a foreign added fat cannot always be accomplished with certainty.

METHOD FOR THE ISOLATION OF THE GLYCERIDES

A number of methods for separating the glycerides in fats and oils have been tried but no comprehensive scheme whose application is sufficiently wide exists. Chevreul, Krafft¹ and others tried the fractional distillation of the glycerides under *vacuo*. It is, however, according to Boemer,² possible to distill only those containing fatty acids with less than 14 carbon atoms; where glycerides with fatty acids having a larger number of carbon atoms are present, decomposition occurs. Heise³ isolated the first mixed glyceride, oleodistearin, by precipitating the etheral solution of mkányi fat with alcohol. Holde⁴ and Okada⁵ separated different fractions of fat dissolved in ether or ether-alcohol by lowering the temperature. Boemer,⁶ who made some very exhaustive researches into the less soluble glycerides in beef and mutton tallow and in lard, isolated these by dissolving the fat in 2 to 3 times its volume of ether, benzol or chloroform and separating out 3 to 4 fractions by lowering the temperature or by adding alcohol. Fractions within 5° C. of each other were combined and taken up in an amount of solvent which would just take all the substance into solution on warming, but which, on cooling, allowed most of it to separate out again. This was continued 20 to 30 times until no substance was left in solution. Boemer and, in fact, the other investigators as well, with the exception to some extent of Hansen,⁷ were not successful in isolating the more soluble glycerides. The less soluble glycerides that were secured were not obtained in amounts that even approximated quantitative proportions. Even after 32 crystallizations from ether, Duffy⁸ did not succeed in obtaining an entirely pure glyceride from 2000 g. of tallow, although the substance isolated amounted to only 8 g.

SOLUBILITY OF GLYCERIDES

With very few exceptions, the usual solvents for fats and oils, such as ethyl ether, benzol, chloroform, carbon disulfide, etc., do not show any marked differences in their solvent action on the various glycerides. Tristearin and tripalmitin, although entirely soluble in ether in the warm, are somewhat less soluble in the cold—less so than other glycerides. However, there are no data based on quantitative measurements. Alcohol, to some extent, exerts a selective solubility on some of the glycerides, those of the lower fatty acids and of the unsaturated fatty acids being more soluble in it than those of the saturated higher fatty acids. Thus,¹ while tributyrin and tricaproin are readily soluble in cold absolute alcohol, tripalmitin and tristearin are almost insoluble in this medium in the cold. The solubility of all the glycerides in alcohol decreases with dilution.² Arnold³ found in a number of fats and oils that the iodine number of the alcohol-soluble portion was higher than that of the part that did not go into solution, showing that the glycerides containing unsaturated acids are more readily soluble in alcohol than those containing the saturated acids. Davidsohn and Wrage,⁴ however, have secured some results that lead them to conclusions that do not entirely bear this out. A large amount of work on the critical temperature of dissolution by Crismer,⁵ Valenta,⁶ Allen,⁷ Cesàro⁸ and others indicates that as the temperature decreases the solubility of the glycerides in alcohol, and in other solvents as well, becomes less and that this is most marked with the glycerides of the saturated higher fatty acids. In general, it may be said that the solubility of the glycerides in alcohol, as in other solvents, decreases with an increase in the number of C-atoms of their fatty acids and that those containing unsaturated fatty acids show a somewhat greater solubility than those containing saturated fatty acids with an equal number of carbon atoms. The fatty acids, themselves, although more readily soluble, show similar relative solubilities when compared with each other. This is, of course, what is generally the case in homologous series and in compounds formed from them.

GENERAL DISCUSSION

Due to the very large number of glycerides and to the very slight differences in solubility existing between them, it seems impossible to secure any precipitant or solvent that will separate the glycerides sharply from each other. The conditions of insolubility must be graded so finely that the very slight differences existing between the glycerides will to some extent be approximated. Neither by the very slow lowering of the temperature of a solution containing the glycerides nor by the very slow addition of a precipitant such as alcohol to their solution is it possible to attain

¹ Ber., 1903, 4343.² Z. Natur. Ges., 14 (1909), 90.³ Arb. lab. Gem., 12 (1896), 340, 13, 302.⁴ Ber., 1901, 3403.⁵ Chem. Ztg., 32 (1908), 1199.⁶ Z. Natur. Ges., 14 (1909), 90, 17 (1909), 353, 25 (1913), 321.⁷ Arch. Hyg., 43 (1902), 1.⁸ J. Chem. Soc., [N] 1893, 199.¹ Lewkowitsch, Oily, Fats and Waxes, 3th ed., 1, pp. 11-12.² Vanderveelde, Jour. de chim. med., 25 (1911), 48.³ Z. Natur. Ges., 14 (1909), 115, 161, 16 (1908), 27.⁴ Chem. Rev. d. Ind., J. Ind., 22 (1911), 108.⁵ Bull. chim. soc. par., 9 (1901), 9 (1900), 10 (1900), 11 (1900).⁶ J. Soc. Chem. Ind., 1883, 201.⁷ Ber., 69 (1886), 180.⁸ Bull. chim. soc. par., 1907, 1034.

this object with the needed refinement. In fact, in the latter case, since certain of the glycerides are distinctly soluble in alcohol, this medium would not serve to throw them out of the increased volume of solution formed by its addition. If a dilute alcohol is chosen there is even less possibility of adjusting conditions with the minute delicacy needed.

OUTLINE OF METHOD

The requirements for securing the requisite refinement in the gradation of the solubility conditions can be much more readily attained when an exactly opposite procedure is pursued, *viz.*, if from an alcohol-ether solution of the glycerides, first the ether and then the alcohol, be removed very gradually. This may be accomplished by aspirating air by means of the water pump through the solution of the glycerides in an appropriate alcohol-ether mixture. At first mainly ether with a small amount of alcohol is suctioned off, but after all the ether has been removed the alcohol continues to go. At the reduced pressure produced by the suction of the water pump the temperature of the liquid drops considerably (to about 5° C.), at which point the differences in the solubilities of the various glycerides are much accentuated. The removal of the solvents can be graded to progress with any desired degree of refinement by adjusting the speed of the suction produced by the water pump. Throughout the process a very thorough agitation of the solution is secured. In this way, by the very gradual removal of minute amounts of the solvents in the general order of their solvent action on the glycerides, accompanied by an equally gradual lowering of the temperature, the many nearly related points of comparative insolubility of the various glycerides are approached so slowly that their separation can be secured to some extent.

At first, of course, the more insoluble glycerides are thrown out of solution, but as the ether, and finally the alcohol, is aspirated off, the other glycerides, soluble in the latter medium, gradually come down as well. Naturally there is no one point at which any one glyceride is entirely precipitated. However, the largest part usually does come down within fairly narrow limits. The conditions are somewhat similar to those met with in the fractional distillation of nearly related liquids.¹ One can expect to secure a glyceride only in its pure state with repeated fractionations after having combined similar fractions. The conditions are complicated by the ready solubility of the glycerides in each other and by their formation with the solvent at times of colloid or emulsoid solutions. It is of course necessary to regulate conditions so that the latter is avoided. Besides ether and alcohol or ether, alcohol and water, any other combination of solvents may be chosen such that those having the greatest solvent action are also the more volatile.

EXPERIMENTAL

GENERAL PROCEDURE—Since by the methods so far proposed it has been possible to isolate only the

less soluble glycerides of fats and oils, the writer undertook the isolation of the more soluble glycerides of a sample of tallow according to the method described. To 100 g. tallow were added 1000 cc. of a mixture of 50 parts ether and 50 parts absolute alcohol, warmed slightly and then allowed to cool. A heavy white residue formed which was filtered off as Residue A. Through the filtrate from this, air was aspirated by the suction of the water pump; the solution became turbid at about 650 cc., but suction was continued until a heavy precipitate had formed, which was filtered off as Residue B. The filtrate from this amounted to about 450 cc. and the suction on it was continued until it had been reduced to 200 cc. On allowing to stand, the turbid liquid separated into two liquid layers. The lower one, which had a very decided yellow color, was separated by means of a separatory funnel as Residue C. Suction on the upper layer was continued until it was reduced to 100 cc.; it became only slightly turbid: it was evaporated on the water bath, but since only a very slight residue was left this was discarded.

Each one of the above residues was now again taken up in a mixture of ether and alcohol: Residue A in a 500 cc. mixture of 10 parts absolute alcohol and 90 parts ether (since only small amounts of alcohol-soluble glycerides were present); Residue B in 300 cc. of a mixture of 40 parts absolute alcohol and 60 parts ether (since this contained a larger proportion of the alcohol-soluble glycerides); and Residue C after evaporating the alcohol and ether with which it had previously formed a solution, in a 100 cc. mixture of 40 parts 95 per cent alcohol, 10 parts water and 50 parts ether (since here the amount of the less soluble glycerides was slight). Through each of these solutions air was now aspirated and in each case 3 to 4 fractions were secured. The melting points of these fractions were taken and those within 5° C. of each other were combined and dissolved again in mixtures of alcohol and ether or of alcohol, water and ether proportioned according to the number, quantity and solubility of the glycerides which could be expected to be present. These were again fractionated and recombined as above until the various fractions from any one solution gave identical melting points. The separation of the solid residue was usually accomplished by pouring both residue and liquid upon a filter paper and drawing off the liquid by means of suction, stirring toward the end with a glass rod so that as much as possible of it was expressed.

Most of the more soluble glycerides would of course be contained in Residue C, but some would also be in the end fractions from Residues A and B. Residue A was fractionated into four parts having, respectively, the melting points, 57°, 56°, 55° and 44° C. Residue B was fractionated into three parts having, respectively, the melting points 50°, 45° and 35° C. On combining the similar end fractions from these, other fractions with the following melting points were secured: 52, 45, 40, 38, 34, 32, 30, 27, 25, 24, 22, 18 and 15° C. These were again recombined and refractionated and those having a melting point below

¹ Young, "Fractional Distillation," 1903, Chapter 7, p. 114.

25° C. combined with Residue C, which was now fractionated according to the procedure outlined, usually from a mixture consisting of either 50 parts ether and 50 parts 95 per cent alcohol or 50 parts ether, 40 parts 95 per cent alcohol and 10 parts water. Those fractions that were nearly related in melting point were combined and refractionated. This was continued until after fractionating the lower melting point fractions eleven times and the higher melting point fractions seven times two distinct yields were secured which seemed on further fractionation to be pure compounds.

To identify a glyceride the constants usually deemed necessary are: melting point, saponification number, neutralization number of the fatty acids (average molecular weight) and the iodine number. In order to obviate the possibility that the substance under examination is not a mixture of several glycerides, it is necessary to determine one of the constants, preferably the melting point, on several fractions. If all the fractions have the same constant the substance may, according to Boemer,¹ be considered a pure glyceride. Another indication that the substance is not a mixture can be obtained by observing whether all or practically all of it is precipitated at one point during the suction instead of gradually.

HIGHER MELTING POINT YIELD

The higher melting point yield from Residue C amounted to only 0.98 g. and gave the following constants:

	Observed Determinations			Calculated or Known Constants for Oleodistearin
	1	2	Average	
Melting Point (Corrected)	44.0	44.4	44.2	44-44.6
Iodine Number	27.0	26.7	26.9	28.6
Saponification Number	187.4	187.4	187.4	189.5
Neutralization Number	197.7	197.7	197.7	197.9

On fractionating the material into three fractions these were found to have melting points (corr.): 44.6, 44.0, 44.4° C. The substance, although the results for the iodine number were slightly low, may be regarded as the glyceride oleodistearin.

This glyceride has been isolated by Heise² from mkányi fat and kokum butter. According to Fritzweiler,³ it also occurs in cocoa butter, and according to Klimont⁴ in Borneo tallow. It has, however, not as yet been isolated from beef or mutton tallow. In appearance it is a white solid substance forming small crystals.

LOWER MELTING POINT YIELD

The lower melting point yield secured from Residue C amounted to approximately 20 g. and gave the following constants:

	Observed Determinations			Calculated or Known Constant for Dioleopalmitin
	1	2	Average	
Melting Point	41.6	40.6	41.1	40-41.2
Iodine Number	31.2	30.6	30.9	30.0
Saponification Number	197.6	196.0	196.8	196.1
Neutralization Number	201.2	204.8	203.8	200.0

Since the melting point was not sharp the iodine number was determined on four fractions of the material.

terial with the following results: 50.7°, 51.8°, 50.6°, 50.3°. The agreement in itself is sufficiently satisfactory to stamp the material as a pure glyceride. However, there is a considerable deviation in this iodine number from that required by theory for dioleopalmitin, to which the other constants correspond quite closely and to which also the observed iodine numbers approach nearer than to any of the other glycerides, except dioleostearin, that can occur in tallow. The glycerides present in any fat are dependent, of course, upon the fatty acids to be found in the fat which in this instance are stearic, palmitic and oleic acids. This deviation in the iodine number may be explained on one of two grounds. It may be due to the admixture of another glyceride with a lower iodine number. However, the number of fractions having practically identical constants would hardly justify this assumption. On the other hand, it is possible that the long-continued passage of air through the solutions containing this substance or its frequent exposure to heat when the solvent was evaporated off may have affected the unsaturated bond. This is borne out in some respects in the literature and may also explain the indistinct melting point. Thus Lewkowitsch¹ reports oxidation of the fatty acids on blowing air through various fats and oils at an elevated temperature and Fahrion² states that the fatty acids are affected by heat. The error due to this cause may possibly be avoided by removing the oxygen from the air before aspirating it through the solution. In order to obviate all possibility of confusion with dioleostearin the saturated fatty acid of the substance was fractionated from an appropriate alcohol-ether mixture according to the general procedure outlined for the glycerides. In this way a saturated fatty acid was secured, three fractions of which had the melting points (corr.): 62.0°, 61.8°, 62.2° C. The melting point of palmitic acid is 62.6° C.

It may therefore be stated that the substance is dioleopalmitin which has been affected to some extent so that it does not add on the theoretical quantity of iodine. At room temperature it is a yellowish liquid, but on solidifying becomes almost white in color.

Besides the two glycerides which were isolated from Residue C, some material remained. Although this was not identified, it probably consisted of a mixture of the two glycerides that were isolated. There was no evidence of the presence of triolein and therefore the dioleopalmitin may, in all probability, be considered the glyceride present in tallow which is most soluble in ordinary solvents.

OLEIN FREE GLYCERIDES

No attempt was made to fractionate completely Residues A and B. It is impossible to insure so well that it was possible to obtain about 25 g. of mono- and glycerides from these two residues after four refractionations. The iodine number of glycerides was determined and it was found that they were very low, as follows:

1. Residue A, 1899	10.0
2. Residue B, 1899	33.0
3. Residue A, 1900	10.0
4. Residue B, 1900	33.0

¹ Z. N. G. 1900, 114, 1900, 260.

² Ibid.

³ J. Chem. Soc. 1902, 911.

⁴ Monatsh., 1904, 35, 1905, 363.

ing to Kreis and Hafner.¹ These two investigators² considered it impossible to secure an olein-free glyceride by crystallization from alcohol, ether, chloroform or other solvents. Boemer³ secured olein-free substance only after numerous crystallizations and then only in comparatively small amounts.

DETECTION OF TALLOW IN BUTTER FAT

The readiness with which this comparatively large amount of olein-free substance was secured led the writer to make comparisons between the different quantities that could be isolated in this way from various other fats. From the results obtained it was indicated that by standardizing conditions the method could be adopted to detect the addition of certain foreign fats to butter fat in quantities that could not be ascertained by means of the usual analytical constants. Thus to 5 g. of butter fat was added a mixture of 80 parts ether and 20 parts 95 per cent alcohol, so that the combined volume amounted to 75 cc. This was reduced by suction to 55 cc. and the resulting precipitate filtered off. This precipitate was again dissolved in a mixture of 70 parts ether and 30 parts 95 per cent alcohol to a total volume of 50 cc. By suction this was reduced to 30 cc., the resulting precipitate again filtered off and weighed: it amounted to 3.8 per cent. When the same sample of butter fat containing 20 per cent added tallow was subjected to this procedure a residue amounting to 9.9 per cent was obtained. The Reichert-Meissl number, which is the constant most characteristic for butter fat, was in the above instances, respectively 36.8 for the pure butter fat and 26.9 for the butter fat containing 20 per cent added tallow. The latter figure is still well above the minimum for butter fat, which runs as low as 22 and at times is even less.⁴ In the case of the residues the difference caused by the 20 per cent added tallow amounts to 106 per cent of the original amount; in the case of the Reichert-Meissl number it amounts to only 27 per cent. It is the intention of the writer to make further investigations of the amount of residue to be secured under standardized conditions from representative samples of butter of undoubted purity.

SUMMARY

The method consists, essentially, in dissolving a fat or oil in two or more solvents, one or more of which is at the same time more volatile and exerts the greater solvent action on the glycerides. First, mainly, this solvent is very gradually removed by aspirating air through the solution, after which the remaining solvent is removed in the same way. This is accompanied by a considerable lowering of the temperature. Due to the slow decrease in temperature and to the gradual removal of the solvents until none is left, the various glycerides by degrees come out of solution in the order of their insolubility in the solution remaining. At the same time it must be pointed out that all of any one glyceride does not come down entirely at

a definite concentration and that in order to secure a chemically pure product the fractionation after combining like fractions must be repeated as often as necessary. The substance may then be secured in amounts approximating its quantitative presence in the fat. The theoretical conditions resemble in many respects those existing during the fractional distillation of a mixture of liquids. Two of the more soluble glycerides of tallow were isolated by this method and an instance given of how a wider and more accurate knowledge of the glycerides in the various fats and oils would prove valuable not only from a scientific standpoint but also in the detection and identification of adulterants.

CHEMICAL LABORATORY, BUREAU OF FOODS & DRUGS
DEPARTMENT OF HEALTH, CITY OF NEW YORK

THE THERMAL VALUES OF THE FATS AND OILS II—THE SULFURIC ACID OR MAUMENE NUMBER

By J. W. MARDEN AND M. V. DOVER

Received June 25, 1917

INTRODUCTORY AND HISTORICAL

The sulfuric acid or Maumené reaction has been a subject of comment ever since Maumené, in 1882,¹ observed that heat was evolved when concentrated sulfuric acid was mixed with various oils. Because the rise in temperature was found to be different for different oils, this thermal value has been used to some extent for identification and detection of adulteration. The drying oils give a higher rise in temperature than the non-drying, the temperature change apparently depending upon the degree of unsaturation of the oil. Archbutt² suggests the following procedure for the determination of the Maumené number. A 200 cc. beaker is packed into a larger beaker with cotton filling the space between the two. This is used as the calorimeter. Fifty grams of oil are weighed into the inner beaker, a thermometer is immersed in the oil and the temperature accurately read. Ten cc. of concentrated sulfuric acid at the same temperature as the oil are pipetted into the oil. The mixture is stirred and the maximum temperature observed. The difference between the initial and final temperature expressed in degrees Centigrade is considered the Maumené number.

In spite of the fact that various modifications of apparatus and various devices for stirring the mixture of oil and acid have been suggested, there is much dispute as to the value of this test for analytical work because only the arbitrary rise in temperature has been taken with no regard to the varying heat capacities of the oils, apparatus, etc. In order that the Maumené test be used on an oil, the apparatus must first be standardized with a sample of known purity and experiments must always be conducted under exactly similar conditions. Furthermore, it has been observed that the rise in temperature depends upon the concentration of sulfuric acid used in the experi-

¹ *Z. Nahr. Genussm.*, **7** (1904), 655.

² *Ber.*, **36** (1903), 1123.

³ *Ibid.*

⁴ Lewkowitsch, "Oils, Fats and Waxes," 5th Ed., **2**, p. 823.

¹ *Compt. rend.*, **35** (1882), 572.

² A very excellent and complete historical discussion of this method is by Lewkowitsch, "Chemical Technology of the Fats and Oils," **1** (1909), 384, The Macmillan Company, New York.

ment. Thomson and Ballantyne¹ observed that when acid between the concentrations of 95 and 99 per cent was used, that if the rise in temperature with oil was divided by the rise in temperature with the same weight of water and same volume of acid, the value obtained was a constant. This value, multiplied by 100, they called the "specific temperature" reaction. This would mean that the Maumené number is directly comparable to the heat of dilution. There seems to be some doubt on this point.²

The heat of bromination has already been determined by one of the authors³ in terms of calories per gram of oil and it seemed possible that the sulfuric acid number could also be determined quickly and accurately in somewhat the same way. A simple and dependable method for the determination of this value based upon an accurate calorimetric method should be of worth to the analyst. For this purpose an inexpensive apparatus has been devised and the Maumené numbers have been determined in terms of calories per gram of oil for about twenty of the common fats and oils. Also the variation in the quantity of heat liberated by the interaction of sulfuric acid of various concentrations and olive oil has been determined. The specific heats of a series of oils are given at the end of this paper.

APPARATUS AND STANDARDIZATION

It was necessary to use two calorimeters in this work. The apparatus used for the determination of the thermal reactions of the oils (Fig. I) consisted of a Dewar tube of 1000 cc. capacity, fitted with a cork and hard rubber stopper which held a large test tube in which the oil and acid were mixed, and stirrer as shown in the figure. A smaller calorimeter (Fig. II) built upon the same principle with a 100 cc. Dewar tube was used for the determination of the specific heats of the oils, which it is necessary to know in order to calculate the thermal value.

TABLE I—HEAT OF DILUTION OF SULFURIC ACID (Brönsted)

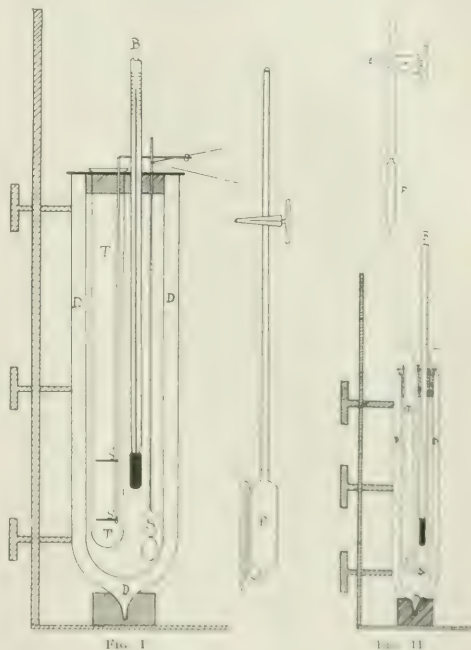
Mols water per mole H ₂ SO ₄	Calories of Heat
1	6.710
1.5	8.790
2	10.020
3	11.640
4	12.830
5	13.710
6	14.370
7	14.890
8	15.260
9	15.580
15	16.660
19	16.830
99	17.660

TABLE II—SPECIFIC HEATS OF DILUTED SULFURIC ACID (Brönsted)

Mols Water per mole H ₂ SO ₄	Specific Heat
0	0.3352
0.4856	0.3786
1	0.4408
2	0.4628
3	0.5012
4	0.5140
5	0.5305
6	0.6152
7	0.6475
8	0.6776
9	0.7029
10	0.7231
11	0.7415
12	0.7584
13	0.771
14	0.7837
15	0.7948
16	0.8041
17	0.8122
18	0.8203
19	0.8271
20	0.8349

Both calorimeters were standardized using the heat of dilution of sulfuric acid which has been accurately determined by Brönsted⁴ (see Table I).

To standardize the large calorimeter (Fig. I), 500 g. of water were weighed into the Dewar flask *D*, about 40 cc. of concentrated sulfuric acid were accurately weighed into the test tube *T*, and 10 cc. of water weighed in the pipette *P*. This was hung in the tube *T*, until the whole system had come to constant temperature, the water in the Dewar tube being stirred with the wire stirrer *S*, all the time the experiment was in progress. When the temperature became constant the water in the pipette *P* was forced by means of a rubber bulb into the acid and *P* was withdrawn. The mixture of acid and water in *T* was stirred with the wire stirrer *S'*. The pipette *P* was again accurately weighed. From the weight of the acid, the concentration of which was accurately known, the heat liberated was calculated. The num-



ber of calories liberated in the reaction divided by the temperature rise, minus the heat capacity of the diluted sulfuric acid and the 100 g. of water in *D*, gives the heat capacity or water equivalent of the apparatus. The specific heat of the diluted sulfuric acid was obtained from the work of Brönsted (see Table II). The heat capacity of the mixture of oil and acid was found to be the same in the top of the test tube as of each. The specific heats of the oils used in giving the heat capacities of the acid oil mixtures are given in Table VI.

The small calorimeter (Fig. II) was calibrated in exactly the same way as the larger calorimeter. 10 g. of water was weighed into the 100 cc. Dewar flask *D*, 1 g. of water was weighed into the small tube *T*, and 1 cc. of

¹ *J. Soc. Chem. Ind.*, 1891, 334.

² Sherman, Dummer, and Kohnstamm, *J. Am. Chem. Soc.*, **34** (1912), 266.

³ THIS JOURNAL, **6** (1916), 171.

⁴ *J. phys. Chem.*, **68** (1904), 693.

pipette, *P*, which when calibrated delivered 0.840 g. of 95.1 per cent sulfuric acid, was hung in the small tube until the whole system had come to constant temperature. The acid was then allowed to mix with the water, the pipette was removed and the mixture of acid and water stirred with the wire stirrer *S'*. The water in the tube *D* was stirred during the whole time of the experiment by means of the wire stirrer *S*, both stirrers being moved vertically by means of a motor.

The strength of the sulfuric acid used in these experiments was determined both by weight titrations and by specific gravity. The heat capacities of the two calorimeters were also found by weighing the parts and calculating the water equivalent from the specific heats; in each case these values checked well. The temperature change in all determinations was noted each minute and the total rise in temperature was calculated in the same way as it is found at present in the calorimetric determination of coal.¹

SULFURIC ACID NUMBER IN CALORIES PER GRAM OF OIL

This determination is made in exactly the same way as the experiment just described for determination of the heat capacity of the apparatus, except for the fact that the oil in question is placed in the pipette instead of water (Fig. 1, *P*), as in the former determination. After the pipette containing the oil has hung in the reaction test tube (Fig. 1, *T*) for a sufficient length of time to allow the whole apparatus to have come to the same temperature, the oil is run into the acid and the rise in temperature observed in the usual manner. The quantities used here give an excess of acid for the amount of oil taken. The rise in temperature, multiplied by the heat capacity of the apparatus, oil and acid, gives the total heat liberated in the reaction. This number, divided by the weight of oil, gives the calories per gram of oil.

TABLE III—HEATS OF REACTION OF OILS WITH EXCESS OF 95.10 PER CENT SULFURIC ACID

Results in Calories per Gram of Oil			
No.	OIL	No.	OIL
1	Turpentine..... 270	11	Lard Oil..... 99.3
2	Sandalwood..... 181.2	12	Peanut..... 89.5
3	Raw Linseed..... 135	13	Rape Seed..... 89.5
4	Boiled Linseed..... 138.4	14	Olve I..... 86.2
5	Cod Liver..... 133.3	15	Olve II..... 85.0
6	China Wood..... 130	16	Olve III..... 81.0
7	Caster..... 116.6	17	Sperm..... 76.8
8	Raw Linseed..... 115(a)	18	Neat's-foot..... 67.0
9	Cottonseed..... 102	19	Cocanut..... 36.1
10	Sesame..... 100.4	20	Liquid Petroleum..... Nil

(a) Found to have been adulterated with mineral oil.

The values in Table III were all run in duplicate and checked to within less than 0.5 per cent. This table shows a wide variation in amount of heat liberated by the various oils and the values are in the same order of magnitude as the corresponding iodine numbers.

The fact that an excess of acid was used in these experiments is shown in Table IV. When the amount of acid is cut in half the thermal value is lowered only about 5 per cent.

TABLE IV—THERMAL VALUE OF OLIVE OIL, WITH VARYING WEIGHTS OF 95.10 PER CENT H₂SO₄

Grams of Acid	7.2	54	36
Thermal Value (Calories per g. Oil).....	86.2	83.3	82.2

The effect of varying the strength of acid used in the above experiments is clearly shown in Table V.

It is obvious that the thermal value varies considerably with the concentration of the acid. At a concentration of 95 per cent acid a variation of one per cent would cause a difference of 5 or 6 calories in the thermal value of olive oil.

TABLE V—EFFECT OF CHANGE OF CONCENTRATION OF H₂SO₄ UPON THERMAL VALUE OF OLIVE OIL

Concentration of H ₂ SO ₄	95.1%	90.6%	82.7%
Thermal Value (Calories per g. Oil).....	86.2	60.0	40.7

SPECIFIC HEATS OF FATS AND OILS

The specific heats of the fats and oils (Table VI) were determined in a manner exactly similar to that in which the heat capacity of the small calorimeter was determined except that 50 g. of the oil in question were put into the Dewar flask instead of water.

TABLE VI—SPECIFIC HEATS OF OILS, FATS AND WAXES

Substance	Specific Heat	Temperature of Determination
Beeswax (a).....	0.499 (L)	65°-100°
(b).....	0.429 (L)	-21°- 3°
Castor Oil (a).....	0.434 (L)	6°
(b).....	0.498	20°- 30°
China Wood Oil.....	0.438	20°- 30°
Cocanut.....	0.511	20°- 30°
Cod Liver Oil.....	0.452	20°- 30°
Cottonseed Oil.....	0.474	20°- 30°
Lard.....	0.483	20°- 30°
Lard Oil.....	0.50 (S)	
Linseed Oil (Boiled).....	0.441	20°- 30°
Linseed Oil (Raw).....	0.474 (S)	
Menhaden Oil.....	0.474 (S)	
Mineral Oil (a) (Liquid Petroleum).....	0.50 (S)	
(b).....	0.416	20°- 30°
Neat's-foot Oil.....	0.457	20°- 30°
Olive Oil (a).....	0.471 (L)	6.6°
(b).....	0.493 (S)	
(c).....	0.475	20°- 30°
Paraffin Oil (Wax).....	0.69 (K)	0°- 20°
Peanut Oil.....	0.490	20°- 30°
Rape Seed Oil.....	0.469	20°- 30°
Sesame Oil.....	0.478	20°- 30°
Sperm Oil.....	0.463	20°- 30°
Turpentine Oil.....	0.42 (K)	18°
(L) Lewkowicz, <i>Loc. cit.</i>		
(S) Sherman, Danziger and Kohnstamm, <i>Loc. cit.</i>		
(K) Kaye and Laby, "Physical and Chemical Constants," Longmans, Green & Co., New York (1911).		

CONCLUSIONS

I—A method has been proposed for the calorimetric determination of the sulfuric acid number of the fats and oils.

II—This method is simple and accurate to 0.5 per cent. If the same weights of acid, oil, and water are always used the heat capacity of the entire system can, under ordinary conditions, be considered constant. With this value once determined the process is no more complicated or tedious than the ordinary coal calorimetric determination. The rise in temperature multiplied by the heat capacity of the system divided by the weight of oil gives the sulfuric acid number in calories per gram of oil. A single determination does not take over one-half hour.

III—Results are given for this calorimetric value, using 95.10 per cent sulfuric acid.

IV—It has been shown that varying the concentration of the acid largely affects the results. If this test is to be used, therefore, some standard concentration of acid should always be employed.

V—A variation in the amount of acid used has but little effect on the thermal value provided there is no change in the concentration.

VI—The specific heats of a series of fats and oils have been determined. There is little variation in the specific heats of the oils examined.

¹ THIS JOURNAL, 6 (1913), 527.

THE DETERMINATION OF FAT IN CERTAIN MILK PRODUCTS¹

By C. K. FRANCIS AND D. G. MORGAN

Received May 19, 1917

Many methods based on the Babcock test have been proposed for use on ice cream, milk powders, etc., but have not received the endorsement of the Association of Official Agricultural Chemists, which is in charge of the methods recognized by the various courts. The Official Method of the Association of Official Agricultural Chemists for the determination of fat in the products mentioned, is known as that of Roesse-Gottlieb, and is based on the use of ether or some other substance having the power to dissolve fats. Objections are made to the method because a special and somewhat expensive apparatus is necessary, and it appears that lower results are obtained when working on powders and semi-liquid preparations.

A number of the more recent methods for the determination of fat were tested by applying them to malted milk and powdered milk, but the most encouraging were those in which sulfuric acid was used. It appears that large quantities of acid were necessary to remove the carbohydrates. Considerable sugar was found in some samples, and when this and other organic matter was carbonized the separation of the fat from the black mass was poor, and in many experiments no fat was obtained. Owing to the extreme affinity of the sulfuric acid for water and carbohydrates, the action of this acid on powders and semi-liquid preparations was severe, and often excessive carbonization resulted. After this had once occurred the addition of more sulfuric acid appeared to have no effect. In an effort to separate the fat, other substances were added to the milk-acid mixture. The presence of small quantities of nitric acid appeared to influence the reaction, and as the preliminary tests seemed to meet with success, the method as herein described was developed.

PREPARATION OF SAMPLES

ICE CREAM—Some special precautions are necessary in order to obtain a representative sample of ice cream. Usually a good sample may be collected in the factory directly from the freezer by withdrawing small portions on a large spoon from different parts of the container and from the blades of the stirrer. When the ice cream is firmly frozen in a packer or can, a butter trier or thief should be used; the trier should be thrust into the cream from top to bottom at least three times, and the separate portions combined into one sample. If the cream has become soft in the container it will be necessary to stir it well with a spoon or paddle before sampling.

If the ice cream is not to be analyzed at once, or is to be forwarded to a laboratory at a distance, it should be allowed to melt at room temperature and a small quantity of bicarbonate of mercury added as a preservative. If a tablet is used it should be finely pulverized and thoroughly mixed with the sample,

using one-fourth of a tablet for every quart of ice cream.

The representative sample, if in good condition, should be allowed to melt at room temperature, but if the fat has separated, it is necessary to heat to about 50° C. If the sample is sour or contains much curd, a few cc. of ammonia may be added. The melted sample should be thoroughly mixed by pouring from one vessel to another and approximately 10 cc. of the uniform sample removed at once with a large bore pipette and 9 g. quickly weighed into a 30 per cent cream test bottle.

EVAPORATED MILK—Mix as under ice cream and weigh 4.5 g. of the sample into a 30 per cent cream test bottle. If the sample is in a diluted form, use a 9 g. sample. In the case of sweetened condensed milk, warm slightly by immersing in warm water before mixing.

MALTED MILK AND DRIED MILK—Mix the entire sample thoroughly and quickly weigh 4.5 g. into a small beaker. Transfer to a 30 per cent cream test bottle with the aid of the least possible amount of hot water. If the sample has a low fat content, as in the case of dried skimmed milk, a 10 per cent milk test bottle, or a skimmed milk test bottle, should be used.

DETERMINATION OF FAT

ICE CREAM AND EVAPORATED MILK—Prepare a mixture of equal parts of glacial acetic and sulfuric acids, and add to the sample 4 to 5 cc. of the mixture at a time, mixing thoroughly after each addition, until a dark brown color develops. Add concentrated nitric acid, 1 to 2 drops at a time, and shake thoroughly after each addition until the action of the acid has subsided, or excessive foaming may result. After two or three such additions, the number of drops may be increased to 5 or 6 if the precautions to prevent excessive foaming are observed. When a light yellow color results, immerse the bottle in boiling water for 3 to 4 minutes, or until the dark brown color returns. Then centrifuge for 5 minutes at 1200 r. p. m., fill nearly to the neck with hot water, and centrifuge an additional 2 minutes. Bring the fat column into the scale portion of the neck with more hot water and centrifuge for another minute, reduce the meniscus with glymol, and multiply the reading by 2 for 9 g. samples and by 4 for 4.5 g. samples.

MALTED MILK—Prepare a mixture of sulfuric and nitric acids (see 1 cc. of H₂O to 1 cc. HNO₃) and add to the sample 4 to 5 cc. of the mixture, shaking thoroughly after each addition until a light yellow color results (this ordinarily requires about 2 cc. to 3 cc. of the mixture). Immerse in boiling water until a dark brown almost black color develops. Now add a sufficient amount of water and return once again to the bath at 2 cc. of HNO₃ to 1 cc. of H₂O, shaking thoroughly after each addition, until a light and easy flow develops and is allowed to settle. Immerse again in boiling water until the dark brown color returns. Centrifuge for 4 minutes, fill nearly to the top of the neck with hot water, and centrifuge 2 minutes. Reduce the fat

¹From BAC 114, Oklahoma Agricultural Experiment Station.

column into the scale portion of the neck with more hot water and centrifuge 1 minute. Reduce the meniscus with glymol and multiply the reading by 4.

DRIED MILK—Add concentrated sulfuric acid, 5 to 6 cc. at a time, until a dark brown, almost black, color develops. Prepare a mixture of sulfuric and nitric acids (10 cc. of H_2SO_4 to 2.5 cc. of HNO_3), and add 0.5 cc. at a time, shaking thoroughly after each addition, until a clear, light red color results (this requires ordinarily 5 to 6 cc. of the mixture). Immerse in boiling water until the dark brown color returns, add more of the mixture until the light red color is produced, and again immerse in the boiling water until the dark brown color appears. Centrifuge 5 minutes and proceed as for malted milk.

DISCUSSION OF RESULTS

The results obtained by this method on different products have been compared with those obtained by the Roese-Gottlieb method, as indicated in the accompanying table.

SAMPLE	COMPARATIVE TESTS—PERCENTAGES OF FAT	
	ROESE-GOTTLIEB METHOD	AUTHORS' METHOD
Ice Cream.....	7.7	7.7
Ice Cream.....	7.58	7.68
Unsweetened Evaporated Milk.....	7.93	7.90
Sweetened Evaporated Milk.....	9.35	9.35
Malted Milk.....	7.06	7.14
Dried Skim Milk.....	1.36	1.29

It appears that our method gives uniformly higher results than the Roese-Gottlieb method. In every case a good separation of fat was obtained free from particles of carbon and bubbles. It is important that the nitric acid be added with care and an excess avoided; too much nitric acid may cause the formation of a large quantity of gas, the gas bubbles continuing to rise for some time and producing a froth which interferes with the reading of the fat column. The action of the acid is more rapid when added to the warm mixture, and it is suggested that the bottle be immersed in warm water while the acid is being added.

SUMMARY

A method for determining fat, including treatment of the samples, in such dairy products as ice cream, evaporated milk, malted, dried skim milk and similar milk products, is described. The procedure is similar to that followed when using the well known Babcock test, but in place of sulfuric acid, mixtures of glacial acetic, sulfuric and nitric acids are prescribed. The fat is separated and read in a Babcock bottle.

CHEMICAL DEPARTMENT
OKLAHOMA AGRICULTURAL EXPERIMENT STATION
STILLWATER, OKLAHOMA

APPLICATION OF THE CRYOSCOPIC METHOD FOR DETERMINING ADDED WATER IN MILK¹

By J. T. KEISTER

Received May 31, 1917

Beckmann and Jordis² determined the freezing point of different samples of normal milk and found that the freezing points varied from -0.55 to $-0.56^{\circ}C$.

¹ Published by permission of the Secretary of Agriculture; read at the meeting of the American Chemical Society, New York City, September 25 to 30, 1916.

² *Forschungsbericht über Lebensmittel*, 2 (1895), 367.

Later J. Winter¹ reported results of similar work and found the freezing point to vary from -0.54 to -0.57° . The freezing points determined by Bords and Genin² showed for normal milk as great variation as -0.44 to $-0.56^{\circ}C$. Hamburger³ found that the freezing point of "fore" milk and "strippings" differed. Pins⁴ states that evening's milk showed a slightly higher freezing point than morning's milk, although his findings were not confirmed by Abati and Sohn⁵ who found no difference. Van Eck⁶ showed that too low temperature of the freezing bath and excessive supercooling of the milk raised the freezing point. Stroecklin⁷ found that the acid content and the freezing point of the sour milk could not serve as a means of accurately calculating the freezing point of the fresh milk. Koeppe,⁸ Van Raoul,⁹ Reicher,¹⁰ Henderson and Meston¹¹ and others have published results of freezing-point determinations of milk where results are reported quite similar to those recorded in the work mentioned here. Monier-Williams¹² showed that the presence of fat is without influence in the determination of the freezing point. He concludes further that neither the proportion of total milk solids nor the non-fatty solids exerts any influence.

The most striking fact found by an examination of the results of the freezing-point determinations of milk in the literature is the slight variation in readings made by the different investigators. No determination of any constituent of milk has given such closely agreeing values as the freezing points recorded in the literature by the different experimenters. The range in temperature is from -0.54 to $-0.57^{\circ}C$, in general. Hence, the value of this determination for detecting added water in milk is evident. One of the chief difficulties encountered in the interpretation of the results of milk analysis is to distinguish between rich milk containing a small amount of added water and naturally thin milk. The freezing-point determinations appear to serve as an index for making this distinction in almost every case.

The freezing point of milk is evidently controlled by substances in solution. Substances like fat exert no influence on the freezing point and as fat is the most variable constituent of milk the most widely varying factor is removed. On this point the majority of observers have agreed, though there are some conflicting statements. It has been shown that the freezing point is independent of breed, age of cow, period of lactation or quantity of milk. It is also claimed that substances which are in colloidal condition, such as albuminoids, affect the freezing point either not at all or to a very slight extent. In any

¹ *Compt. rend.*, **121** (1895), 696; **123** (1896), 1298; **124** (1897), 777.

² *Ibid.*, **123** (1896), 425.

³ *Mon. sci.*, **666** (1897), 462.

⁴ Dissertation, Leipzig, 1910.

⁵ *Milchzeitung*, **28** (1899), 177.

⁶ *Chem. Weekblad.*, **12** (1914), 108.

⁷ *Ann.*, **56**, 4 (1911), 23.

⁸ *Jahr. Kochen- und Backkunst*, **47** (1908), 308.

⁹ *Chem. Weekblad.*, **11** (1914), 206.

¹⁰ *Ibid.*, **11** (1914), 323.

¹¹ *Proc. Roy. Soc. Queensland*, **24** (1913), 168.

¹² Report Local Govt. Board Pub. Health (Great Britain), *Food Reports* **22** (1914).

TABLE I—ANALYSIS AND FREEZING POINT OF MILK OF INDIVIDUAL COWS

BREED	Cow No.	Age of Cow Yrs.	Time since Calving mos.	Milking Time	Milk Lbs.	Per cent Total Solids	Per cent Fat	Per cent Solids-not-Fat	Per cent Ash	FREEZING POINT IN ° C.		
						Rose-Gottlieb Method				Milk	Water	Diff.
Holstein.....	1	5	11 mos.	Noon	9.0	12.16	3.49	8.67	0.79	-0.553		
				P.M.	8.4	11.85	3.31	8.54	0.81	-0.551		
	2	3	9 mos.	Noon	15.2	12.72	3.95	8.77	0.67	-0.548		
				P.M.	12.5	12.21	3.26	8.95	0.72	-0.544		
Grade Holstein.....	3	9	6 mos.	A.M.	15.0	12.16	3.18	8.98	0.71	-0.542		
				P.M.	7.1	11.27	3.54	7.63	0.73	-0.585		
Holstein.....	4	7		A.M.	10.0	11.45	3.63	7.83	0.69	-0.538		
				P.M.	13.2	12.32	3.24	9.08	0.71	-0.548		
	5	3	5 mos.	A.M.	17.2	11.55	3.41	9.14	0.67	-0.541		
				P.M.	10.4	11.36	2.32	8.04	0.67	-0.548		
	6	4	5 wks.	A.M.	13.2	11.50	3.47	8.03	0.72	-0.560		
				P.M.	14.8	13.40	4.20	9.20	0.70	-0.570		
Grade Holstein.....	7	7	2 1/2 mos.	A.M.	18.1	12.68	4.17	8.51	0.71	-0.549		
				P.M.	17.6	11.46	3.46	8.00	0.75	-0.563		
	8	7	1 mo.	A.M.	15.0	11.12	3.40	7.72	0.72	-0.580		
				P.M.	24.8	10.85	3.14	7.71	0.72	-0.559		
	9	9	2 mos.	A.M.	18.1	10.62	3.11	7.51	0.69	-0.589		
				P.M.	18.5	13.84	4.99	8.85	0.73	-0.549		
Holstein.....	10	3	4 mos.	A.M.	18.0	12.89	4.05	8.84	0.72	-0.550	0.029	
				P.M.	10.0	12.31	3.31	9.00	0.69	-0.553	0.021	
Grade Holstein.....	11	7	3 mos.	A.M.	13.0	12.32	3.62	8.70	0.74	-0.562	0.027	
				P.M.	13.5	12.96	4.12	8.84	0.63	-0.541	0.025	
Holstein.....	12	8	2 1/2 mos.	Noon	26.1	12.58	4.01	8.57	0.71	-0.574		
				P.M.	21.0	11.95	3.46	8.49	0.69	-0.566	0.032	
Part Jersey.....	13	8 or 9	5 weeks	A.M.	30.2	11.59	3.07	8.52	0.72	-0.576	0.035	
				P.M.	11 approx.	12.61	4.43	7.18	0.72	-0.566	0.034	
Part Durham.....	14	6 or 7	5 mos.	P.M.	7	14.17	4.65	9.52	0.76	-0.557	0.033	
Part Jersey.....	15	15	2 1/2	8 or 10 mos	P.M.	5	15.90	9.10	0.74	-0.552		
Part Jersey.....	16	18 or 20	1 mo.	P.M.	12	11.67	7.80	6.89	0.69	-0.552		
Herd Milk.....						12.63	3.89	8.73	0.73	-0.563		
Herd Milk with 5 per cent added water.....						12.07	3.66	8.41	0.71	-0.534		
Herd Milk with 8 per cent added water.....						11.66	3.46	8.20	0.68	-0.514		
Market Milk.....										-0.549		

case, as the molecular weight of these substances is very high their relative effect upon the freezing point would be very small. The only constituents, therefore, that exert any appreciable influence upon the freezing point of milk are lactose and the soluble salts, which later are composed largely of the chlorides of the alkali metals. In this connection it should be noted that there appears to be a more or less constant relation between the amounts of lactose and sodium chloride present in the milk. When there is any increase of lactose a decrease of sodium chloride is found, and *vice versa*. Therefore, there is a tendency for any influence exerted on the freezing point by these substances to be balanced. This is shown by the work of L. W. Ferris of this laboratory in a separate paper under the title "The Detection of Added Water in Milk by Means of a Simplified Molecular Concentration Constant,"¹¹ the investigation being made at the same time and upon the same samples as were used in the freezing-point measurements here reported.

Another factor which exerts an influence upon the freezing point of milk is the per cent of acid in the sample which, if present in considerable amount, might lead to erroneous conclusions, as with increased acidity of the milk an increased depression or lowering of the freezing point takes place. Therefore, it is necessary to make the test on samples before any considerable amount of acid has developed if confidence is to be placed in the results.

In the work recorded here the samples of milk were authentic and represent portions from complete milkings, both morning and evening, in every case except cows Nos. 1 and 2, which were milked morning, noon and evening. The freezing points of the separate samples were determined as recorded in the tables and the maximum variations of the freezing points of milks from individual cows are shown.

The freezing point figures in Table I represent the mean of two and sometimes of three readings, the usual

range in variation of readings on the same sample being 0.001 to 0.003. It should be noted that Samples 3, 5, 7, 8 and 16 represent the lowest grade or thinnest milk that could be found, having in mind when obtaining them the difficulty encountered in ordinary milk analysis in distinguishing between naturally thin milk and rich milk containing small amounts of added water. The results of these five samples are shown not to give abnormal freezing-point figures.

To obtain accurate results, it is very necessary to control the amount of supercooling. As a result of some experiments on the effect produced by different degrees of supercooling, it was found that by reducing the supercooling to the extent of approximately 0.5° the freezing point was lowered approximately and uniformly 0.01°. The results are recorded in Table II. The samples used in these experiments were fresh market milk.

TABLE II—THE EFFECT ON THE FREEZING POINT OF FRESH MARKET MILK OF DIFFERENT DEGREES OF SUPERCOOLING

Test No.	Degrees of Supercooling	Freezing Point ° C.	Degree of Supercooling	Freezing Point ° C.	Difference ° C.
1.	0.9 to 1.05	-0.553	0.5 to 0.6	-0.547	0.011
		-0.553		-0.545	0.008
		-0.552		-0.545	0.007
2.	1.0 to 1.1	-0.553	0.5 to 0.6	-0.547	0.011
		-0.553		-0.547	0.011
3.	1.0	-0.553	0.5 to 0.6	-0.547	0.011
		-0.553		-0.547	0.011
4.	1.3 to 1.4	-0.589	0.5 to 0.6	-0.588	0.009
		-0.586		-0.588	0.014
5.	1.00 to 1.1	-0.551	0.5 to 0.6	-0.547	0.011
		-0.551		-0.547	0.011
		-0.551		-0.547	0.011

As the amount of acidity developed in milk has been found to influence its freezing point, a few determinations were made on milks in which different degrees of souring had developed. The results of these determinations are recorded in Table III. The samples used in these experiments were purchased market milk of presumably normal composition, except in the case of sample 4, which shows the presence of added water. These results show that the freezing point is, on an average, lowered approximately 0.003° for each 0.1 per cent increase in acidity. The figures

¹¹To appear in next issue of this journal.

here recorded represent the mean of two and sometimes of three readings, the range of variation in readings of the same samples being 0.001 to 0.003°.

TABLE III—EFFECT OF ACIDITY UPON THE FREEZING POINT OF PASTEURIZED MARKET MILK

Sample No.	Per cent Acid as Lactic	Freezing Point ° C.	Lowering of Freezing Point Due to Acid	Average Lowering for each 0.01% of Acid
1.....	0.15	—0.545		
0.18	—0.548			
0.42	—0.637	0.092	0.0030	
2.....	0.15	—0.539		
0.18	—0.548			
0.34	—0.602	0.063	0.0037	
3.....	0.18	—0.496		
0.21	—0.515			
0.24	—0.522			
0.27	—0.536	0.040	0.0044	
4.....	0.15	—0.552		
0.17	—0.555			
0.20	—0.558			
0.46	—0.646	0.084	0.0027	
5.....	0.16	—0.541		
0.18	—0.546			
0.22	—0.564	0.023	0.0038	

DESCRIPTION OF APPARATUS

The apparatus used consisted of an ordinary Beckmann thermometer graduated to 0.01° divisions and a sample tube made from tubing about 22 mm. in diameter and 1.5 mm. thick. The entire tube is about 19 cm. long and has the upper length of about 3.5 cm. widened to 30 mm. diameter to carry a stopper which serves to hold the Beckmann thermometer and the usual wire stirrer. This tube below the collar was fitted into a large test tube to allow the smallest amount of air space between the walls. A piece of thin walled rubber tubing was fitted over the top of the outer tube, making a tight joint at the shoulder of the inner tube. A glass jar of approximately two quarts capacity held the freezing mixture, the jar being wrapped in cotton or other material to assist in maintaining low temperature and a box of suitable dimensions with an opening in the top through which the thermometer passed, provided with a sliding shelf in the box at proper point for the easy removal of jar. A stand held the thermometer in position and a lens aided accurate readings.

PROCEDURE

Fifteen to twenty cc. of the sample of milk previously cooled nearly to the freezing point were placed in the tube. To obtain a temperature of -4° C., a freezing mixture of shaved ice and salt was prepared in the proportions of 40 to 50 g. of salt : 900 to 1000 g. of ice mixed with sufficient water to fill all air spaces. The thermometer was placed in the sample, and the tube lowered into the freezing mixture so that all of the milk was below the surface of the freezing bath. When the mercury column was 1° below the true freezing point the sample was stirred gently at the rate of two strokes per second to break up any ice particles formed. Too rapid stirring must be avoided to prevent the generation of heat mechanically. A rapid rise of the mercury column was noted. The highest point it reached was slightly above the freezing point. Then slow uniform stirring was continued until the mercury remained stationary for one minute when the reading was taken. The thermometer and tube were then removed and warmed with the heat of the hand or in water at 40° C. until the temperature of the sample

raised 1 or 2° and all ice crystals were melted. These operations were repeated and the freezing point taken two or three times. The freezing point of recently boiled distilled water is determined in exactly the same manner as in the case of milk; the difference between the reading obtained on distilled water and that on milk represents the freezing point of the sample. It is necessary to check up the freezing point of distilled water frequently as slight variations occur due to changes in the glass.

DISCUSSION

SUPERCOOLING—As already stated, it is very necessary to control the supercooling in order to obtain concordant results. The results of experiments to determine this demonstrate the necessity of keeping the amount of supercooling uniform and within narrow limits and further emphasize the importance of uniformity and proper control of conditions in all work of this character. This was also proved by Bordas and Genin in their report of work on the freezing point of milk. It should be stated that experience with the form of apparatus used by the writer showed that a supercooling of about 1 to 1.2° was the most satisfactory and the results recorded in this paper represent readings made with an average supercooling of approximately 1.1°. Readings made with milk when the supercooling was about 0.5 to 0.6° were not satisfactory because of the tendency of the mercury column to dart up and down and not remain stationary, as when a greater amount of supercooling was allowed. It may be safely stated, therefore, that it is not necessary in case of milk to keep the amount of supercooling down to the least possible amount so long as uniformity is maintained. An amount of supercooling of 1 to 1.3° was used in this work since it seemed to give the best working conditions and also concordant results.

ACIDITY—It was found that an increase of acidity from 0.15 per cent, which is about the average figure for fresh milk, to 0.24 per cent, which increase is not at all unusual, lowered the freezing point about 0.25 to 0.3 per cent which approaches the amount of lowering produced by the presence of 5 per cent of added water (see Table I). This same effect was found to be produced with samples preserved with formaldehyde. Therefore, a sample of milk in which a considerable amount of acid has developed or which is preserved with formaldehyde and containing a small percentage of added water might easily pass as normal milk by the freezing-point test. A too rapid stirring of the sample while freezing must be avoided to prevent the generation of heat. Our experience is in accordance with that of other observers on this point, *viz.*, the stirring should be so regulated as to reduce the amount of heat generated to a minimum and at the same time be sufficient to break up any ice crystals as they are formed. By rapid stirring a rise of 0.01° or more in the freezing point may easily be effected. A rate of one or two strokes of the stirrer per second is most satisfactory, which condition is determined largely by the behavior of the mercury column.

CONCLUSIONS

I—The freezing-point figure of milk is the most constant one yet obtained and the safest basis upon which to draw conclusions as to the presence or absence of added water.

II—The freezing-point figures on the milks of sixteen individual cows examined show that the presence of 5 per cent added water can be detected in the majority of cases by this method and in any case place the sample in the suspicious class.

III—The presence of water added to fresh milk in excess of 5 per cent can be detected with certainty by the freezing-point measurement. The use of sufficient formaldehyde for preservation was found to lower the freezing point.

IV—It is essential that the test be applied only to reasonably fresh milk as the presence of acidity to the extent of 0.1 per cent beyond the normal for fresh milk (0.15 per cent) counteracts the amount of decrease in the freezing point depression produced by the presence of approximately 5 per cent of added water.

V—The method is practical in milk control work in that the test need be applied only to samples of doubtful character.

DAIRY LABORATORY AND LABORATORY OF FOOD CONTROL
BUREAU OF CHEMISTRY, WASHINGTON, D. C.

INSOLUBLE PHOSPHORIC ACID IN ORGANIC BASE GOODS

By E. O. THOMAS

Received June 2, 1917

The Official Method¹ for the determination of the citrate-insoluble phosphoric acid in fertilizers while giving all the available phosphoric acid in acid phosphate does not give all of the available in certain classes of organic materials. However, when this same material is batched into a complete fertilizer more available phosphoric acid (or what is the same thing, less insoluble phosphoric acid) is obtained, due to a relatively larger amount of citrate solution acting on the material. Particular reference is here made to base goods made by acidulating garbage tankage without any addition of phosphate rock. By the Official Method this material ranges from 0.95 per cent to 1.80 per cent insoluble phosphoric acid. That the Official Method does not give the true available phosphoric acid in this material is shown by the following experiments. A sample of this base goods containing 17.82 per cent moisture showed by the Official Method 1.56 per cent insoluble phosphoric acid; by increasing the amount of citrate solution used per 2.0 g. of base the results in Table I were obtained.

That the Official Method gives all of the available phosphoric acid in acid phosphate is shown by the test (Table I) on two samples of acid phosphate.

A complete fertilizer made on the following formula using no phosphate material but base goods (Table I) and acid phosphate No. 2 (Table I) gave the re-

sults given in Table I on insoluble phosphoric acid when deviating from the Official Method.

500 lbs. Base Goods (1.56% Insol. P_2O_5)
900 lbs. Acid Phosphate No. 2 (0.12% Insol. P_2O_5)
520 lbs. Kanana Nitrogen
80 lbs. Muriate of Potash

The calculated amount of insoluble phosphoric acid in the complete fertilizer mixture is 0.44 per cent, or 0.09 per cent more than that found. As the Official Method is shown to take care of all the available phosphoric acid in acid phosphate it is fair to

TABLE I—RESULTS ON 2-GRAM SAMPLES WITH VARYING AMOUNTS OF NEUTRAL AMMONIUM CITRATE SOLUTION, GRAVITY, 1.09 (100 Cc. Neutral Ammonium Citrate Solution Used in Official Method)

Cc. Neutral Ammonium Citrate Solution	Per cent Base Goods	Per cent Insoluble Phosphoric Acid No. 1	Per cent Acid Phosphates No. 2	Complete Fertilizer
100	1.56	1.41	0.12	0.35
133	1.44	1.44	0.09	0.28
200	1.38	1.35	0.10	0.26
400	1.05	1.42	0.08	0.28
800	0.88	1.37	0.08	0.20
1200	0.80
1600	0.70

assume that this gain of 0.09 per cent available is derived from the 500 lbs. of base goods, or a gain to the buyer of 0.36 unit of available phosphoric acid per ton. Leaving out of consideration the other materials in this mixture, of the 2.0 g. taken for analysis, 0.5 g. is base goods which is acted on by 100 cc. of citrate solution; i. e., the ratio of 2.0 g. base goods to 400 cc. citrate solution. The insoluble phosphoric acid found in the base goods using 400 cc. citrate solution (Table I) was 1.05 per cent, a gain in available of 0.51 per cent over that found by the Official Method.

By following all details of the Official Method, except the using of 100 cc. of *N/10* normal citric acid in place of the 100 cc. ammonium citrate as suggested by Rudnick,¹ this sample of base showed 1.78 per cent insoluble phosphoric acid. Using 100 cc. 2.0 per cent citric acid to replace the ammonium citrate this same base showed 1.15 per cent insoluble. This latter figure is comparable with that obtained when using 400 cc. citrate solution in the digestion, namely, 1.05 per cent, and is also comparable with the figures obtained when this garbage base is batched (*vis.*, in complete fertilizer, Table I) not to exceed 500 lbs. to the ton. As shown in Table I, there is a gain of 0.36 per cent available phosphoric acid per ton of base goods when this material is batched at the rate of 500 lbs. per ton of complete fertilizer and the Official Method is used. This gain of 0.36 per cent plus the 1.15 per cent found when using the 2.0 per cent citric acid solution gives 1.51 per cent insoluble phosphoric acid, very close to the amount found by the Official Method, *vis.*, 1.56 per cent.

CONCLUSION

The Official Method for the determination of citrate-insoluble phosphoric acid gives the true value of acid phosphate, but some modification should be made for the analysis of materials of the character of acidulated garbage tankage.

814 PEARCE BUILDING
NEWBOLD, VIRGINIA

¹ Jour. A. O. A. C., 1, No. 4, Part 2, p. 4.

¹ THIS JOURNAL, 6 (1914), 486.

LABORATORY AND PLANT

DISCONTINUOUS EXTRACTION PROCESSES

By L. F. HAWLEY¹

Received May 8, 1917

The operation by which a soluble substance is removed from an accompanying insoluble material by washing with a suitable solvent is a common and important operation in chemical industrial processes; the terms lixiviation, leaching, percolation, extraction, diffusion, filtration, decoction, decantation, washing and others are applied in different industries to the same general operation and on account of this varied nomenclature there seems to be a lack of appreciation of the fact that the fundamental principle is the same in each of these operations, whatever name is applied to it.

Most of us have a hazy idea that in such an operation several separate washings with fresh solvent will remove more soluble material than a single washing with the same total amount of solvent, or that a multiple extraction, in which the same solvent is used in proper order on several charges of material, is more efficient than repeated washings with fresh solvent, but when we are asked why, in what way, or especially, how much, the answer is not forthcoming. In certain single cases, as a result of long experience, we may be able to give satisfactory answers, but the general case has not been developed, so far as is known to the writer. The following discussion is for the purpose of developing the general case and giving a quantitative treatment of the subject.

THE SIMPLEST CASE—In order to simplify the conditions to a point where a mathematical treatment is readily possible we will first assume an ideal case in which the original material to be treated consists of small particles of an impermeable, insoluble substance, wet with a strong solution of the substance to be extracted; these conditions would be well met by a mass of small glass beads wet with a strong salt solution, *i. e.*, containing only as much of the solution as would remain behind after draining. If a mass of this kind is shaken with a certain amount of water and as much as possible of the water is then drained off, how much of the original salt remains with the beads? In this particular example it is easy to conceive that after shaking with the water a weaker solution is formed and that the concentration of the part drained off is the same as the concentration of the part remaining; therefore, the portion of the salt remaining on the beads after such a treatment depends only on the relation between the volume of solution drained off and the volume of the solution retained.

SOLVENT RATIO—If, for instance, 5 volumes of solution are drained off and one volume is retained, then $\frac{5}{6}$ of the salt is removed and $\frac{1}{6}$ remains with the beads. This ratio, *volume removed : volume retained*, is of fundamental importance in considering any extraction problem and will hereafter be called the *solvent ratio*,

and designated by *a*. With any solvent ratio *a*, a single washing will remove $\frac{a}{a+1}$ of the original soluble substance present, leaving behind $\frac{1}{a+1}$. If the amount of solvent retained is known, then the amount of soluble material removed can be computed from the amount of solvent removed.

SUCCESSIVE TREATMENTS WITH FRESH SOLVENT

By carrying this same conception a little farther, the amount of soluble material remaining after two or more successive treatments with the same amount of solvent can be computed. If $\frac{1}{a+1}$ is left behind after one treatment with solvent ratio *a* then $\frac{1}{(a+1)^2}$ is left after two such treatments, $\frac{1}{(a+1)^3}$ after 3, etc.¹

Table I is computed from these formulas and gives the percentage of soluble material removed after different numbers of treatments with varying solvent ratios. The total volumes of the resulting solutions are also shown for comparison; these volumes are expressed in terms of the amount of solvent retained.

TABLE I—PERCENTAGE EXTRACTION WITH DIFFERENT SOLVENT RATIOS AND DIFFERENT NUMBERS OF TREATMENTS; REPEATED WASHINGS WITH FRESH SOLVENT*

TREATMENTS:	1	2	3	4
Solvent Ratio	Per cent Ex-tracted	Volume of Solu- tion Per cent Ex- tr.	Vol. of Sol. Per cent Ex- tr.	Vol. of Sol. Per cent Ex- tr.
1.....	80.00	1 75.00	2 87.50	3 93.75
2.....	66.67	2 88.89	4 96.30	6 98.76
3.....	75.00	3 93.75	6 98.44	9 99.61
4.....	80.00	4 96.00	8 99.20	12 99.84
5.....	83.33	5 97.22	10 99.54	15 99.92
6.....	85.71	6 97.96	12 99.71	18 99.96
7.....	87.50	7 98.44	14 99.81	21 99.98
8.....	88.89	8 98.76	16 99.86	24 99.98
9.....	90.00	9 99.00	18 99.90	27 99.99
10.....	90.90	10 99.17	20 99.92	30 99.99

* Just previous to the publication of this paper the writer's attention was called to a similar table in "Cyaniding Gold and Silver Ores," Julian and Smart, Chapter 31.

Table I shows the correctness of the common notion that in washing with a limited amount of solvent it is better to wash several times with small portions than once with the whole amount; besides this the results which can be obtained with different amounts of solvent and different methods of application are shown quantitatively. For instance, 6 volumes of solvent, if used in one treatment, may give only 85.7 per cent extraction (solvent ratio 6), but if used in two equal parts separately will give 93.75 per cent (solvent ratio 3), or in three parts, 96.29 (solvent ratio 2).

¹ See Ostwald's "Foundations of Analytical Chemistry" sections on the Theory of Washing Precipitates and on Adsorption Phenomena. Ostwald says that his similar formulas "do not agree at all with observed facts" on account of the adsorption phenomena which were not considered in their calculation but he is speaking of analytical results where 00.01 per cent might be a large error. In commercial extraction where 00.1 per cent might be a negligible discrepancy between calculated results and observed facts the effect of adsorption would not seriously interfere with the accuracy of the formulas. Finely divided analytical precipitates would also show adsorption phenomena to a much greater degree than would the coarser granular or fibrous materials commonly used in extraction processes.

¹ Chemist in Forest Products, Forest Products Laboratory, Madison, Wisconsin.

Even more striking examples are that 4 volumes of solvent in 4 equal parts give a better extraction (93.75 per cent, solvent ratio 1) than 10 volumes used all at once (90.9 per cent, solvent ratio 10), and that 8 volumes in 4 parts give the same results (98.76 per cent, solvent ratio 2) as 16 volumes in two parts (solvent ratio 4).¹

MULTIPLE EXTRACTION

These simple cases have served to clarify our views of the terms "retained solvent" and "solvent ratio" and we can now proceed to the more efficient and more complex process of multiple extraction. It can be readily seen from the consideration of the results of any series of repeated washings with fresh solvent, as shown in Table I, that as the number of washings increase the solvent is used less and less efficiently, *i. e.*, the same amount of solvent removes less and less salt. For instance, when using enough solvent each time so that the solvent ratio is 4, washing No. 1 removes 80 per cent; washing No. 2, 16 per cent; No. 3, 3.2 per cent; No. 4, 0.64 per cent. After these last washings the solution contains so little of the salt that it could very evidently be used to better advantage as solvent on a fresh charge of beads than as a finished solution. By means of a procedure whereby the weaker solutions are used over again, either on new charges of the original material or on charges which have been already extracted by stronger solutions, the final solution can be obtained in much more concentrated form than by using the fresh solution only once; *i. e.*, the solvent is used more efficiently.

The most rational method of applying the solvent to obtain this effect is according to the counter-current principle, in which each lot of solvent is used on charges of beads containing successively more and more salt and in which each charge of beads is treated with solvents containing successively less and less salt. Another way of considering the counter-current principle is that each lot of solvent progresses in one direction, meeting charges of beads which have been treated fewer and fewer times until it finally treats a fresh charge, is fully concentrated, and is removed from the system, while each charge of beads progresses in the other direction, meeting solvents which have been used fewer and fewer times until finally it is treated with fresh solvent, is completely washed, and removed from the system. We will now endeavor to develop the formulas which will express the amount of soluble material removed by varying solvent ratios and varying numbers of treatments, according to this counter-current principle.

DEVELOPMENT OF FORMULAS These formulas are more difficult to work out on account of the fact that on the start with fresh solvent and fresh material the results are different from those obtained after the process has been in operation for some time. This

¹ It will not be necessary to consider the case in which unequal portions of solvent are used for each of the mathematical cell, but that if x is a constant, and a is a maximum when $a = 1$, and therefore with the same total amount of solvent and equal portions give better results than the same number of unequal portions.

is shown in the following table, which traces the course of the operation from the time of starting with fresh materials until the results become practically constant when a solvent ratio of 2 is used in a series of two extractions:

TABLE II—TABLE SHOWING DETAILED COURSE OF EXTRACTION IN SERIES.

Cell No.	TWO TREATMENTS. SOLVENT RATIO 2		AFTER	
	BEFORE	Added Solvent	Beads	Solvent
1.....	100.00	0	33.33	66.67
2.....	100.00	66.67	55.56	44.44
3.....	55.56	0	18.52	37.04
4.....	100.00	37.04	45.62	54.38
5.....	45.62	0	15.23	30.45
6.....	100.00	30.45	43.48	56.52
7.....	43.48	0	14.49	28.99
8.....	100.00	28.99	43.00	56.99
9.....	43.00	0	14.33	28.66
10.....	100.00	28.66	42.89	57.11
11.....	42.89	0	14.30(a)	28.59(a)
12.....	100.00	28.59	42.86(c)	57.14(d)

$$(a) = r \quad (b) = ax \quad (c) = \frac{ax + 1}{a + 1} \quad (d) = \frac{(ax + 1)a}{a + 1} = 1 - r$$

In this table the figures represent percentages of salt, 100 per cent being the amount in a fresh charge of beads. For instance, 100 per cent in the column headed "Beads" signifies a fresh charge of beads, while 0.0 per cent in the "Solvent" column indicates fresh solvent. After the first treatment of fresh beads with fresh solvent 33.33 per cent of the original salt remains on the beads and 66.66 per cent are removed with the solvent. This solvent containing 66.66 per cent of the salt on a charge is added to a fresh charge of beads (100 per cent salt) and by mixing and draining off $\frac{1}{3}$ (55.5 per cent) of the total 166.66 per cent remains behind on the beads while $\frac{2}{3}$ (111.1 per cent) is removed in the solvent drained off. The beads containing 55.5 per cent salt are now treated with fresh solvent which removes 37.04 per cent, leaving 18.52 per cent. In this way the extraction is continued, the figures in italics representing the amount of salt left on the beads after two washings and the figures in parentheses representing the amount removed from the system in the solvent after the second washing. It will be noted that these two figures gradually become smaller until they are practically constant at about 14.30 per cent and 28.59 per cent, respectively, and since together they represent the final disposition of the 100.00 per cent of salt added with each fresh charge of beads they will finally reach a limit at which the sum of the two will be 100.00. It is now possible to determine the value of both these figures in terms of the solvent ratio a .

If the amount of salt finally left on the beads is called x , then the salt in the solution drained off after the treatment is ax , since the ratio between these figures is the solvent ratio a . The solution drained off containing ax is added to a fresh charge of beads and the total salt in the mixture is then $ax + 1$; by the treatment this amount is divided in two parts, one remaining on the beads and the other drained off, which are so each other as $1 : a$. That is, the part remaining on the beads is $\frac{1}{a+1}$, and the part drained

$$\text{off is } \frac{ax}{a+1} \quad (a) = r \quad (b) = ax$$

By using latter figures, the amount of salt in the final solution is $\frac{ax + 1}{a + 1}$ and

that $\frac{a}{a+1} (ax+1) = 1-x$; clearing of fractions, $a^2x + a = a - ax + 1 - x$, or, $x = \frac{1}{a^2 + a + 1}$.

In a multiple extraction with two treatments in series the amount of unextracted salt is then $\frac{1}{a^2 + a + 1}$ and the amount of extracted salt is $\frac{a^2 + a}{a^2 + a + 1}$ when $a =$ the solvent ratio.

In the same way the amount of salt extracted by multiple extraction with 3, 4, or more treatments in series can be expressed in terms of the solvent ratio. The details of the development of the formulas need not be repeated and the results only will be given. For a series of 3 treatments the unextracted salt is $\frac{1}{a^3 + a^2 + a + 1}$, for 4 treatments $\frac{1}{a^4 + a^3 + a^2 + a + 1}$, etc.

Table III shows the percentage extraction obtainable with different solvent ratios and different number of treatments, as computed from these formulas.

TABLE III—PERCENTAGE EXTRACTION WITH DIFFERENT SOLVENT RATIOS AND DIFFERENT NUMBERS OF TREATMENTS. MULTIPLE EXTRACTION

Solvent Ratio	Number of Treatments*					
	1	2	3	4	5	6
1.....	50.00	66.67	75.00	80.00	83.33	85.71
2.....	66.67	85.71	93.33	96.77	98.42	99.21
3.....	75.00	92.31	97.50	99.17	99.73	99.91
4.....	80.00	95.24	98.82	99.71	99.93	...
5.....	83.33	96.77	99.36	99.87	99.97	...
6.....	85.71	97.67	99.61	99.94
7.....	87.50	98.24	99.75	99.96
8.....	88.89	98.63	99.83	99.98
9.....	90.00	98.90	99.88	99.99
10.....	90.90	99.10	99.91

*Number of treatments must, of course, be integral but solvent ratios may be fractional. The results obtainable with fractional solvent ratios may be determined by substitution in the formulas or by inspection and interpolation in the tables. It should be noted that with solvent ratios less than unity the value of $\frac{1}{1+a+a^2+a^3+\dots+a^n} = 1 - a^n$, i. e., however many treatments are given with a solvent ratio of, say, 0.8 not less than $1 - 0.8 = 0.2$ of the original soluble material will be left unextracted. This is the only instance where the mathematical conception of the percentage extraction as a function of the solvent ratio seems to apply directly to continuous extraction; continuous extraction may be considered as discontinuous extraction in an infinite number of cells and, therefore, even in theoretically perfect continuous extraction, the solvent ratio must be unity or greater (the amount of solvent drawn from the system must be equal to or greater than the amount left on the extracted material) in order to obtain complete recovery of soluble material.

In these cases of multiple extraction the amount of solvent in the final solution is proportional to the solvent ratio only and is not affected by the number of treatments and, therefore, the following examples can be derived from the table. Three volumes of solvent in 5 treatments give better extraction (99.73 per cent) than 6 volumes in 3 treatments (99.61 per cent). Two volumes of solvent in 6 treatments in series give better extraction (99.21 per cent) than 4 volumes in 3 treatments (98.82 per cent), or than 10 volumes in 2 treatments (99.10 per cent). Other examples can be figured out in the same way.

COMPARISON OF MULTIPLE EXTRACTION WITH REPEATED WASHINGS WITH FRESH SOLVENT

With these two tables showing the results obtainable in extraction by repeated washings with fresh solvent and by multiple extraction, respectively, we are now in position to make comparisons between these two methods. For convenience in making the com-

parison, Table IV is prepared which is simply a combination of Tables II and III.

This table shows plainly the advantages of multiple extraction in the way of removing a greater proportion of the soluble material per unit of solvent used.

EXTRACTION OF MATERIAL NOT WET WITH SOLVENT

The foregoing conclusions were all obtained on the assumptions: (1) that the soluble substance was already in solution before the extraction process was started, and (2) that the material to be extracted was wet with the amount of solution normally retained after draining. There are several instances in commercial practice where both these assumptions would hold but there are many instances where neither would hold and we will now develop the formula for multiple extraction and for repeated washings with fresh solvent, similar to the preceding, except that the original material will be assumed dry and with the soluble substance in solid form. A concrete case would be a mass of glass beads whose surfaces were encrusted with a layer of salt or which were uniformly mixed with finely ground salt. In this case another assumption must be made in order to make the results capable of simple mathematical treatment, viz., that all the salt is dissolved during the first treatment with solvent.

SOLVENT RATIOS—Extraction under this second set of conditions will give results the same as under the first set of conditions, except that when the beads are treated with solvent for the first time part of the solvent added will be retained and the solvent ratio will be less than when the same amount of solvent is added to wet beads. After the first treatment, however, the beads will be wet and just as much solvent as is added will be drained off. The solvent ratio for the first treatment will, therefore, be different from that for the other treatments. For instance, if a mass of dry beads is treated three times with fresh solvent, each time with twice as much solvent as the beads retain after draining, the solvent ratio will be 1 for the first treatment and 2 for the other two treatments;¹ and only 5 of the 6 volumes of solvent used will be found in the final solution, the other 1 volume being retained by the beads. Or in multiple extraction, if twice as much solvent is used as is retained by the beads the solvent ratio will be 1 in the first treatment the beads receive and 2 in the other treatments, however many there may be.

¹ This is not the most efficient way to use 6 volumes of solvent in three extractions, since better extractions can be obtained by dividing the solvent into three such parts that the solvent ratio is the same each treatment (see footnote p. 867). For instance, if $2\frac{1}{2}$ volumes are used in the first treatment and $1\frac{1}{2}$ volumes in each of the others, the solvent ratio would be $\frac{2}{3}$ for each treatment and the unextracted salt would be $(\frac{2}{3})^3 = 5.2$ per cent; while with solvent ratios of 1, 2 and 2, respectively, for the three treatments the unextracted salt would be $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2} = \frac{1}{8} = 5.55$ per cent. But these differences are very small, especially with high solvent ratios, or large number of extractions and in order to make the results comparable with multiple extractions equal amounts of solvent will be used for each extraction instead of dividing, so as to give equal solvent ratios. In multiple extraction the relative amounts of solvent used in different treatments cannot be controlled because fresh solvent is used only for the last treatment of a charge and the previous treatments can use only this same amount over again.

PERCENTAGE RECOVERY AND VOLUME OF EXTRACT WITH DIFFERENT SOLVENT RATIOS AND DIFFERENT NUMBER OF TREATMENTS

TABLE IV—MATERIAL SATURATED WITH SOLVENT AT OUTSET
x = Multiple Series Extraction, y = Repeated Fresh Solvent Extraction

Solvent Ratio	1 TREATMENT		2 TREATMENTS		3 TREATMENTS		4 TREATMENTS		5 TREATMENTS		6 TREATMENTS	
	Vol. of Sol. x	Per cent Recovery y	Vol. x	% Rec. y	Vol. x	% Rec. y	Vol. x	% Rec. y	Vol. x	% Rec. y	Vol. x	% Rec. y
1.....	1	50.00	1	66.67	2	75.00	1	75.00	3	87.50	1	80.00
2.....	2	66.67	2	85.71	4	88.89	2	93.33	6	96.30	1	96.77
3.....	3	75.00	3	92.31	6	93.75	3	97.50	9	98.44	3	99.17
4.....	4	80.00	4	95.24	8	96.00	4	98.82	12	99.20	4	99.71
5.....	5	83.33	5	96.77	10	97.22	5	99.36	15	99.54	5	99.87
6.....	6	85.71	6	97.67	12	97.96	6	99.61	18	99.71	6	99.94
7.....	7	87.50	7	98.24	14	98.44	7	99.75	21	99.81	7	99.96
8.....	8	88.89	8	98.63	16	98.76	8	99.83	24	99.86	8	99.98
9.....	9	90.00	9	99.00	18	99.00	9	99.88	27	99.90	9	99.99
10.....	10	90.90	10	99.10	20	99.17	10	99.91	30	99.92	10	40

TABLE V—MATERIAL NOT SATURATED WITH SOLVENT AT OUTSET
x = Multiple Series Extraction, y = Repeated Fresh Solvent Extraction

Solvent Ratio*	1 TREATMENT		2 TREATMENTS		3 TREATMENTS		4 TREATMENTS		5 TREATMENTS		6 TREATMENTS	
	Volume of Ex. tract x	Per cent Recovery y	Vol. x	% Rec. y	Vol. x	% Rec. y	Vol. x	% Rec. y	Vol. x	% Rec. y	Vol. x	% Rec. y
1.....	0	0	0	0	1	50.00	0	0	2	75.00	0	0
2.....	1	50.00	1	75.00	3	83.33	1	93.75	7	98.15	1	96.88
3.....	2	66.67	2	88.89	5	91.66	2	96.30	9	98.76	2	99.59
4.....	3	75.00	3	93.75	7	95.00	3	98.44	11	99.00	3	99.61
5.....	4	80.00	4	96.00	9	96.67	4	99.20	14	99.44	4	99.84
6.....	5	83.33	5	97.22	11	97.62	5	99.54	17	99.66	5	99.92
7.....	6	85.71	6	97.96	13	98.21	6	99.71	20	99.78	6	99.96
8.....	7	87.50	7	98.44	15	98.61	7	99.81	23	99.85	7	99.98
9.....	8	88.89	8	98.77	17	98.89	8	99.86	26	99.89	8	99.98
10.....	9	90.00	9	99.00	19	99.09	9	99.90	29	99.92	9	99.99

* For all treatments after the first. Solvent ratio is $a-1$ on the first treatment.

FORMULAS—With these conclusions in regard to the solvent ratios when extracting dry material, the formulas expressing the percentage extraction under varying conditions can be developed just as was done for wet material. The details need not be worked out again and the results only will be given. In repeated treatments with fresh solvent where the solvent ratio is $a-1$ for the first treatment and a for the other treatments, the formula expressing the amount of unextracted soluble material after one treatment is $\frac{1}{a}$; after 2 treatments $\frac{1}{a(a+1)}$; 3 treatments $\frac{1}{a(a+1)^2}$; etc. In multiple extraction where the solvent ratio is $a-1$ for the first treatment and a for the other treatments, the amount of unextracted salt after one treatment is $\frac{1}{a}$; after 2 treatments, $\frac{1}{a^2}$; after 3 treatments, $\frac{1}{a^3}$; etc.

Table V gives the computations from these formulas for different solvent ratios and different numbers of treatments, that is, it gives a comparison between repeated washings with fresh solvent and multiple extraction when the original material is not saturated with the solvent on the start.

The figures in Table V show relationships similar to those of Table IV and the general conclusions on the advantages of multiple extraction hold here also. As a general comparison between Tables IV and V it can be said that, under similar conditions as to the amount of original solvent used and number of treatments, a somewhat less complete extraction but a greater concentration of solution is found, when the original material is not saturated with solvent.

OTHER METHODS OF MANIPULATION

In the foregoing it has been intimated perhaps that the solvent ratio was variable at will by simply varying the amount of solvent used on a charge of material,

but in practice it has been found that the amount of solvent used per charge is determined largely by the character of the material to be extracted, the most practicable amount being about that much required just to cover the charge (to fill the interstices between the solid particles). If much more than this amount is used that portion of the solvent above the charge is not used efficiently and tends to be less concentrated than that in contact with the charge. If much less than this amount is used the upper part of the charge not in contact with solvent is not as thoroughly extracted as the lower part of the charge. Therefore, in practice the solvent ratio is fixed within fairly narrow limits since the two terms of the ratio *volume drained off* (volume required to cover minus volume retained after draining) and *volume retained after draining* both depend upon the nature of the material to be extracted.

TWO CONSECUTIVE TREATMENTS WITH FRESH SOLVENT—The same general effect on concentration of solution and on percentage of complete extraction as is obtained by changing the solvent ratio may be obtained, however, by changing the method of applying the solvent without changing the solvent ratio. In certain cases where the value of the recovered product is high and the cost of the recovery process after extraction is relatively low in comparison with the cost of extraction or in cases where the insoluble part of the charge is the valuable part, it might be desirable to increase the percentage recovery of soluble material at the expense of decreased concentration of solution without increasing the amount of extracting apparatus. These results can be brought about by giving each charge two treatments with fresh solvent instead of only one, as has been discussed in the methods previously studied. The concentrations of the solutions are practically the same as those obtained by doubling the solvent ratio, but the percentage recovery is better in all cases,¹ as shown in Table VI.

¹ If the same amount of solvent is used in each treatment, the concentration of the solution will be lower in the second treatment than in the first.

TABLE VI—PERCENTAGE EXTRACTION WHEN EVERY CHARGE IS WASHED TWICE WITH FRESH SOLVENT

Solvent Ratio	NUMBER TREATMENTS PER CHARGE						
	1	2	3	4	5	6	7
1	75.00	85.71	91.67	95.00	96.97	98.15	98.75
2	88.89	96.00	98.55	99.47	99.81	99.93	99.99
3	94.75	98.36	99.57	99.80	99.97	99.99	99.99
4	96.00	99.17	99.83	99.96	99.99	99.99	99.99
5	97.22	99.53	99.92	99.99	99.99	99.99	99.99
6	97.96	99.70	99.96	99.99	99.99	99.99	99.99
7	98.44	99.80	99.98	99.99	99.99	99.99	99.99

* Every alternate lot of solvent is used in one more treatment than the previous lot.

** With the same solvent ratio the volume of solution is twice as great in this case as in the case where every charge is washed only once with fresh solvent, as in Table III.

The formulas from which the table was prepared are shown below.

Number of Treatments	Solvent Used Times	FRACTION UNEXTRACTED
2	1 & 2	$1/(a^2 + 2a + 1)$
3	1 & 2	$1/(a^3 + 3a^2 + 2a + 1)$
4	2	$1/(a^4 + 4a^3 + 4a^2 + 2a + 1)$
5	2 & 3	$1/(a^5 + 5a^4 + 7a^3 + 4a^2 + 2a + 1)$
6	3	$1/(a^6 + 6a^5 + 11a^4 + 8a^3 + 4a^2 + 2a + 1)$
7	3 & 4	$1/(a^7 + 7a^6 + 16a^5 + 15a^4 + 8a^3 + 4a^2 + 2a + 1)$

These denominators form a series in which any term $A_n = AA_{n-1} + AA_{n-2} + 1$ and the following arrangement also shows their series relationship:

$$\begin{aligned}(a+1)^2 &= a^2 + 2a + 1 \\(a+1)^3 &= a^3 + 3a^2 + 2a + 1 \\(a+1)^4 &= a^4 + 4a^3 + 4a^2 + 2a + 1 \\(a+1)^5 &= a^5 + 5a^4 + 7a^3 + 4a^2 + 2a + 1 \\(a+1)^6 &= a^6 + 6a^5 + 11a^4 + 8a^3 + 4a^2 + 2a + 1 \\(a+1)^7 &= a^7 + 7a^6 + 16a^5 + 15a^4 + 8a^3 + 4a^2 + 2a + 1\end{aligned}$$

This method of treatment is really a combination of ordinary multiple extraction with repeated washings with fresh solvent and the results are naturally a mean between these two simple methods of extraction.

ONE TREATMENT WITH FRESH SOLVENT FOR EVERY TWO CHARGES—The opposite case, where high concentration of solution is desired, even at the expense of incomplete extraction or longer series of extraction, can be obtained by treating only every alternate charge of material with fresh solvent, every other alternate charge getting its final treatment with solvent which has been used once before; in this way two charges of extracted insoluble material are removed from the system for every one lot of solvent removed. Table VII shows the results obtained by this method of manipulation. The data in Table VII were obtained from the formulas listed below this table.

Of course, these two methods of manipulation can also be carried out as well on material not wet with solvent at the outset (see p. 868), but it is not thought worth while to include the results obtained under such conditions as they show only the same general relationship between "wet" and "dry" extractions as has already been mentioned on p. 869.

APPLICATION TO COMMERCIAL CONDITIONS

For the mathematical treatments an ideal case was assumed in which the insoluble portion of the original material does not prevent the complete dissolving of the soluble portion or the complete intermingling of the solution added and the solution already present, its only effect being to prevent the complete draining off of the solution. Such conditions are closely approached in the concrete examples

TABLE VII—PERCENTAGE EXTRACTION BY ONE TREATMENT WITH FRESH SOLVENT FOR EVERY TWO CHARGES

Solvent Ratio	NUMBER TREATMENTS PER CHARGE						
	1	2	3	4	5	6	7
1(b)	42.86	45.83	47.50	48.48	49.07	49.43	49.63
2	68.75	71.93	76.30	79.55	82.00	84.03	85.37
3	76.36	83.97	88.43	91.62	93.79	95.37	96.41
4	82.57	89.89	93.61	96.05	97.49	98.41	98.93
5	86.39	93.12	96.09	97.89	98.81	99.35	99.69
6	88.92	95.04	97.42	98.76	99.37	99.69	99.84
7	90.71	96.27	98.18	99.21	99.63	99.84	99.91
8	92.03	97.10	98.66	99.47	99.77	99.91	99.94
9	93.04	97.68	98.98	99.63	99.85	99.94	99.96
10	93.83	98.10	99.20	99.73	99.90	99.96	99.99

(a) Every alternate charge gets one less treatment than the previous charge.

(b) With the same solvent ratio the volume of solution is only one-half as great as in the case where every charge gets one treatment with fresh solvent (Table III) and only one-fourth as great as in Table VI.

Number of Treatments	Solvent Used Number Times	PERCENTAGE UNEXTRACTED*
1	2	$\frac{a^2 + 2a + 1}{2a^2 + 2a + 1}$
1 & 2	3	$\frac{a^3 + 3a^2 + 2a + 1}{2a^3 + 3a^2 + 3a + 1}$
2	4	$\frac{a^4 + 4a^3 + 4a^2 + 2a + 1}{2a^4 + 2a^3 + 4a^2 + 4a + 1}$
2 & 3	5	$\frac{a^5 + 5a^4 + 4a^3 + 7a^2 + 5a + 1}{2a^5 + 2a^4 + 4a^3 + 8a^2 + 11a + 2}$
3	6	$\frac{a^6 + 6a^5 + 14a^4 + 8a^3 + 15a^2 + 6a + 1}{2a^6 + 2a^5 + 4a^4 + 8a^3 + 16a^2 + 16a + 1}$
3 & 4	7	$\frac{a^7 + 7a^6 + 4a^5 + 8a^4 + 15a^3 + 16a^2 + 7a + 1}{2a^7 + 2a^6 + 4a^5 + 8a^4 + 16a^3 + 16a^2 + 15a + 2}$
4	8	$\frac{a^8 + 8a^7 + 4a^6 + 8a^5 + 16a^4 + 20a^3 + 22a^2 + 8a + 1}{2a^8 + 2a^7 + 4a^6 + 8a^5 + 16a^4 + 20a^3 + 22a^2 + 8a + 1}$

* These numerators form a series in which any term equals the previous term plus the second previous term multiplied by a or $A_n = A_{n-1} + AA_{n-2}$.

These denominators are a series in which any term $A_n = A_{n-1} + A_{n-1} + AA_{n-2}$, or the series can also be expressed as follows to show the relationship between the various terms.

$$\begin{aligned}a_1 &= a + 1 \\a_2 &= (a + 1)^2 - a^2 \\a_3 &= (a + 1)^3 - a^3 \\a_4 &= (a + 1)^4 - 2a^2(a + 1) \\a_5 &= (a + 1)^5 - 3a^2(a + 1)^2 \\a_6 &= (a + 1)^6 - 4a^2(a + 1)^3 + a^4 \\a_7 &= (a + 1)^7 - 5a^2(a + 1)^4 + 3a^2(a + 1) \\a_8 &= (a + 1)^8 - 6a^2(a + 1)^5 + 6a^2(a + 1)^2 \\a_9 &= (a + 1)^9 - 7a^2(a + 1)^6 + 10a^2(a + 1)^3 - a^6\end{aligned}$$

of glass beads wet with a solution of salt or encrusted with solid salt if the treatment with solvent is accompanied by thorough mixing, such as might be accomplished by boiling or mechanical agitation. These conditions could also be approximated in any commercial process in which the soluble substance is held at or near the surface of the particles of the original material to be extracted, but when the soluble substance is distributed evenly throughout each particle and the particles are large, then the ready dissolving of the soluble substance is hindered and the theoretical extraction might not be obtained. In this case, however, the soluble substance protected from action of the solvent by the large size of the particle really has no effect in the process whatever and should not be considered in any study of the course of the extraction. For instance, if 10 per cent of the soluble substance is completely protected from action of the solvent the course of the extraction will still be according to the mathematical formula, except that the theoretical limit of possible extraction is now 90 per cent of the actual soluble material present instead of 100 per cent; that is, all figures are reduced by 10 per cent.

If there is no agitation of the solid charge itself,

but only circulation of the solvent, as by boiling, it is possible that by packing together of parts of the charge and by the flow of solvent through channels around the packed portions a certain proportion of the charge would never be acted upon by solvent. This part of the charge unacted on by solvent would affect the course of the extraction in exactly the same way as the soluble substance near the center of the large particles, *i. e.*, the mathematical formulas would apply but all the figures would be reduced by a percentage equal to the percentage of the total charge not reached by the solvent. If, however, certain portions of the charge not reached by the solvent during the first application of solvent to the charge are reached during later applications, then the course of the extraction does not follow the formulas. But it is believed that this action takes place only to a very small extent in commercial processes and it can be safely asserted that any commercial extraction process in which such action of the solvent does occur is in general an inefficient process, inefficient because it requires a number of separate treatments to effect the complete solution which might better be obtained in a single treatment with longer time or with some other improved condition.

This method of looking at the operation of an extraction process shows the advantages to be obtained by keeping the solutions from the different treatments very well separated; imperfect draining of the solvent from a charge before applying the next solvent is equivalent to decreasing the solvent ratio (because the solvent ratio varies inversely as the amount of solvent left in the charge) and decreased solvent ratio means decreased yields, other conditions being the same.

In certain cases the extraction process is run in a manner that may be called semi-continuous, that is, each charge is boiled or otherwise agitated with its particular lot of solvent while shut off from the rest of the system (discontinuous), then all the extractors are connected together and one pumping serves to force the solvent from each extractor to the next in series (continuous in that the solvent is being pumped in at the same time it is being drawn off). This method of moving the solvent may be the result of an attempt at economy (in making one pumping take the place of several) or it may be in imitation of the continuous method of extraction.

Whatever the origin of this method, it is very faulty; the economy in pumping is false economy and the simultaneous movement of the different solvents, which is advantageous in continuous extraction, is here actually disadvantageous. The main reason for the poor results of this method lies in the fact that the only way to obtain a high solvent ratio (and correspondingly high per cent extraction) is to drain off one lot of solvent as completely as possible before applying the next lot. It can readily be seen that if one lot of solvent is used to force out another lot there is certain to be mixing of the two solvents in the process (aside from the necessary mixing due to the old solvent which is naturally retained by the solid part of the

charge); in very long narrow extractors this mixing might be negligible, but in any apparatus of commercially practicable size and shape the mixing would be serious. Any mixing of this sort has the same effect as decreasing the solvent ratio, that is, it decreases the percentage extraction.¹

APPLICATION TO EXPERIMENTAL WORK

Another important use for this conception of extraction will be found in the simplification of experimental work on new extraction processes; with the formulas and tables at hand it may no longer be necessary to run complete tests in series extraction in order to determine how many treatments and how much solvent are necessary. Instead, a single experimental treatment will determine the solvent ratio and percentage extraction and from these figures it should be possible to compute the results from different number of treatments. The effect of variations in methods of treatment, in time, pressure, temperature, etc., can also be determined as well in a single extraction as in a series and then the results can be expanded to any length series by use of these formulas.

For instance, suppose that in treating a certain material with solvent, 1 volume of solvent was retained and 4 volumes were drained off; if 80 per cent of the soluble substance were found in the 4 volumes of solution then no change in time, pressure, or other factors would be necessary for perfect extraction and the results obtainable from various numbers of treatments in series could be found from Table III, solvent ratio 4. If, however, only 72 per cent were found, it would indicate that $72/80 = 90$ per cent would be the maximum that could be expected under such conditions of extraction, however long a series were used. If some change, such as an increase of pressure, gave 76 per cent in first treatment with fresh solvent and with solvent ratio 4, then $76/80 = 95.0$ per cent would be the maximum that could be expected with the new conditions of pressure; that is, the maximum increase in yield, due to the increase in pressure, would be 5.0 per cent. The yields obtainable with varying numbers of treatments can be determined from Table III by using, respectively, 90 per cent and 95 per cent of the yield percentages given in that table.

CONCLUSION

A mathematical conception of the process of discontinuous extraction has been developed by means of which the relative yields (total and per unit of solvent) obtainable by various methods of extraction are theoretically determined. This conception, if applicable in practice, will be useful in the study of commercial processes and in the simplification of experimental work on extraction.

FOREL PRODUITS, LABORATOIRES
MARSEILLE, FRANCE

¹ In a continuous extraction process the continuous movement of the solvent through the solid material in each extractor have definite effect on the results obtained by the series extraction. In a series extraction the solvent is used to force out another lot of solvent, and this mixing of the two solvents in the process (aside from the necessary mixing due to the old solvent which is naturally retained by the solid part of the charge) in very long narrow extractors this mixing might be negligible, but in any apparatus of commercially practicable size and shape the mixing would be serious. Any mixing of this sort has the same effect as decreasing the solvent ratio, that is, it decreases the percentage extraction.

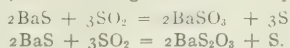
AN INVESTIGATION OF THE WET THIOPEN PROCESS¹

By A. E. WELLS

Received July 31, 1917

In the last several years, the Bureau of Mines has devoted considerable study to various proposed methods for eliminating or recovering sulfur dioxide from smelter smoke. Among these has been included a critical study of the Wet Thiopen Process. The results of the investigations on this process are given in U. S. Bureau of Mines *Bulletin* 133, "The Wet Thiopen Process for Recovering Sulfur from Sulfur Dioxide in Smelter Gases," by A. E. Wells.

The Wet Thiopen Process is based on the fact that when barium sulfide, either in finely divided water suspension or in solution, is added to a solution of sulfur dioxide, the following reaction takes place:



In carrying out the process, the gases are first cooled and cleared of all dust and fumes, then passed through an absorption tower in which the sulfur dioxide is absorbed in water or mother liquor. To the solution of sulfur dioxide is added powdered barium sulfide, when the reactions given above take place.

The precipitate containing the sulfite, thiosulfate, and sulfur is settled, and the mother liquor is returned to the absorption tower. The settled precipitate is then filtered and dried. The elemental sulfur and one-half the sulfur from the thiosulfate is distilled and the sulfur vapors are condensed. The residue, consisting of barium sulfite or sulfate is then reduced to the sulfide, which is returned to the operation as a precipitant.

In the investigations of the Bureau, all the operations involved in the process were studied, both on a laboratory scale, and on a scale that may be considered semi-commercial, and the technical possibilities of the process were determined.

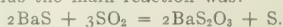
In the experiments concerning the absorption of sulfur dioxide in water or mother liquor, the gases, cooled to about 25° C. and containing from 3.5 to 10 per cent sulfur dioxide, were caused to ascend at a velocity of about 2 ft. per second, through a tower containing for 40 ft. of its height a checkerwork of wooden blocks. This checkerwork caused the descending stream of the solvent to be broken up into thin sheets or drops and allowed intimate contact of the gases with the solvent.

It was demonstrated in these experiments that with water as the absorbing agent, it is possible to obtain a high extraction of the sulfur dioxide, and at the same time obtain solutions which will contain within 10 per cent of the amount of sulfur dioxide that, theoretically, the solution could contain in equilibrium with the gas concentration, *i. e.*, the concentrations may be within 10 per cent of the theoretical saturation values. These theoretical saturation values are obtained by calculation, applying the Law of Partial Pressures to the values obtained with a pure gas and given in Landolt-Börnstein's "Physikalisch Chemische Tabellen," 4th ed., page 597.

With the mother liquor as an absorbing medium, it is possible to obtain solutions containing 30 per cent more SO₂ than is theoretically possible in water, and at the same time retain the greater portion of the sulfur dioxide. The concentrations obtained in these tests were within 10 per cent of those obtained in a small glass absorption tower by the engineers of the Thiopen Company in some earlier tests.

From these absorption tests, it was evident that for a commercial operation, the percentage of SO₂ in the gases should be at least 5 per cent, and the absorbing liquor should be cool, *i. e.*, less than 25° C.; otherwise the volume of solution to be handled for a given amount of sulfur dioxide absorbed would be very large. Furthermore, a fairly constant concentration of the sulfur dioxide in the gases is necessary if saturated solutions and a high absorption of the sulfur dioxide are to be obtained at the same time.

On adding barium sulfide to the sulfur dioxide solution, either in dry pulverized condition, in water suspension or in solutions, in amounts equivalent to effect the reactions given above, the reactions were found to take place immediately. The principal barium product was the thiosulfate rather than the sulfite. Thus the main reaction was:



If sufficient barium sulfide had been added to combine with most of the SO₂, there were very few barium salts left in solution, and the specific gravity of the solution did not go above 1.03. With a large excess of SO₂ in solution after the BaS had reacted, there was a re-solution of some of the barium as thiosulfate.

The best practical method for incorporating the barium sulfite was found to be by making an emulsion of the BaS in a portion of the sulfur dioxide solution and stirring this emulsion into the bulk of the solution in an agitator tank.

The precipitate settled readily, if the mother liquor contained a slight excess of SO₂ after precipitation. If this solution after precipitation contained an excess of BaS [or Ba(SH)₂ + Ba(OH)₂], the precipitate was slimy and settled rather slowly.

In the larger scale tests, a settling capacity equivalent to the volume of solution being precipitated in 20 minutes was ample for satisfactory settling. The overflow of supernatant liquor contained some light flakes of sulfur which did not increase in the cycles nor interfere in the pumps or absorption towers. The settled precipitate did not contain more than 50 per cent water.

This precipitate was dewatered still further on a canvas filter using vacuum. In large scale operations no difficulty would be experienced in reducing the moisture in the precipitate to about 25 per cent, in a standard filtering apparatus, using moderate suction or pressure.

The ease and efficiency with which the settling, decantation and filtering operations are carried out are dependent largely on the condition under which the precipitation takes place. Thus, it is necessary that the sulfur dioxide content of the solution coming from the tower shall be fairly constant, or the attention of an

¹ Author's abstract of Bureau of Mines *Technical Paper*, 133

attendant will be necessary to see that the solution is not too acid or too alkaline after precipitation.

The further drying of the precipitates preliminary to the distillation of the sulfur must be effected by steam coils or by a special type of drying furnace in which there would be no danger of overheating, with attendant loss of sulfur.

In the distillation operations, it was found that the sulfur began to distil rapidly at 180°C . and from that temperature up to 450°C ., the boiling point of sulfur, the rate of distillation would depend upon the rapidity with which the vapors were removed from the retort as well as the temperature.

In all cases, whether the precipitate consisted of $2\text{BaS}_2\text{O}_3 + \text{S}$ or whether a considerable proportion of the precipitate $2\text{BaSO}_3 + 3\text{S}$ was also present, the sulfur was completely distilled at 450°C . The distilled and condensed sulfur was practically pure. The residual product from the distillation was barium sulfite and sulfate.

In the reduction of the barium sulfite or sulfate, by mixing the residue with carbon, coke or coal and heating to a temperature between 750 and 1200°C ., there was some tendency for the formation of small amounts of the oxides and carbonates of barium. When the reduced material was used as a precipitate these reacted very slowly with the SO_2 in the dilute solutions from the absorption towers. Therefore, they became "inert" substance, diluting the active BaS , and increasing in amount in each cycle of operations.

If the reduction was effected in a direct fired furnace where the products of combustion passed over the material, the proportion of these inert compounds was greater than if the reduction was brought about by carbon of high purity, quickly, at a high temperature, and in a furnace externally heated.

The use of a coal containing a high percentage of ash also adds "inert" substances to the reduced material in each cycle, and therefore as pure carbon as possible is desirable as reducing agent.

The oxide or carbonate can be connected to the sulfite by agitation with a strong sulfur dioxide solution, or to the sulfate by treatment with sulfuric acid. When reductions are effected in a direct fired furnace, probably 10 per cent of the material would have to be treated with strong sulfur dioxide solution or sulfuric

acid in each cycle to keep the barium as sulfite in sulfate to be reduced again to the sulfide.

If coal, high in ash, is used as reducing agent, and the amount of insoluble matter increases to a certain amount, it will be necessary to leach the entire amount of reduced material, getting the BaS into reduction and discarding the insoluble material.

With the addition of these supplementary operations, it is believed that the technical operation of the process can be carried out successfully for the recovery of sulfur from sulfur dioxide in waste smelter gases. The indications are that, at least in some localities, the process can be applied on a commercial scale which will allow the production of sulfur at a cost of about \$12 per ton.

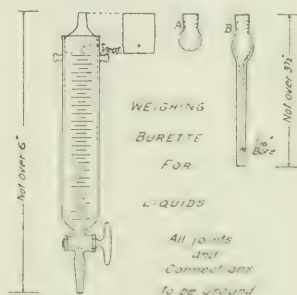
WEIGHING BURETTE FOR LIQUIDS

By W. ED. BURKHARD

Received July 9, 1917

The weighing burette illustrated below has been found very valuable.

The capacity which determines the diameter of the burette is governed by the material to be analyzed.



The cup *A* is used to prevent fuming while weighing, etc. *B* is made preferably for oleum or other material that would cause spattering. In case of "oleum over 20 per cent" the water into which the acid is to be run has a layer of neutral fine Glauber's salt crystals. By keeping the tip of *B* in the crystals all spattering is avoided. The attachment is left in the solution while titrating.

GENERAL CHEMICAL COMPANY
BAYONNE WORKS, BAYONNE, N. J.

ADDRESSES

THE VAPOR PRESSURE AND VOLATILITY OF SEVERAL HIGH-BOILING METALS—A REVIEW¹

By J. H. JOHNSON

Received July 19, 1917

The question as to the vapor pressure of a metal at a given temperature, or its boiling point at a particular pressure, often arises, as a knowledge of this property is valuable in connection with a number of problems. But the somewhat scanty data to be found in the literature refer, for any one metal, to a small

number of pressures, and in many cases to a single vapor pressure only. That of one atmosphere, therefore, in order to ascertain the vapor pressure at any particular temperature one must in general plot the curve and extrapolate. This procedure is tedious and trouble and is moreover not feasible when only one point on the curve has been determined by experiment; more can be learned, as we shall see, by plotting at one time the available data for all the metals hitherto investigated. In so doing we can set up equations which enable us to calculate the vapor pressure at any temperature with as much certainty as is inherent in the experimental results. For account of the greatly increased availability and usefulness of the data on

¹ Presented at the Symposium on the Chemistry and Metallurgy of Zinc, 54th Meeting American Chemical Society, Kansas City, April 19 to 24, 1917.

rearranged in this way, in comparison with their present form, it seemed worth while to publish a brief note on the matter. More accurate experimental data than we now possess would be highly desirable; but the figures presented in the table, which at least give the order of magnitude of the vapor pressure at the several temperatures, will suffice for many purposes.

Search of the literature has revealed very few investigators who have made direct observations of the vapor pressure of metals of high boiling point. The earliest of these is Barus,¹ who worked with zinc, cadmium and bismuth (as well as some other substances). He heated the metal in a closed crucible provided with a connection to a vacuum pump and with a réentrant tube in which the thermoelement to measure the temperature was placed; his criterion of boiling was that the temperature observed should vary with variations in pressure. Barus realized clearly that his results leave something to be desired, and considered that his boiling temperature would tend to be too high, particularly at the lower pressures. His original data follow:

TABLE I—BOILING POINTS OF ZINC, CADMIUM AND BISMUTH AS GIVEN BY BARUS; PRESSURE IN MM., TEMPERATURE IN DEGREES CENTIGRADE

ZINC				CADMIUM				BISMUTH*			
p	t	p	t	p	t	p	t	p	t	p	t
10	582	42	710	26	675	22	549	63	606	32	1199
40	710	35	699	67	731	25	552	84	622	32	1206
65	732	28	684	158	792	26	565	226	686	32	1211
96	757	62	736	264	833	32	574	274	704	32	1215
101	772	99	758	375	864	75	620	342	722	39	1213
156	785	166	802	473	884	105	639	510	752	34	1204
271	837	264	838	570	904	157	667	563	760	32	1207
345	857	368	863	654	916	189	681	636	770	40	1214
425	873	477	884	771	933	262	702	656	772	34	1206
535	897	557	900	292	706	755	785	39	1221
764	933	653	914	355	724
...	...	775	925	381	729
...	489	745	33	1215
...	517	750
...	624	760	42	1233
...	644	766
...	656	766
...	756	772

* The values for pressures of about 90 mm. given in the original have been omitted because Barus considered that these values were lower than the corresponding boiling points.

Berthelot² made a series of determinations of the boiling point at atmospheric pressure of zinc and cadmium by a method similar to that used by Barus; the individual determinations differ by several degrees, the mean result being 920° for zinc and 778° for cadmium. The method followed by Fery³ was such that accurate results could hardly be expected; he gives 704° for the boiling point of zinc and 2100° for that of copper.

The procedure adopted by Greenwood⁴ is in principle the same as that followed by Barus. The metal was confined in a long graphite crucible, lined where necessary with pure magnesia; the temperature was taken as that of the wall of the crucible, as measured on an optical pyrometer.

"The measurements of the boiling points were carried out by slowly raising the temperature of the crucible and observing the surface of the metal from above through an absorbing glass. At first the surface of the molten metal remains perfectly still, but as the boiling point is approached a slight agitation of the surface is observed which soon becomes vigorous. In the case of the metals studied, the difference between the temperature indicated when a gentle agitation is first apparent and that at which the ebullition has become so violent that globules of metal are being ejected from the top of the tall crucible does not exceed 100°. By taking the boiling point as the temperature at which ebullition becomes decided, quite concordant results were obtained in different experiments. From a study of a large number of metals in this manner, it appears probable that the temperature at which the vaporization becomes sufficiently rapid to cause a decided projection of drops

from the surface may be taken with fair approximation as the boiling point."

A current of gas, either hydrogen or nitrogen, was passed through the apparatus; when nitrogen was employed, the temperature readings, though concordant in similar experiments, were always considerably higher (50 to 100°) than those obtained in a hydrogen atmosphere. Greenwood attributes this effect to the ease with which hydrogen permeates the crucible walls, removing and diluting the column of heavy vapor; but considers "that the values observed in hydrogen approximate more closely to the boiling points of the metals at atmospheric pressure."

In a later paper Greenwood¹ describes similar experiments at pressures less than one atmosphere. At these low pressures, there were no noteworthy differences between the results obtained in hydrogen and in nitrogen; ebullition was quite sharply defined (in general more clearly than at atmospheric pressure) and the results of individual experiments showed a very satisfactory concordance. He also made a few observations, following

TABLE II—GREENWOOD'S RESULTS ON THE BOILING POINTS OF METALS; PRESSURE IN ATMOSPHERES, TEMPERATURE CENTIGRADE

METAL	p	t	METAL	p	t	METAL	p	t
Zinc.....	6.3	1120	Lead....	0.14	1320	Chromium	1	2200
	11.7	1230		0.35	1420			
	21.5	1280		1.0	1525	Tin.....	0.13	1970
	53	1510		6.3	1870		0.35	2100
Magnesium....	1	1120		11.7	2100		1.0	2270
Bismuth.....	0.13	1200	Aluminum	1	1800	Copper....	0.13	1980
	0.34	1310		1.0	1920		0.34	2180
	1.0	1420	Manganese	1	1900		1.0	2310
	11.7	1950	Silver....	0.14	1660	Nickel....	1	2400
Antimony.....	16.5	2060		0.35	1780			
	1	1440		1.0	1955	Iron.....	1	2450

essentially the same procedure, at higher pressures where the boiling temperatures were low enough to admit of this. Greenwood's original data, most of which represent the mean of several observations, are brought together in Table II.

Heycock and Lamplough⁵ record the following observations, but give no description of the procedure adopted:

BOILING POINT	Cadmium	Zinc
At 1 atmosphere pressure.....	765.9	905.7° C.
Change per mm. at 760 mm.....	0.12	0.133° C.

The vapor pressure of arsenic has been determined recently by Gibson⁶ and by Preuner and Brockmüller⁷ by direct measurement by means of a quartz manometer constructed on the principle of the Bourdon gauge; their results, which agree satisfactorily, are given in Table III.

TABLE III—EXPERIMENTAL DATA ON THE VAPOR PRESSURE OF ARSENIC; PRESSURE IN MM., CENTIGRADE TEMPERATURE

GIBSON		PREUNER AND BROCKMÜLLER	
p	t	p	t
...	...	6.....	400
26.0	469.4	19.....	450
31.6	476.3	32.....	476
50.9	488.3	42.....	488
67.4	499.9	61.....	500
96.2	512.3	90.....	512
131.6	526.4	130.....	526
269.9	557.4	268.....	557
334.1	568.9	334.....	569
...	...	430.....	580
...	...	580.....	600

Von Wartenberg⁸ has published observations, made by the dynamic method, on the vapor pressure of high-boiling metals at temperatures at which the vapor pressure of the metal is very small. The essential feature of this method is to pass a measured volume of gas over the metal, kept at the desired temperature, and determine the loss of weight of the metal. From these observations the vapor pressure at that temperature can readily be calculated on the basis that the actual partial

¹ C. Barus, *Bull. U. S. Geological Survey*, **108**, 1893; *Phil. Mag.*, **39** (1890), 141.

² D. Berthelot, *Compt. rend.*, **131** (1900), 380. He also refers to several earlier determinations of these two boiling points, but these have now only historical interest.

³ *Ann. chim. phys.*, [7] **28** (1903), 428. He also gives results for a brass containing 63 Cu : 37 Zn.

⁴ "An Approximate Determination of the Boiling Points of Metals." *Proc. Roy. Soc. London (A)*, **83** (1909), 396.

⁵ "The Influence of Pressure on the Boiling Points of Metals." *Proc. Roy. Soc. London (A)*, **83** (1910), 483. His other papers (*Trans. Faraday Soc.*, **7** (1911), 151; *Z. physik. Chem.*, **76** (1911), 484; *Z. Elektrochem.*, **18** (1912), 319) merely recapitulate the results.

⁶ *Proc. Chem. Soc.*, **28** (1912), 4; *Chem. News*, **105** (1912), 66.

⁷ Dissertation, Breslau, 1911.

⁸ *Z. physik. Chem.*, **81** (1913), 167.

⁹ *Z. Elektrochem.*, **19** (1913), 482.

pressure of the metal in the gas stream is equal to its vapor pressure, a basis which can be secured by proper experimentation, provided always that the vapor density is known. His mean results, expressed in atmospheres and degrees centigrade, follow:

LEAD		SILVER ¹		THALLIUM	
p	t	p	t	p	t
1.05×10^{-4}	808	1.90×10^{-3}	1178	7.40×10^{-4}	634
2.30×10^{-3}	996	1.08×10^{-3}	1316	1.75×10^{-3}	783
2.20×10^{-2}	1176	5.10×10^{-3}	1435	3.20×10^{-2}	970

¹ In another paper (*Z. Elektrochem.*, **19** (1913), 489) Von Wartenberg points out that the vapor pressure of silver is twice as great in presence of oxygen as in an indifferent gas, and attributes this to the temporary formation of oxide which decomposes again at lower temperatures; by this means one may get a considerable sublimate of silver at 1300°. Similar effects have been observed with tungsten.

Moreover, he concluded that the vapor pressures of both copper and platinum are less than 10^{-5} atmosphere at 1360°, and found that of tin to be appreciable though he was unable to calculate it because the vapor density of tin is not known.

The vapor pressure of three high-boiling metals has been investigated recently by Langmuir¹ and by Langmuir and Mackay,² who measured the rate of loss of weight of a wire maintained at a definite temperature in an exceptionally good vacuum; from these results the vapor pressures were calculated by means of a formula derived on the basis of the kinetic theory of gases and the Clausius-Clapeyron equation. The metals studied were platinum, molybdenum and tungsten; the calculated boiling points at two pressures are subjoined.

BOILING TEMPERATURE—ABSOLUTE			
Pressure, mm.	Platinum	Molybdenum	Tungsten
10^{-8}	1740	2020	2600
760	4180	3890	5100

Thus these three metals have boiling points at far higher temperatures than the more common metals which we are here considering, so in what follows we shall not deal further with them.³

Quite recently Egerton⁴ has published determinations of the vapor pressures of zinc, cadmium (and mercury) at temperatures at which the vapor pressure is very small (0.01 mm. and smaller); the method, originally used by Knudsen⁵ for mercury, depends upon the kinetic flow of molecules through small apertures.

TABLE IV. VAPOR PRESSURE IN MM. AND DEGREES CENTIGRADE OF CADMIUM AND ZINC, ACCORDING TO EGERTON

CADMIUM		ZINC	
t	p	t	p
169	1.9×10^{-4}	257	1.2×10^{-4}
178	3.6	268	1.7
189	8.5	280	4.2
198	2.7×10^{-4}	291	8.4
210	5.3	312	2.1×10^{-3}
222	1.0×10^{-3}	331	5.2
229	1.8	341	7.7
240	2.9	363	1.8×10^{-3}
250	4.7		
260	8.0		
262	1.3×10^{-3}		

The rate of flow, through an aperture of known "resistance," of the vapor of the metal, kept at constant temperature, was measured, whence, on the basis of the kinetic theory, the corresponding vapor pressure can be calculated. His mean results appear in Table IV.

¹ *Phys. Rev.*, **2**, 143 (1916).

² *Id.*, **4**, 1913.

³ The equations to the respective vapor pressure curves, as given in the original follow:

$$\text{For Pt. } \log p = -5800/T - 1.36 \log T + 14.000$$

$$\text{Mo. } \log p = -35500/T - 1.36 \log T + 10.134$$

$$\text{W. } \log p = -14400/T - 0.97 \log T + 11.500$$

⁴ *Phil. Mag.*, **33**, 191 (1917).

⁵ *Ann. Physik.*, **29**, 1900, 1901.

REDUCTION OF THE DATA

The experimental results as a whole are not so accurate as one would wish to have them, and it is difficult to estimate the uncertainty which attaches to them. Von Wartenberg considers that Greenwood erred in choosing as his final values those observed in hydrogen, and that the true boiling point, *i. e.*, the temperature at which the liquid is in equilibrium with a pressure of one atmosphere of its own vapor should lie higher even than that observed in nitrogen. In any case we must take the results as they are, remembering merely that they are approximate; but for many purposes this is ample. The experimental data, if they are to be useful, must be reduced; this was accomplished in the following way:

The slope of the vapor-pressure curve at any point is given

by the relation $\frac{d \ln p}{dT} = \frac{\Delta H}{RT^2}$ where ΔH is the heat of vaporization per mole at the absolute temperature T . If we integrate this on the assumption¹ that ΔH is independent of T (an assumption which in many cases is not seriously in error) we obtain as the

$$\text{equation to the curve, } \ln p = \frac{-\Delta H}{RT} + \text{constant} \quad (1)$$

$$\text{which is of the form, } \log p = -A(1/T) + B \quad (2)$$

$$\text{or, } 1000/T = -A' \log p + B'$$

where $A' = 1000/A$, and $B' = A'B = 1000B/A$.

Accordingly, if we plot values of $\log p$ against the corresponding values of $1/T$, the graph will be a straight line if the above assumption holds, and nearly linear, although the assumption does not hold rigorously; in any case the curve thus obtained is such that we may interpolate readily and even extrapolate with some degree of safety.

The actual data for each metal were plotted on a large scale in this way, and the points were found to lie as close to a straight line as would be expected; accordingly, the best straight line was drawn through each series of points. The graphs are reproduced in Fig. 1, from which it is manifest that the inclination (and hence A' in Equation 3) decreases regularly as we pass from metals of lower to metals of higher boiling point. We are therefore justified in assuming, for the purpose of the present approximation, that the A' values for those metals for which only a single determination was made, would follow the same regular sequence. The values of A' derived from the curves were plotted against the respective boiling points, and by interpolation at the appropriate temperatures, values of A' for the other metals were deduced and the corresponding lines drawn (not reproduced in Fig. 1). From the curves values of $1/T$ for a series of rounded values of p were read by inspection, whence the corresponding values of t (*i. e.*, the boiling temperature centigrade) are readily derived, the latter are tabulated in Table V for all of the metals.

As regards the accuracy of these figures little can be stated, except that they are probably as good as the original data. The extrapolation which we have made implies that there is no melting nor inversion within the temperature range, but the error caused by the fact that they are deduced is not great.

It would undoubtedly be desirable to have correct values for ΔH as $\Delta H = RT^2 \frac{d \ln p}{dT}$, an assumption which leads to the equation $\log p = -\Delta H/RT + \text{constant}$. The use of this equation, which is quite troublesome to work with, and which leads to the same result as that obtained by means of the simpler equation, $\log p = -A(1/T) + B$, can be shown that it is less than 0.01 mm. for the metals here considered, and accordingly, as above, the error in the values here obtained for the mean of temperature and pressure would be less than 0.01 mm. than those derived from the simpler equation. The error in the values obtained by means of the simpler equation is not greater than 0.01 mm. for the metals here considered.

$$\text{For Pt. } \log p = -5800/T - 1.36 \log T + 14.000$$

$$\text{Mo. } \log p = -35500/T - 1.36 \log T + 10.134$$

$$\text{W. } \log p = -14400/T - 0.97 \log T + 11.500$$

and they are reproducible within the limits of the range of accuracy.

because for a metal the heat of fusion or of inversion is very small compared to the heat of vaporization. In any case the figures tell us the order of magnitude of the vapor pressure of the pure

point at one atmosphere. The position of arsenic is anomalous, presumably because of the fact that its vapor is at these temperatures polyatomic, wherefore ΔH is not constant and conse-

TABLE V—APPROXIMATE BOILING TEMPERATURES* IN DEGREES OF METALS AT VARIOUS PRESSURES

METAL	Melting Temperature	p in mm. mercury									
		10^{-3}	10^{-2}	10^{-1}	1	10	50	100	760		
Cadmium	321	230	270	330	410	500	590	630	780		
Zinc	419	290	350	430	540	630	700	780	920		
<i>Aluminum</i>	660	380	440	520	620	730	860	920	1120		
Thallium	303	580	570	660	710	910	1030	1060	1300		
Bismuth	271	540	620	720	840	990	1130	1200	1440		
<i>Antimony</i>	630	540	620	720	840	990	1130	1200	1440		
Lead	327	620	710	820	960	1130	1360	1460	1640		
<i>Aluminum</i>	660	730	830	950	1090	1280	1440	1530	1800		
<i>Manganese</i>	1245	790	890	1030	1150	1360	1580	1630	1900		
Silver	960	920	1030	1160	1320	1520	1700	1790	2090		
Chromium	1510	980	1090	1230	1400	1610	1800	1890	2200		
Tin	232	1010	1130	1270	1440	1660	1850	1940	2260		
Copper	1083	1080	1200	1340	1520	1740	1930	2030	2350		
Nickel	1452	1100	1220	1370	1550	1780	1970	2070	2400		
Iron	1520	1120	1250	1400	1590	1820	2010	2110	2450		
Arsenic		830	220	260	310	360	420	490	530	630	

* i , e , the temperature at which the vapor pressure is 10^{-3} mm., etc.

metal, and suffice for many practical purposes; it is probable that the boiling temperatures given are minimum values; conversely that the vapor pressures as calculated from the formulae are maximum values.

TABLE VI—VALUES FOR THE SEVERAL METALS, OF THE COEFFICIENTS IN THE FORMULAE AND OF THE HEAT OF VAPORIZATION ΔH PER MOLE

METAL†	$\log p = A/T + B/1000$		$T = A'/\log p + B'$		$\Delta H = 4.579A$
	A	B	A'	B'	
Arsenic	6670	10.47	0.150	1.570	30500
Cadmium	5460	8.04	0.183	1.473	25000
Zinc	6290	8.14	0.139	1.294	28800
Magnesium	7250	8.09	0.138	1.116	33200
Thallium	8850	8.50	0.113	0.961	40500
Bismuth	9010	8.12	0.111	0.902	41300
Antimony	9010	8.12	0.111	0.902	41300
Lead	9900	8.05	0.101	0.813	45400
<i>Aluminum</i>	11500	8.41	0.087	0.732	52600
<i>Manganese</i>	12300	8.55	0.081	0.694	56300
Silver	14300	8.97	0.070	0.628	65500
Chromium	14900	8.91	0.067	0.597	68200
Tin	15100	8.83	0.066	0.583	69000
Copper	16400	9.14	0.061	0.557	75000
Nickel	16700	9.12	0.060	0.547	76500
Iron	17000	9.10	0.059	0.537	77800

† The figures for the metals named in italics are derived from a single observation only.

quently the simple equation does not apply so well. Attention is drawn to the constancy of the values of B (which, however, show an undoubted trend); from which it is evident that one could get a fair idea of the vapor pressure of a metal at any

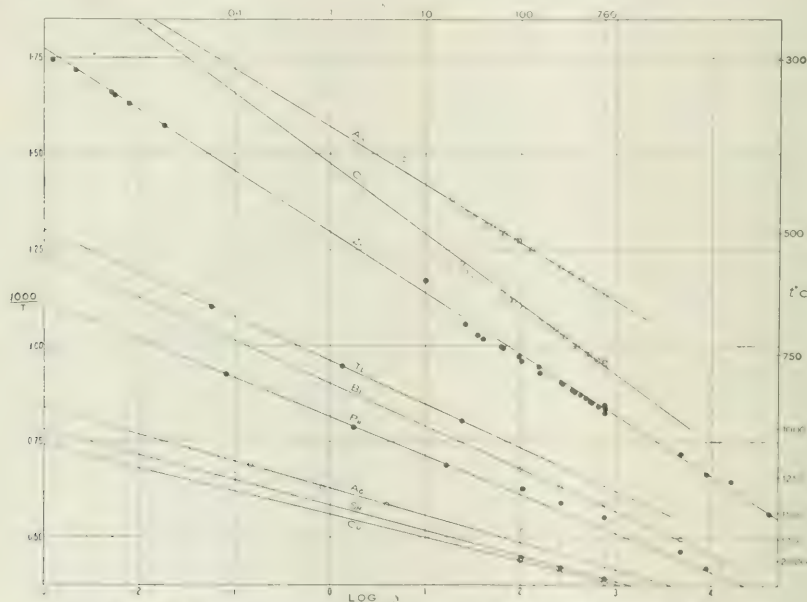


FIG. 1—THE VAPOR PRESSURE OF THE SEVERAL METALS; GRAPHS OF $\log p$ AGAINST $1000/T$. THE CIRCLES REPRESENT THE POINTS DETERMINED EXPERIMENTALLY

In Table VI are brought together the respective values of A , B (Equation 2), A' and B' (Equation 3) as derived from the graphs, for each of the metals; by means of these one can readily calculate the vapor pressure at any desired temperature or the boiling temperature under any specified pressure. This table also gives approximate values of the molar heat of vaporization, derived from A ; for, by comparison of Equations (1) and (2), it is obvious that $\Delta H = 2.303 RA = 4.579A$ calories. Here again therefore, we observe that the values of A are such that there is a parallelism between heat of vaporization and boiling

temperature if it has been determined at a single temperature.

REMARKS ON VAPOR PRESSURE AND VOLATILITY OF METALS

The values given in Table V or calculable from the appropriate formula, refer only to the pure metal. The vapor pressure of a metal in solution will always be smaller, depending upon its actual concentration, or better its effective mole fraction, in the solution. When $1/n$ of the total moles present are moles of X , the mole fraction of X is $1/n$, and its partial vapor pressure is

$1/n$ of that of pure X at the same temperature;¹ but it is to be borne in mind that the mole fraction is not necessarily given by the gross molecular proportion of X in the mixture, for part of it may be present in other molecular species, *e. g.*, as a compound.

It has been argued that a better separation of two metals (*e. g.*, of zinc and cadmium) by distillation could be achieved by regulating the pressure;² but within the practicable range of temperature there is little advantage to be gained in this way unless it should happen that there is a change in constitution of the mixture (*e. g.*, the formation of a compound, the unmixing of a solution, or *vice versa*) within this range, for, when a mixture of a specified composition and constitution is distilled at a series of temperatures, the degree of separation achieved in each case depends upon the ratio of the vapor pressure of zinc to that of cadmium; but between 500 and 1000° this ratio ranges only from about $1/7$ to $1/4$, so that there would be no substantial advantage in conducting the distillation of mixtures of these two metals at one temperature rather than at another. On the other hand, in cases where the metals form a compound, a much better separation would be possible by distilling at a temperature below the dissociation point of this compound than at a higher temperature; nevertheless such a course may not be practicable because of the slowness of distillation at the low temperature requisite.

For a given temperature the amount of material volatilized and carried by a current of indifferent gas can be calculated very easily from the vapor pressure; but this estimate will usually exceed the actual amount because (1) of lack of purity, (2) of incomplete saturation. Both these factors are likely to be met with in practice; thus Welch and Duschak³ found the vapor pressure of As_2O_3 in a typical flue dust to be only about one-half of that of pure As_2O_3 at the same temperature, and that the flue gas was not even saturated with respect to the flue dust which it carried. The completeness of saturation depends, other things being equal, upon the rate of volatilization under the particular conditions; this rate is very much greater in a very good vacuum than it is in an atmosphere of indifferent gas,⁴ and depends very markedly upon the excellence of the vacuum maintained.⁵ There have been numerous experiments on the volatilization of metals in a vacuum;⁶ these we shall briefly review.

¹ This is absolutely true in many cases, and is true as a first approximation in all cases. With respect to this whole question see papers on the vapor pressures of amalgams by J. H. Hildebrand, *J. Am. Chem. Soc.* **35** (1913), 501; by Hildebrand and Eastman, *Ibid.*, **35** (1913), 909; **37** (1915), 2452; also Hildebrand, *Ibid.*, **38** (1916), 1452. In how far the above considerations apply to solid solutions is open to question; there is reason for believing that the above rule does not apply to X when the proportion of X present in a solid solution is very small.

² And it has been implied that this could be done by regulating the pressure of some indifferent gas.

³ "The Vapor Pressure of Arsenic Trioxide," Bureau of Mines, *Technical Paper*, **81**, 1915.

⁴ The fact that the rate of volatilization is much less in an atmosphere of indifferent gas than *in vacuo* is the basis of the nitrogen filament lamp, for by this means the filament may be run at a higher temperature and consequently with increased efficiency, without unduly shortening its life.

⁵ Nair and Turner, *J. Chem. Soc.*, **108** (1913), 1524, observing that the amount of zinc volatilized is much diminished by imperfection of the vacuum, determined the amounts of zinc (and cadmium) volatilized in 30 minutes under various pressures of air, hydrogen and carbon monoxide, and ascertained in each case the temperature required under these conditions for complete volatilization of a given amount of metal in 30 min. As one would expect, this temperature is lowest in a vacuum, successively higher for hydrogen, carbon monoxide, air, and for any one gas increases with the pressure. Their observations for zinc in air at several pressures, follow:

P.	0	1	20	50	80	500	600 mm.
Temp. required	460	500	600	660	680	750	840° C.

Incidentally they observed that at 500° zinc oxidizes very slowly in vacuum, probably because the air is displaced by the heavier zinc vapor; in moving an oxidation is rapid.

⁶ With respect to this whole question particularly on its theoretical side, see recent papers by Langmuir, *e. g.*, *J. Am. Chem. Soc.* **38** (1916), 2749, where numerous references are given.

Demargay¹ observed the occurrence of vaporization *in vacuo* in periods of 24 to 48 hours as follows: Cd at 160°, Zn at 184°, Sb and Bi at 293°, Pb and Sn at 360°; and similar observations were recorded by Kraftt.² Later Kraftt and Bergfeld³ investigated the lowest temperature at which they could observe metal to vaporize in a cathode-ray vacuum in the course of a few hours, with the following results: Cd, 150°; Zn, 180°; Bi, 270°; Pb, 335°; Ag, 680°; Au, 1070°. Reference to the several formulae as given above shows that at the above temperatures the vapor pressure of each metal was of the order 10^{-5} mm., thus adding another instance of the actuality of such very small vapor pressures.

By taking advantage of these differences one may achieve a more or less complete separation of two metals; the completeness of the separation depends upon the ratio of the partial vapor pressures of the two metals in the mixture, a ratio which, as we have seen, does not vary markedly with change of the pressure (or, of course, temperature) at which distillation is performed. Tiede and Fischer⁴ showed that lead could be separated from tin by heating in a vacuum. Berry,⁵ on heating mixtures of zinc and magnesium in a well evacuated bent glass tube, found that both zinc and magnesium distill off, leaving the compound $MgZn_2$; and also, at a somewhat higher temperature, that this compound distills unchanged. In another paper⁷ he states that copper and cadmium heated in vacuum at 600° can be separated quantitatively; that cadmium and magnesium volatilize together; and that the distillate from mixtures of magnesium and lead at 680° contains only traces of lead. Vialay has patented⁸ a process of separating zinc and aluminum from their alloys by heating the alloy slowly to 1200°, in a thin layer, preferably in a vacuum.

Groves and Turner⁹ record a series of experiments, the main results of which follow. Zinc when heated *in vacuo* begins to volatilize appreciably at 375°; from 60:40 brass volatilization of zinc is appreciable at 520°, from 70:30 brass at 550°. When brass is heated *in vacuo* at 1080° the zinc is quantitatively removed in half an hour. An alloy of zinc and iron at 500° loses only zinc, and that very slowly; at 600° some iron comes over with the zinc. Their further observations on volatilization *in vacuo* can be summarized as follows:

I—No appreciable loss of weight occurs after heating at 1100° *in vacuo* for half an hour with Cu-Al, Cu-Ni, Cu-Sn, Cu-Fe.

II—Quantitatively separable Cu-Bi, Cu-Pb in 35 min. at 1100°; Cu-Zn in 30 min. at 1100°; Fe-Zn at 500°, but at 1000° more than half the iron had volatilized; Pb-Sn.

III—Excess of more volatile metal removed, leaving a compound; Au-Zn, leaving AuZn; Cu-Sb, leaving Cu_3Sb ; Au-Cd, leaving AuCd; Mg-Zn, leaving $MgZn_2$.

IV—More volatile metal is completely removed, Cu-Al.

V—Two or more metals volatile together from Au-Zn mixtures little silver comes over at 600°, but more and more at higher temperatures; Ag-Pb; Pb-Zn; Zn-Cd.

In a later paper¹⁰ Thompson and Turner present results on the rate of volatilization in a vacuum of copper and alloys containing from 10 to 90 per cent Cu. They found that alloys containing more than 50 per cent copper volatilize appreciably by this means, but that a little copper is also volatilized from the

¹ *Ann. Chem. Phys.*, **95**, 185.

² *Ann. Chem. Phys.*, **36**, 100.

³ *Ibid.*, **38**, 100.

⁴ *Langmuir, J. Am. Chem. Soc.*, **3** (1911), 181, and references therein.

⁵ *Langmuir, J. Am. Chem. Soc.*, **34**, 1111 (1912).

⁶ *J. Ind. Eng. Chem.*, **4**, 86 (1912).

⁷ *J. Ind. Eng. Chem.*, **4**, 17 (1912).

⁸ *J. Ind. Eng. Chem.*, **4**, 17 (1912).

⁹ *J. Ind. Eng. Chem.*, **10**, 101 (1918).

¹⁰ *Ibid.*, **11**, 711.

¹¹ *J. Ind. Eng. Chem.*, **12**, 11 (1920).

alloys carrying less than 40 per cent Cu. Some work on the vapor pressure of zinc from brass was done by Hansen¹ and by others,² the several results being tolerably concordant.

There are, moreover, scattered observations on volatilization of metals at atmospheric pressure. Bengaugh and Hudson³ and Bassett⁴ present results on the rate of loss of zinc from brass at various temperatures. Rose⁵ made experiments on the estimation of zinc in coinage bronze by volatilization; he found that, though only 0.1 per cent of the zinc volatilized at 1200° in two hours, a period of two hours at 1375° sufficed to remove all but 0.3 per cent of the zinc, this volatilization being accompanied by a loss of about 0.2 per cent of the tin and copper. Again, in the process of refining zinc by distillation it has been observed that other metals, notably lead,⁶ tend to come over with the zinc unless the distillation is conducted slowly.

Butts⁷ has discussed the vaporization of copper in wire-bar furnaces, and cites data which indicate that this occurs to an appreciable extent at 1120°. Mostowitsch and Pletneff⁸ made experiments on the volatility of gold in atmospheres of various gases, and state that it is not appreciably volatile at 1400° in an atmosphere of oxygen, nitrogen, carbon monoxide or carbon dioxide but that in hydrogen volatility is noticeable at 1250°; the latter effect they attribute to the formation of an unstable compound, but an alternative explanation may be that offered by Greenwood⁹ to account for the lower boiling points in hydrogen observed by him.

The various observations summarized above are in general harmony with what one would expect from the vapor pressure, although they could not have been predicted precisely from a knowledge of the vapor pressure alone. There are two observations to which I wish to revert for a moment—those namely of Groves and Turner and of Thorneycroft and Turner, who found that some iron or copper came over with the zinc when the respective binary alloys were distilled under certain circumstances, the temperature, however, corresponding to a very small vapor pressure of the less volatile metal. This may be accounted for in two ways,¹⁰ which in essence do not differ materially: (1) that the particles of vapor of the less volatile metal are entrained by the blast of zinc vapor just as the gas from the vessel to be exhausted is entrained by the blast of mercury vapor in the condensation pump;¹¹ (2) that when all the zinc particles surrounding a given iron (or copper) particle have vaporized, the iron particle is left unattached, and so is carried over into the distillate. This question could readily be elucidated by making series of experiments with mixtures containing different (small) proportions of iron (or other metal) in which the rate of distillation is varied within wide limits. In any case this observation shows that one cannot with safety deduce, from the calculated partial pressure of the components, the composition of the distillate except when the rate of distillation is very small—in other words, the theory applies strictly only to static conditions. Nevertheless a knowledge of the vapor pressure of metals is a prerequisite to any intelligent treatment of the volatility of metals.

SUMMARY

The data in the literature on the vapor pressure and volatility of metals have been reviewed and collated, and thus made more

¹ *Proc. Am. Inst. Metals*, **1912**, 111

² Collated by Gillett: "Brass Furnace Practice," Bur. of Mines, *Bull.* **73** (1914), 126.

³ *J. Ind. Metals*, **4** (1910), 101. ⁴ *This Journal*, **4** (1912), 164.

⁵ T. K. Rose, *J. Soc. Chem. Ind.*, **33** (1914), 170; *C. A.*, **8**, 1722.

⁶ See German patent No. 286,557, Aug. 12, 1915; *Metall und Erz*, **12** (1915), 330, where means to obviate this in a process of electrothermic distillation are described.

⁷ A. Butts, *Met. and Chem. Eng.*, **16** (1917), 84.

⁸ Mostowitsch and Pletneff, *J. Russ. Met. Soc.*, **1916**, 410; through *Met. and Chem. Eng.*, **16** (1917), 153.

⁹ See Scherer, p. 874.

¹⁰ It is, of course, possible that the compound of zinc with copper or iron has an appreciable vapor pressure and distils as such.

¹¹ See Langmuir, "The Condensation Pump; an Improved Form of High Vacuum Pump," *Gen. Elec. Review*, **1916**, 1060.

readily available. Formulae are given by means of which the vapor pressure at any temperature can be calculated with an accuracy in the result not inferior to that of the original data; and the temperatures corresponding to a series of pressures are tabulated.

RESEARCH DEPARTMENT
AMERICAN ZINC LEAD AND SMELTING COMPANY
ST. LOUIS, MISSOURI

DISCUSSION

N. T. BACON criticized the statement that every substance has some vapor pressure at any temperature. This is the theory on which Nernst has built much of his work, but Mr. Bacon's study has led him to believe it false. Instead, he believed that each substance had a critical temperature, below which it could not exist in gaseous form, being the counterpart of the temperature above which it cannot exist in liquid form.

In conversation a few months ago, Dr. Irving Langmuir had at first denied this, but when asked what the concentration of platinum vapor would be at 0° C., he calculated it out by extrapolation and found, as a result, a value so small that several hundred thousand worlds would have been required as the space proportion for a single molecule.

As, to maintain a vapor pressure in any space, enough molecules must be present to maintain equal pressure in all dimensions, theoretically a minimum of three is required for the unit of space under consideration. Any smaller number could be looked upon as merely sporadic particles, like particles of dust, of which it would be difficult to postulate whether they were in solid, liquid, or gaseous condition.

Either would necessarily acquire something like gaseous velocity by contact with other molecules in any atmosphere, until they finally dropped under gravity or adhered to the walls by adsorption. This theory is built on the idea that the old assumption is false, that all molecules are perfectly elastic. Now that we recognize atoms as having a multiplicity of parts, it is easy to see how by distortion of these, from a normal form by collision with some other particle, the kinetic energy of a molecule might be transformed into heat. We know very little of the temperature of gaseous molecules, except as manifested by their kinetic energy, but if heat is being continuously withdrawn through the walls of a system, the higher temperatures resulting from collisions with the wall will be cut down first, and thus the secondary equilibrium disturbed, which might have resulted in throwing back the molecule by local overheating.

Some of Dr. Langmuir's experiments seem to indicate this, though he has not interpreted them so, for he has noted that as the temperature approaches that of liquid air, molecules of one kind after another cease to be reflected from the walls and form adsorption films on the walls.

This is just what should happen by the theory of a critical temperature of each gas. This does not mean that there would be no molecules of each kind left in the atmosphere, but rather that no vapor saturation pressure remains.

A new definition of saturated vapor tension seems called for. It has been defined as the condition of equilibrium between the gaseous and liquid phases, so that for each molecule impinging on the liquid surface and condensing there, a fresh one is driven off by the resulting latent heat. This postulates a liquid phase, whereas, in many cases, when saturation is produced by condensation or cooling, the saturation must result solely from an oversupply of gaseous molecules. As, for many substances, the vapor tension as calculated by extrapolation would not be sufficient to maintain a single molecule in the volume of the apparatus employed, is it not obvious that this cannot serve as a satisfactory hypothesis to explain chemical phenomena even though the system based on it agrees pretty well with observed phenomena?

PRACE DALE, R. I.

THE PYROGENESIS OF HYDROCARBONS

This material is copyrighted by the Institute of Petroleum Technologists and is reprinted here by official permission of the Council of the Institute of Petroleum Technologists, from the *Journal of the Institution of Petroleum Technologists*, Volume 3, No. 9 (December, 1916), pp. 36 to 120. Numbers in parentheses after names of authors mentioned are those of entries in the bibliographic indexes, pp. 899-900.

PART I—HISTORICAL AND BIBLIOGRAPHICAL

By E. LAWSON LOMAX

In submitting to the Members of the Institution the following papers on "Pyrogenesis of Petroleum," we have endeavored in a general way to illustrate the various stages through which development has taken place.

The subject, however, is so vast that it is impossible adequately to deal with it in a single evening, but we hope at some future date to have the honor to present to you in greater detail some of the features of the particular processes or types of processes which are being worked at the present time.

The products of the pyrogenetic treatment of petroleum may be divided into four general classes, *viz.*, permanent gas, illuminating oils, aromatic hydrocarbons, and volatile fuels for internal-combustion engines. These classes also represent roughly the lines on which development has taken place.

Although the manufacture of permanent gas is of secondary importance to us as an Institution, the earliest work on the pyrogenesis of petroleum was started with this end in view, and it is as well briefly to refer to the pioneer work on the subject. The use of illuminating gas made from oil was proposed as early as 1792 by Murdock, and in 1805, as well as in 1821, Henry(2a) described the gas obtained by cracking animal oils, fats and waxes, noticing the formation of ethylene. Between these two dates, John Dalton(1a), in 1809, carried out the first scientific investigation on the pyrogenetic decomposition of hydrocarbons by subjecting ethylene and methane to the action of electric sparks.

It is evident that about this time the question of the production of gas from oil occupied the attention of inventors and scientists, for a few years later, in 1825, we have the classic discovery of benzene by Faraday(3a) in the products obtained by action of heat upon oil, during the course of which work he also noticed the presence of unsaturated hydrocarbons which are very reactive to sulfuric acid.

The work of Dalton on the decomposition of ethylene and methane by electric sparks inspired later workers on the same lines such as Marchand(4a), Magnus(5a), Quet(7a), Hoffmann and Buff(8a), and De Wilde(12a), who all worked on the decomposition of ethylene by heat, and described some of the products of the reactions.

In 1866-67, the famous French chemist, Berthelot(13a, 14a, 15a) published the results of a brilliant series of researches on the action of heat on various hydrocarbons. He showed that acetylene heated alone in a closed space at the temperature at which glass softens, is decomposed, forming liquid hydrocarbons, 97% of the acetylene having disappeared at the end of 30 minutes. In the presence of coke, acetylene is decomposed almost wholly to carbon and hydrogen, and in the presence of iron, half of the hydrogen is released in a free state with the formation of empyreumatic hydrocarbons, the reaction proceeding more rapidly, and at lower temperature. When acetylene is mixed with other gases, such as hydrogen, methane, ethane or carbonic oxide, the reaction proceeds more slowly, and ethylene is formed.

He also showed that the action is reversible at higher temperatures. Under the same conditions: ethylene gave ethane, acetylene and tarry products; ethane gave ethylene; ethylene and hydrogen in equal parts gave ethane, and at dull red heat equilibrium was established between ethylene, hydrogen and ethane, acetylene and ethylene in equal parts gave as principal product a body which was either an isomer or identical with crotonylene, acetylene and benzene in equal parts gave naphthalene.

At this temperature, which he presumed to be 600 to 700° C., hydrocarbons react by direct affinity, and, starting with the lowest hydrocarbon, all the members of the series can be synthesized.

In a later paper he gives the results of passing various hydrocarbons through a porcelain tube heated to bright redness: benzene gave diphenyl, chrysene and a resinous body, but no anthracene or naphthalene, toluene gave benzene, undecylated toluene, naphthalene in large quantity, a crystalline hydrocarbon volatile at 200° C., a large portion of a liquid hydrocarbon which he called benzyl, also anthracene and bodies analogous to chrysene, benzene and ethylene mixed gave styrene, naphthalene and anthracene, styrolene gave benzene and acetylene, styrolene and hydrogen mixed gave benzene, and ethylene, styrolene and ethylene mixed gave principally naphthalene and some benzene, styrolene and benzene mixed gave principally

anthracene, also naphthalene and diphenyl; benzene and naphthalene mixed gave anthracene; diphenyl gave benzene and chrysene. Xylene gave toluene as principal product, also benzene, naphthalene, anthracene and unchanged xylene; cumolene gave toluene and xylene in large quantities—also benzene, cumolene, naphthalene, anthracene, chrysene and benzerythrene in smaller amounts. The results of this work stand to the present day, the whole study being worthy of the great author.

Shortly before this, the attention of the oil industry was directed to the question of increased production of illuminating oils by "cracking," an operation which was accidentally discovered in 1861, owing to the carelessness of a stillman, who built a strong fire under his still, and left it running, intending to return in about an hour. He did not, however, return till about four hours later, when he found the still running a light colored distillate of lower specific gravity than that which was passing when he left. Experiment showed that a portion of the distillate had condensed upon the upper cooler part of the still, and, dropping back on to the hot residue was decomposed into lower-boiling constituents.

This discovery had, however, to some extent been anticipated by Silliman in 1855(6a), who advanced the theory that several of the products of distillation of petroleum were results of heat and chemical change during distillation. The discovery led to a large amount of technical and scientific work on the increased production from petroleum of illuminating oil, which at that time was the most valuable product obtained.

In 1865, Young(3) took out a patent for increasing the yield of burning oils by distillation under a pressure of about 20 lbs., which was followed in 1866 by that of Vincent and others(4), in which the vapors were partly cooled at the still-head, the condensates being allowed to fall back on the hot residues; and a provisional patent in 1869 by Scot and MacIvor(7).

In the meantime, the question was being discussed by Hirsch(17a), Silliman(18a), and Peckham(19a), from a theoretical standpoint; an account of his process was published by Young in 1867(16a), which was followed in 1871-73 by the famous researches of Thorpe and Young(21a) on the effect of distilling solid paraffin under pressure, together with a description of products formed boiling below 200° C., these products consisting of paraffins and olefines as follows: amylene, pentane, hexylene, hexane, heptylene, heptane, octylene, octane, nonylene, nonane, undecylene, undecane and possibly caprylidene, but with no trace of benzene.

An interesting item in connection with this research was communicated to us by your Past President, Sir Boverton Redwood, to the effect that it is not generally known that this research of Thorpe and Young was carried out with a view to determining what actually took place during distillation as carried out according to Young's Patent of 1865(3).

In 1864 and 1868, Vohl(22, 23) describes the treatment of heavy petroleum residues by passing them through hot tubes packed with lime or iron filings, in order to obtain burning oils.

Previous to this, attempts had been made to remove the tars formed in the manufacture of oil-gas for the production of aromatic hydrocarbons.

In 1869, a patent with this end in view was taken out by "Le Societe pour l'etude d'un proc.," followed by that of Breitenlohner(24) in 1870, while in 1870, Vohl(23) describes the production of aromatic hydrocarbons from heavy petroleum residues through iron tubes heated to red heat.

In 1877, Jacobson(25) showed that by the combination of allylene and acetylene the heavy benzene homologues present in coal tar can be formed, and in the same year, Vohl(24) showed that no phenol or cresol is formed in making benzene from the same contained in 1881 by Jacobson(26). A year later, Liebermann, Liebermann and Herz(27) and Liebermann and Wulff(28) published almost simultaneously accounts of processes for the production of aromatic hydrocarbons from benzene and toluene, by passing them through heated tubes with various packings. Liebermann used iron filings for these purposes. Aromatic hydrocarbons formed by these processes were obtained by Amberg(29) who claims that some of the most complex hydrocarbons are formed in combination with a combination of hydrogen as H₂, C₂H₂, C₂H₄.

In 1914, Pittman(30) and his associates are concerned with the pyrogenetic treatment of American oil, stating that the degree

of saturation of the resulting products varies with the temperature, pressure and time of reaction. He isolated acetylene, butylene, crotonylene, benzene, styrolene and bodies similar to naphthalene and acenaphthene.

In 1884, Greville Williams described (34a) and took out a patent (10) for a process for separating aromatic hydrocarbons from the tar produced during the manufacture of oil-gas, and almost simultaneously, Armstrong and Miller (35a) published the results of their well-known investigation on the liquid obtained by the compression of oil-gas, followed two years later by the examination of the gas itself and of the tar deposited prior to compression. In these investigations they isolated benzene, toluene, xylenes (*o*-, *m*- and *p*-), mesitylene, pseudocumene, naphthalene, crotonylene, isobutylene, ethylene, propylene, amylene, hexylene, and heptylene, with only traces of paraffins and naphthenes, and also showed that the unsaturated compounds are easily polymerized, these hydrocarbons, when freshly made, being volatile in steam. They stated that at the higher temperatures required for oil-gas manufacture, normal paraffins are completely decomposed into olefines, acetylenes, benzenes, etc., and that it is not improbable that the benzenes are products, in a direct line, of the action of heat on the paraffins, and not built up from hydrocarbons of the acetylene series.

In 1885, Redwood (36a) described the manufacture of aromatic hydrocarbons from Russian ostakti as carried out by Nobel Bros., by means of which benzene, naphthalene and anthracene were obtained, while in the same year, Hirzel (14) secured a patent for the production of aromatic hydrocarbons by passing petroleum vapors through a retort packed with porous material and heated to red heat, which is apparently the first attempt at pyrogenation in the vapor phase as distinct from the vaporization and pyrogenation in the same retort. A patent was also brought out by the Riebeckische Montanwerke (16) in which it was claimed that by distilling oil under a pressure of 3 to 6 atmospheres, the yield of light oils was increased and the residues could be used for the preparation of lubricants.

Nikiforoff's well-known patent (17) in which the oil was decomposed in two stages, the first stage being at a temperature of 525 to 550° C. in cast-iron retorts, and the second at 700 to 1200° C. under a pressure of two atmospheres in retorts similar to those employed in the Pintsch gas process, was brought out in 1886, claim being made for a 12% yield of benzol as well as other aromatic hydrocarbons (52a), and in the same year, Burns (18) took out a patent for a process in which the oil-vapor from a special still was decomposed in retorts packed with scrap iron and coke.

The American chemists, Norton and Andrews (37a), studied the action of heat on hexane, isohexane and pentane. Hexane decomposed at a bright-red heat gave ethylene, propylene, butin (butadiene), amylene, hexylene and benzol as well as small quantities of saturated hydrocarbons boiling between 100 and 160° C. Treated at 550° C., hexane was not decomposed; at 600° C. there was no formation of gas, but the recovered hexane contained traces of unsaturated compounds, while at 700° C. decomposition with the evolution of gas took place and propylene, butylene, amylene, hexylene and butin (butadiene) were formed, but no benzene. Isohexane decomposed at bright-red heat gave ethylene, propylene, butylene, amylene, hexylene and butin (butadiene). Normal pentane decomposed at bright-red heat gave ethylene, propylene, butin (butadiene) and traces of other unsaturated hydrocarbons.

Day (38a) showed that ethylene begins to decompose when heated at 350° C., and that when heated at 400° C. for a sufficient time, it is entirely decomposed, with the formation of methane, ethane and liquid products, while Norton and Noyes (39a) showed that at low red heat, ethylene gives benzol, naphthalene, propylene, butylene, di-vinyl, methane, ethane, carbon and possibly anthracene, the di-vinyl being similar to the crotonylene identified by Armstrong and Miller and the butin of Norton and Andrews.

Krämer and Böttcher (40a), in 1887, stated that aromatic hydrocarbons are formed by superheating aliphatic hydrocarbons or by heating them under pressure but that under the same condition naphthenes are not formed.

Studying methods of increasing yields of illuminating oils from petroleum, Lisenko (41a) found that when petroleum is distilled, it is not only split up into its constituents, but certain parts of the higher-boiling fraction are decomposed into bodies of lower boiling point, the yield of these varying with the time of heating. By heating residues from Caucasian petroleum at 434 to 501° C., the yield of kerosene was increased by 30%.

Benton (19) took out a patent for this purpose in which the oil was heated in a coil at 371 to 537° C. under a pressure of 500 lbs. per sq. in., and then led into an evaporating chamber connected with a condenser; in 1889, Redwood and Dewar (20) patented their well-known process for increasing the yield of light oils from residues by distillation and condensation under

pressure. This process gave very good results while it was worked. It was designed with a view to increasing the yields of kerosene from Russian oil, and thus decreasing the amount of ostakti produced, which was then somewhat of a drug on the market, but the employment of ostakti as a fuel came into prominence about this time, and it became as valuable as the kerosene which was produced from it, and so the process was abandoned for the time at least.

The demand for a motor-fuel to replace petrol had not yet arisen, so the work in the next decade was confined to the production of aromatic hydrocarbons, and to scientific investigations of the products formed by pyrogenetic treatment of petroleum hydrocarbons, the researches being carried out on both simple hydrocarbons and mixtures thereof.

In 1892 (43a) and again in 1894-95 (50a), Lewes published the results of his investigations on the decomposition of ethylene, in which he states that if ethylene is passed through a tube heated to 800 to 900° C. it is decomposed to acetylene and methane: $3C_2H_4 = 2C_2H_2 + 2CH_4$. If the products are maintained in the heat zone, the acetylene is polymerized to benzene; on raising the temperature to 1000° C. the benzene gives naphthalene, which on further heating to 1100° C. is decomposed to acetylene, which in turn breaks down to carbon and hydrogen. At 900° C., ethane gives up hydrogen with the formation of ethylene. He also showed that aromatic hydrocarbons are present in the tar formed, as well as possibly normal hexane, hexylene, normal heptane, heptylene, and nonane.

Boissieu (44a) showed that mazout on dry distillation yielded aromatic hydrocarbons; Dvorkovitz (47a) also showed that in the manufacture of oil-gas large amounts of aromatic hydrocarbons were obtained, and in 1894, Noyes, Blinks and Mory (48a) examined oil-gas produced at 750 to 1000° C., finding in the gas, ethylene, propylene and a compound C_8H_6 which gave a crystalline tetrabromide, and in the tar, small amounts of the benzene homologues, but large amounts of naphthalene and some anthracene and chrysene. Tocher (49a) in the same year showed that in oil-gas produced at 500 to 600° C., unsaturated hydrocarbons predominate in both the gas and the liquid formed, but at higher temperatures, the gaseous products are ethylene, methane and hydrogen.

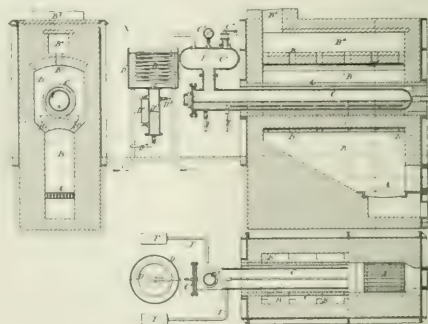


FIG. 1.—REDWOOD AND DEWAR PROCESS

Haber and his colleagues in 1896-97 (53a) stated that at 600 to 800° C., hexane gives amylene, methane and benzene, with a little ethane and very little carbon and hydrogen, the olefine being always the bigger hydrocarbon. Trimethylethylene under the same conditions also gives benzene, therefore the benzene is not a direct product of hexane but is due to polymerization of acetylene. Benzene decomposed at 900° C., giving diphenyl. At 900 to 1000° C., the products are mainly methane, ethylene, hydrogen, carbon and tar.

Worstall and Burwell (57a) in 1897 decomposed crude heptane and octane at 900° C., obtaining the same class of products in both cases: *i. e.*, gas, liquid hydrocarbons, tar and graphitic coke. The tar contained benzene, toluene, xylenes (*o*-, *m*- and *p*-), naphthalene, anthracene, phenanthrene and chrysene, with unchanged heptane or octane, but no paraffins, naphthenes or acetylenes. They stated that at bright-red heat all hydrocarbons of the formula C_nH_{2n+2} gave the same products.

Zaloziecki (58a) in the same year found that petroleum heated in a sealed tube to not over 250° C., undergo intra-molecular changes; *i. e.*, isomerization of the hydrocarbons other than those of the paraffin series.

Pamfilov (59a) obtained aromatic hydrocarbons from petroleum by passing it through a coiled tube at a temperature below that required for making oil-gas, and Boleg (60a) showed

that by distilling hydrocarbons under 3 to 6 atmospheres pressure, the yield of light products is increased.

During this period several patents were registered for the production of aromatic hydrocarbons from petroleum and petroleum residues by Hlawaty and Friedmann(21), Dvorkovitz(24), Smith(26), Young(27), Dvorkovitz(28), Meikle(32), and Meffert(33).

The processes of Meikle and Meffert are the first in which is mentioned the use of steam in the retorts along with oil, although the subject had been investigated previously by Coquillon and Henriviaux(42a). Several patents also were taken out for the manufacture of oil-gas and lighter products from petroleum by Laing(22), Yeadon and Adgie(23), Laing(25), Horsfall(29), the Soc. Internationale de Procédés A. Siegle(30), Siegle(31), and Ragosin(34).

In the meantime, Engler and his pupils had commenced a series of researches on the origin of petroleum, some of the work of which bears directly on pyrogenesis.

In 1893, Engler and Singer(45a) obtained solid paraffin of m. p. 49 to 51° C., by the dry distillation of fish oil, and, in 1897, Engler(54a), by distilling animal fats under pressure, obtained oils containing little nitrogen, which were, however, of light gravity and low boiling point, and did not account for the oils of high gravity, molecular weight and boiling point found in petroleum. He proposed to ascribe the production of these higher compounds to the gradual polymerization of the lower ones, and gave instances of small increases of specific gravity on standing.

In the same year, along with Lehmann(55a), he examined the products of the distillation of fish oil under pressure, identifying the olefines from hexylene to nonylene, paraffins, benzene, toluene, metaxylene, mesitylene and pseudo-cumene, while the presence of naphthenes was not conclusively proved. In another paper he showed, in conjunction with Jezioranski, Grüning and Schneider, that the residues from the distillation of petroleum boiling above 200° C., decomposed on heating in open vessels or under pressure, giving the lower members of the paraffin and olefine series from C_4 to C_{10} , along with aromatic hydrocarbons and some naphthenes, but when heated *in vacuo* distilled without decomposition. Later, in 1906, Engler and Rosner(74a) examined the gas produced in the cracking of Baku crude oil, finding it to consist mainly of methane, ethane, hydrogen, and unsaturated hydrocarbons.

Krämer and Spilker(62a), in 1900, gave the results of distilling Baku residues at 450° C. under 20 atmospheres pressure, light oils being formed, and in 1901, Edeleanu(63a) obtained aromatic hydrocarbons by superheating certain fractions from Rumanian crude oil, while Singer(65a), in 1903-04, showed that, with Rumanian petroleum, cracking takes place at as low a temperature as 200 to 300° C.

Ipatiev, in 1904(69a), stated that in the distillation of petroleum under pressure, at the higher pressures the evolved gases become continually poorer in hydrogen, in spite of the higher temperatures required to maintain the higher pressures. The pressures employed in his work were from 120 to 340 atmospheres.

Collie, in 1906(71a), submitted ethylene to the action of a silent electric discharge, obtaining a liquid which was a mixture of high-boiling hydrocarbons, with hydrogen remaining, while Jackson and Lawrie(72a) submitted acetylene to a high-frequency discharge obtaining a solid polymer of benzene which, on heating, gave methane, hydrogen and a volatile oil. In the same year, Pring and Hutton(73a) stated that carbon and hydrogen united directly at 1850° C., methane and acetylene being formed.

Bone and Coward, in 1908(78a), working on the thermal decomposition of methane, ethane, ethylene and acetylene, refuted this statement and stated that at high temperatures only methane was formed. They also stated that although acetylene is the principal product of the decomposition of ethylene at low temperatures, yet Lewis's equation (47) is wrong, but that when acetylene is the principal product in the decomposition there is always a marked secondary formation of aromatic hydrocarbon. Above 1800° C. they supposed the primary effect to be the elimination of hydrogen with a simultaneous becoming or dissolution of the bond, giving rise to radicals such as $\cdot CH_2$, $\cdot CH$ and $\cdot CH_3$, which, however, can have only a relative existence, and may subsequently re-form H_2C , CH , CH_2 , CH_3 and CH_4 . They held, however, directly to carbon and hydrogen, or α , be directly hydrogenated. A study of the paper in detail is well worth the time spent on it.

In 1910, Pring(79a) repeated the experiment of Pring and Hutton(73a), showing that carbon and hydrogen combined at all temperatures above 1850° C., that above 1900° C. the percentage of methane began to increase with temperature, and above the temperature acetylene is decomposed to ethylene and methane.

Later, in 1911, Pring and Lamberton(81a) showed that in addition to methane and acetylene the formation of ethylene has been detected between 1250 and 1450° C.

THE USE OF CATALYSTS

In 1897, Sabatier and Senderens showed that if ethylene is passed at 300° C. over finely-divided nickel (made by reducing the oxide by heating in a current of hydrogen, and cooling in the same atmosphere), the issuing gas is mainly methane with 10 to 50% of hydrogen, and at lower temperatures ethane is also formed. This peculiar property of finely divided nickel and other metals was further investigated by these two scientists, and they showed in 1899(61a) that by passing acetylene and hydrogen over finely divided nickel, copper, iron or cobalt at moderately low temperatures, liquid hydrocarbons containing paraffins, olefines and aromatic hydrocarbons are formed, together with ethylene and ethane, the proportion of liquid products formed increasing with the temperature, and that an increase in the proportion of acetylene used increased the amount of benzene formed. Later they showed that when a mixture of ethylene and hydrogen was passed over finely divided metals, similar products were formed. The same reaction was tried with platinum black with similar results, but spongy platinum was found not to be so reactive. They also showed that by varying the ratios of the gaseous hydrocarbons and the hydrogen the character of the liquid products could be changed. In 1905(70a) they showed that at 160° C. benzene is hydrogenated by catalysts, such as finely divided nickel, etc., to cyclo-hexane, and that by passing cyclo-hexane over the same materials at 270 to 280° C., it is reduced to benzene. The results of this work of Sabatier and Senderens excited the interest of other investigators, and in 1906, Ipatiev(75a) showed that ethylene, when heated in a sealed tube at 400 to 450° C. with finely-divided iron or copper, readily polymerized, but at higher temperatures much methane, ethane and hydrogen are also formed, while, in presence of an excess of hydrogen, methane is the chief product.

When benzene derivatives are heated with dry hydrogen in presence of iron, copper or aluminum at 400 to 450° C., Ipatiev stated that the benzene nucleus is not hydrogenated even at very high pressures (220 atmospheres), but that in presence of nickel it is slowly but quantitatively converted into cyclo-hexane.

In 1907, Kuznetsov(76a) stated that methane, ethane, ethylene and acetylene are decomposed into their elements by passing over red hot finely-divided aluminum.

Mailhe(79a), in 1908, used finely-divided nickel, copper, iron or cobalt to bring about molecular cleavages. Above 250° C., benzene was decomposed to carbon and methane and cyclo-hexane to benzene and methane.

In 1910, Ostromislenski and Buryanads(82a), working on Russian crude petroleum, showed that in presence of nickel at 600 to 700° C., it breaks down completely to gas and coke, the gas consisting of 72 to 75% hydrogen, and the remainder being saturated paraffins, while naphtha in presence of iron-gauze breaks down to acetylene, which polymerizes to benzene.

Ipatiev and Dowgiewleitch, in 1911(89a), found that hexane and cyclo-hexane, passed through an iron tube heated to 650 to 700° C., were decomposed, the reaction being accelerated by aluminum. The products of the reaction contained paraffins, olefines and hydrogen, but no aromatic hydrocarbons. Under high pressure, hexane decomposed with explosive violence, but cyclo-hexane under high pressure, and in presence of alumina, gave olefines, cyclo-paraffins and benzene derivatives, the formation of methyl cyclopentane taking place only in presence of catalysts. In the same year Zimshikov(90a) showed that palladium black reduces cyclo-hexane and methyl cyclo-hexane to benzene and hydrogen, and toluene and hydrogen, respectively. The reaction commences at 170° C., and proceeds rapidly at 200 to 350° C. No other hydrocarbon derivatives were formed. At 180 to 190° C. in presence of hydrogen, the reverse action takes place. These experiments and methyl cyclopentane are not acted on by H_2 , CH_4 , C_2H_6 , C_3H_8 , C_4H_{10} , C_5H_{12} , C_6H_{14} , C_7H_{16} , C_8H_{18} , C_9H_{20} , $C_{10}H_{22}$, $C_{11}H_{24}$, $C_{12}H_{26}$, $C_{13}H_{28}$, $C_{14}H_{30}$, $C_{15}H_{32}$, $C_{16}H_{34}$, $C_{17}H_{36}$, $C_{18}H_{38}$, $C_{19}H_{40}$, $C_{20}H_{42}$, $C_{21}H_{44}$, $C_{22}H_{46}$, $C_{23}H_{48}$, $C_{24}H_{50}$, $C_{25}H_{52}$, $C_{26}H_{54}$, $C_{27}H_{56}$, $C_{28}H_{58}$, $C_{29}H_{60}$, $C_{30}H_{62}$, $C_{31}H_{64}$, $C_{32}H_{66}$, $C_{33}H_{68}$, $C_{34}H_{70}$, $C_{35}H_{72}$, $C_{36}H_{74}$, $C_{37}H_{76}$, $C_{38}H_{78}$, $C_{39}H_{80}$, $C_{40}H_{82}$, $C_{41}H_{84}$, $C_{42}H_{86}$, $C_{43}H_{88}$, $C_{44}H_{90}$, $C_{45}H_{92}$, $C_{46}H_{94}$, $C_{47}H_{96}$, $C_{48}H_{98}$, $C_{49}H_{100}$, $C_{50}H_{102}$, $C_{51}H_{104}$, $C_{52}H_{106}$, $C_{53}H_{108}$, $C_{54}H_{110}$, $C_{55}H_{112}$, $C_{56}H_{114}$, $C_{57}H_{116}$, $C_{58}H_{118}$, $C_{59}H_{120}$, $C_{60}H_{122}$, $C_{61}H_{124}$, $C_{62}H_{126}$, $C_{63}H_{128}$, $C_{64}H_{130}$, $C_{65}H_{132}$, $C_{66}H_{134}$, $C_{67}H_{136}$, $C_{68}H_{138}$, $C_{69}H_{140}$, $C_{70}H_{142}$, $C_{71}H_{144}$, $C_{72}H_{146}$, $C_{73}H_{148}$, $C_{74}H_{150}$, $C_{75}H_{152}$, $C_{76}H_{154}$, $C_{77}H_{156}$, $C_{78}H_{158}$, $C_{79}H_{160}$, $C_{80}H_{162}$, $C_{81}H_{164}$, $C_{82}H_{166}$, $C_{83}H_{168}$, $C_{84}H_{170}$, $C_{85}H_{172}$, $C_{86}H_{174}$, $C_{87}H_{176}$, $C_{88}H_{178}$, $C_{89}H_{180}$, $C_{90}H_{182}$, $C_{91}H_{184}$, $C_{92}H_{186}$, $C_{93}H_{188}$, $C_{94}H_{190}$, $C_{95}H_{192}$, $C_{96}H_{194}$, $C_{97}H_{196}$, $C_{98}H_{198}$, $C_{99}H_{200}$, $C_{100}H_{202}$, $C_{101}H_{204}$, $C_{102}H_{206}$, $C_{103}H_{208}$, $C_{104}H_{210}$, $C_{105}H_{212}$, $C_{106}H_{214}$, $C_{107}H_{216}$, $C_{108}H_{218}$, $C_{109}H_{220}$, $C_{110}H_{222}$, $C_{111}H_{224}$, $C_{112}H_{226}$, $C_{113}H_{228}$, $C_{114}H_{230}$, $C_{115}H_{232}$, $C_{116}H_{234}$, $C_{117}H_{236}$, $C_{118}H_{238}$, $C_{119}H_{240}$, $C_{120}H_{242}$, $C_{121}H_{244}$, $C_{122}H_{246}$, $C_{123}H_{248}$, $C_{124}H_{250}$, $C_{125}H_{252}$, $C_{126}H_{254}$, $C_{127}H_{256}$, $C_{128}H_{258}$, $C_{129}H_{260}$, $C_{130}H_{262}$, $C_{131}H_{264}$, $C_{132}H_{266}$, $C_{133}H_{268}$, $C_{134}H_{270}$, $C_{135}H_{272}$, $C_{136}H_{274}$, $C_{137}H_{276}$, $C_{138}H_{278}$, $C_{139}H_{280}$, $C_{140}H_{282}$, $C_{141}H_{284}$, $C_{142}H_{286}$, $C_{143}H_{288}$, $C_{144}H_{290}$, $C_{145}H_{292}$, $C_{146}H_{294}$, $C_{147}H_{296}$, $C_{148}H_{298}$, $C_{149}H_{300}$, $C_{150}H_{302}$, $C_{151}H_{304}$, $C_{152}H_{306}$, $C_{153}H_{308}$, $C_{154}H_{310}$, $C_{155}H_{312}$, $C_{156}H_{314}$, $C_{157}H_{316}$, $C_{158}H_{318}$, $C_{159}H_{320}$, $C_{160}H_{322}$, $C_{161}H_{324}$, $C_{162}H_{326}$, $C_{163}H_{328}$, $C_{164}H_{330}$, $C_{165}H_{332}$, $C_{166}H_{334}$, $C_{167}H_{336}$, $C_{168}H_{338}$, $C_{169}H_{340}$, $C_{170}H_{342}$, $C_{171}H_{344}$, $C_{172}H_{346}$, $C_{173}H_{348}$, $C_{174}H_{350}$, $C_{175}H_{352}$, $C_{176}H_{354}$, $C_{177}H_{356}$, $C_{178}H_{358}$, $C_{179}H_{360}$, $C_{180}H_{362}$, $C_{181}H_{364}$, $C_{182}H_{366}$, $C_{183}H_{368}$, $C_{184}H_{370}$, $C_{185}H_{372}$, $C_{186}H_{374}$, $C_{187}H_{376}$, $C_{188}H_{378}$, $C_{189}H_{380}$, $C_{190}H_{382}$, $C_{191}H_{384}$, $C_{192}H_{386}$, $C_{193}H_{388}$, $C_{194}H_{390}$, $C_{195}H_{392}$, $C_{196}H_{394}$, $C_{197}H_{396}$, $C_{198}H_{398}$, $C_{199}H_{400}$, $C_{200}H_{402}$, $C_{201}H_{404}$, $C_{202}H_{406}$, $C_{203}H_{408}$, $C_{204}H_{410}$, $C_{205}H_{412}$, $C_{206}H_{414}$, $C_{207}H_{416}$, $C_{208}H_{418}$, $C_{209}H_{420}$, $C_{210}H_{422}$, $C_{211}H_{424}$, $C_{212}H_{426}$, $C_{213}H_{428}$, $C_{214}H_{430}$, $C_{215}H_{432}$, $C_{216}H_{434}$, $C_{217}H_{436}$, $C_{218}H_{438}$, $C_{219}H_{440}$, $C_{220}H_{442}$, $C_{221}H_{444}$, $C_{222}H_{446}$, $C_{223}H_{448}$, $C_{224}H_{450}$, $C_{225}H_{452}$, $C_{226}H_{454}$, $C_{227}H_{456}$, $C_{228}H_{458}$, $C_{229}H_{460}$, $C_{230}H_{462}$, $C_{231}H_{464}$, $C_{232}H_{466}$, $C_{233}H_{468}$, $C_{234}H_{470}$, $C_{235}H_{472}$, $C_{236}H_{474}$, $C_{237}H_{476}$, $C_{238}H_{478}$, $C_{239}H_{480}$, $C_{240}H_{482}$, $C_{241}H_{484}$, $C_{242}H_{486}$, $C_{243}H_{488}$, $C_{244}H_{490}$, $C_{245}H_{492}$, $C_{246}H_{494}$, $C_{247}H_{496}$, $C_{248}H_{498}$, $C_{249}H_{500}$, $C_{250}H_{502}$, $C_{251}H_{504}$, $C_{252}H_{506}$, $C_{253}H_{508}$, $C_{254}H_{510}$, $C_{255}H_{512}$, $C_{256}H_{514}$, $C_{257}H_{516}$, $C_{258}H_{518}$, $C_{259}H_{520}$, $C_{260}H_{522}$, $C_{261}H_{524}$, $C_{262}H_{526}$, $C_{263}H_{528}$, $C_{264}H_{530}$, $C_{265}H_{532}$, $C_{266}H_{534}$, $C_{267}H_{536}$, $C_{268}H_{538}$, $C_{269}H_{540}$, $C_{270}H_{542}$, $C_{271}H_{544}$, $C_{272}H_{546}$, $C_{273}H_{548}$, $C_{274}H_{550}$, $C_{275}H_{552}$, $C_{276}H_{554}$, $C_{277}H_{556}$, $C_{278}H_{558}$, $C_{279}H_{560}$, $C_{280}H_{562}$, $C_{281}H_{564}$, $C_{282}H_{566}$, $C_{283}H_{568}$, $C_{284}H_{570}$, $C_{285}H_{572}$, $C_{286}H_{574}$, $C_{287}H_{576}$, $C_{288}H_{578}$, $C_{289}H_{580}$, $C_{290}H_{582}$, $C_{291}H_{584}$, $C_{292}H_{586}$, $C_{293}H_{588}$, $C_{294}H_{590}$, $C_{295}H_{592}$, $C_{296}H_{594}$, $C_{297}H_{596}$, $C_{298}H_{598}$, $C_{299}H_{600}$, $C_{300}H_{602}$, $C_{301}H_{604}$, $C_{302}H_{606}$, $C_{303}H_{608}$, $C_{304}H_{610}$, $C_{305}H_{612}$, $C_{306}H_{614}$, $C_{307}H_{616}$, $C_{308}H_{618}$, $C_{309}H_{620}$, $C_{310}H_{622}$, $C_{311}H_{624}$, $C_{312}H_{626}$, $C_{313}H_{628}$, $C_{314}H_{630}$, $C_{315}H_{632}$, $C_{316}H_{634}$, $C_{317}H_{636}$, $C_{318}H_{638}$, $C_{319}H_{640}$, $C_{320}H_{642}$, $C_{321}H_{644}$, $C_{322}H_{646}$, $C_{323}H_{648}$, $C_{324}H_{650}$, $C_{325}H_{652}$, $C_{326}H_{654}$, $C_{327}H_{656}$, $C_{328}H_{658}$, $C_{329}H_{660}$, $C_{330}H_{662}$, $C_{331}H_{664}$, $C_{332}H_{666}$, $C_{333}H_{668}$, $C_{334}H_{670}$, $C_{335}H_{672}$, $C_{336}H_{674}$, $C_{337}H_{676}$, $C_{338}H_{678}$, $C_{339}H_{680}$, $C_{340}H_{682}$, $C_{341}H_{684}$, $C_{342}H_{686}$, $C_{343}H_{688}$, $C_{344}H_{690}$, $C_{345}H_{692}$, $C_{346}H_{694}$, $C_{347}H_{696}$, $C_{348}H_{698}$, $C_{349}H_{700}$, $C_{350}H_{702}$, $C_{351}H_{704}$, $C_{352}H_{706}$, $C_{353}H_{708}$, $C_{354}H_{710}$, $C_{355}H_{712}$, $C_{356}H_{714}$, $C_{357}H_{716}$, $C_{358}H_{718}$, $C_{359}H_{720}$, $C_{360}H_{722}$, $C_{361}H_{724}$, $C_{362}H_{726}$, $C_{363}H_{728}$, $C_{364}H_{730}$, $C_{365}H_{732}$, $C_{366}H_{734}$, $C_{367}H_{736}$, $C_{368}H_{738}$, $C_{369}H_{740}$, $C_{370}H_{742}$, $C_{371}H_{744}$, $C_{372}H_{746}$, $C_{373}H_{748}$, $C_{374}H_{750}$, $C_{375}H_{752}$, $C_{376}H_{754}$, $C_{377}H_{756}$, $C_{378}H_{758}$, $C_{379}H_{760}$, $C_{380}H_{762}$, $C_{381}H_{764}$, $C_{382}H_{766}$, $C_{383}H_{768}$, $C_{384}H_{770}$, $C_{385}H_{772}$, $C_{386}H_{774}$, $C_{387}H_{776}$, $C_{388}H_{778}$, $C_{389}H_{780}$, $C_{390}H_{782}$, $C_{391}H_{784}$, $C_{392}H_{786}$, $C_{393}H_{788}$, $C_{394}H_{790}$, $C_{395}H_{792}$, $C_{396}H_{794}$, $C_{397}H_{796}$, $C_{398}H_{798}$, $C_{399}H_{800}$, $C_{400}H_{802}$, $C_{401}H_{804}$, $C_{402}H_{806}$, $C_{403}H_{808}$, $C_{404}H_{810}$, $C_{405}H_{812}$, $C_{406}H_{814}$, $C_{407}H_{816}$, $C_{408}H_{818}$, $C_{409}H_{820}$, $C_{410}H_{822}$, $C_{411}H_{824}$, $C_{412}H_{826}$, $C_{413}H_{828}$, $C_{414}H_{830}$, $C_{415}H_{832}$, $C_{416}H_{834}$, $C_{417}H_{836}$, $C_{418}H_{838}$, $C_{419}H_{840}$, $C_{420}H_{842}$, $C_{421}H_{844}$, $C_{422}H_{846}$, $C_{423}H_{848}$, $C_{424}H_{850}$, $C_{425}H_{852}$, $C_{426}H_{854}$, $C_{427}H_{856}$, $C_{428}H_{858}$, $C_{429}H_{860}$, $C_{430}H_{862}$, $C_{431}H_{864}$, $C_{432}H_{866}$, $C_{433}H_{868}$, $C_{434}H_{870}$, $C_{435}H_{872}$, $C_{436}H_{874}$, $C_{437}H_{876}$, $C_{438}H_{878}$, $C_{439}H_{880}$, $C_{440}H_{882}$, $C_{441}H_{884}$, $C_{442}H_{886}$, $C_{443}H_{888}$, $C_{444}H_{890}$, $C_{445}H_{892}$, $C_{446}H_{894}$, $C_{447}H_{896}$, $C_{448}H_{898}$, $C_{449}H_{900}$, $C_{450}H_{902}$, $C_{451}H_{904}$, $C_{452}H_{906}$, $C_{453}H_{908}$, $C_{454}H_{910}$, $C_{455}H_{912}$, $C_{456}H_{914}$, $C_{457}H_{916}$, $C_{458}H_{918}$, $C_{459}H_{920}$, $C_{460}H_{922}$, $C_{461}H_{924}$, $C_{462}H_{926}$, $C_{463}H_{928}$, $C_{464}H_{930}$, $C_{465}H_{932}$, $C_{466}H_{934}$, $C_{467}H_{936}$, $C_{468}H_{938}$, $C_{469}H_{940}$, $C_{470}H_{942}$, $C_{471}H_{944}$, $C_{472}H_{946}$, $C_{473}H_{948}$, $C_{474}H_{950}$, $C_{475}H_{952}$, $C_{476}H_{954}$, $C_{477}H_{956}$, $C_{478}H_{958}$, $C_{479}H_{960}$, $C_{480}H_{962}$, $C_{481}H_{964}$, $C_{482}H_{966}$, $C_{483}H_{968}$, $C_{484}H_{970}$, $C_{485}H_{972}$, $C_{486}H_{974}$, $C_{487}H_{976}$, $C_{488}H_{978}$, $C_{489}H_{980}$, $C_{490}H_{982}$, $C_{491}H_{984}$, $C_{492}H_{986}$, $C_{493}H_{988}$, $C_{494}H_{990}$, $C_{495}H_{992}$, $C_{496}H_{994}$, $C_{497}H_{996}$, $C_{498}H_{998}$, $C_{499}H_{1000}$, $C_{500}H_{1002}$, $C_{501}H_{1004}$, $C_{502}H_{1006}$, $C_{503}H_{1008}$, $C_{504}H_{1010}$, $C_{505}H_{1012}$, $C_{506}H_{1014}$, $C_{507}H_{1016}$, $C_{508}H_{1018}$, $C_{509}H_{1020}$, $C_{510}H_{1022}$, $C_{511}H_{1024}$, $C_{512}H_{1026}$, $C_{513}H_{1028}$, $C_{514}H_{1030}$, $C_{515}H_{1032}$, $C_{516}H_{1034}$, $C_{517}H_{1036}$, $C_{518}H_{1038}$, $C_{519}H_{1040}$, $C_{520}H_{1042}$, $C_{521}H_{1044}$, $C_{522}H_{1046}$, $C_{523}H_{1048}$, $C_{524}H_{1050}$, $C_{525}H_{1052}$, $C_{526}H_{1054}$, $C_{527}H_{1056}$, $C_{528}H_{1058}$, $C_{529}H_{1060}$, $C_{530}H_{1062}$, $C_{531}H_{1064}$, $C_{532}H_{1066}$, $C_{533}H_{1068}$, $C_{534}H_{1070}$, $C_{535}H_{1072}$, $C_{536}H_{1074}$, $C_{537}H_{1076}$, $C_{538}H_{1078}$, $C_{539}H_{1080}$, $C_{540}H_{1082}$, $C_{541}H_{1084}$, $C_{542}H_{1086}$, $C_{543}H_{1088}$, $C_{544}H_{1090}$, $C_{545}H_{1092}$, $C_{546}H_{1094}$, $C_{547}H_{1096}$, $C_{548}H_{1098}$, $C_{549}H_{1100}$, $C_{550}H_{1102}$, $C_{551}H_{1104}$, $C_{552}H_{1106}$, $C_{553}H_{1108}$, $C_{554}H_{1110}$, $C_{555}H_{1112}$, $C_{556}H_{1114}$, $C_{557}H_{1116}$, $C_{558}H_{1118}$, $C_{559}H_{1120}$, $C_{560}H_{1122}$, $C_{561}H_{1124}$, $C_{562}H_{1126}$, $C_{563}H_{1128}$, $C_{564}H_{1130}$, $C_{565}H_{1132}$, $C_{566}H_{1134}$, $C_{567}H_{1136}$, $C_{568}H_{1138}$, $C_{569}H_{1140}$, $C_{570}H_{1142}$, $C_{571}H_{1144}$, $C_{572}H_{1146}$, $C_{573}H_{1148}$, $C_{574}H_{1150}$, $C_{575}H_{1152}$, $C_{576}H_{1154}$, $C_{577}H_{1156}$, $C_{578}H_{1158}$, $C_{579}H_{1160}$, $C_{580}H_{1162}$, $C_{581}H_{1164}$, $C_{582}H_{1166}$, <

used as catalysts, but they soon became coated with carbon. Yields up to 59% diphenyl were obtained.

In 1912, also, Zelinski and Herzenstein(96a) showed that by passing a mixture of cyclo-hexane and ethyl cyclo-pentane over palladium black at 300° C., till no further hydrogen was evolved, the methyl cyclo-pentane could be recovered unchanged, the cyclo-hexane being converted to benzene, thus showing selective catalysis; similar results were obtained with fractions from Baku naphtha.

Jones, in 1915(113a), heated various hydrogenated aromatic hydrocarbons in presence of porous porcelain: at 500° C., cyclo-hexane gave benzene and higher olefines, ethane, methane, ethylene, hydrogen, traces of acetylene and unchanged cyclo-hexane; at 530° C., methyl cyclo-hexane gave similar products to cyclo-hexane; at 420° C., 1,4-dihydronaphthalene gave naphthalene, hydrogen, methane, and traces of higher olefines and ethylene, and at 530° C., 1,2,3,4-tetrahydronaphthalene gave naphthalene, benzene, higher olefines, methane, ethane, ethylene and hydrogen.

In the same year, Tchitchibabin(122a) stated that the effect of heat on acetylene in the presence of different catalysts consists of three principal processes: (1) Local decomposition of the acetylene into carbon and hydrogen, accompanied by polymerization into aromatic hydrocarbons; (2) condensation to solid hydrocarbons, similar to cuprene; (3) hydrogenation of acetylene and aromatic hydrocarbons with formation of hydrocarbons of the paraffin, olefine and cyclic series.

Zelinski, in 1915(130a), stated that in cracking petroleum for aromatic hydrocarbons improved yields of benzene and toluene are obtained by using alumina and titanium oxide as catalysts.

Slater, in 1916(131a), found that while several surface-catalysts increased, silica retarded the velocity of decomposition of methane.

This scientific investigation of the effects of catalysts on the decomposition of hydrocarbons naturally reacted on the technical side of the subject, and since 1906 many processes for the production of light spirits by the action of catalysts have been patented.

Day, in 1906(36), proposed to distill oils under pressure in the presence of hydrogen, or an absorbable hydrocarbon, and a catalyst, such as palladium black or spongy platinum, in order to produce light saturated oils.

In 1908, Sabatier(39) took out his first patent on the treatment of oil in presence of catalysts, in order to obtain from heavy oils or lamp oils a spirit boiling below 150° C. The vapors of the heavy oils are passed over finely-divided metals at 400° C., or dull red heat, and the product from this reaction, which consists mainly of unsaturated hydrocarbons, is then hydrogenated in presence of finely-divided metals at 150 to 300° C.

Phillips and Bulteel, in 1909(43), patented a process for the production of light oils from heavier mineral oils by heating in presence of hydrogen or hydrogenized gases and a catalyst such as powdered nickel, a rapid gyratory motion being imparted to the mixture of oil-gas and catalyst as it entered the retort.

Hausman and Pilat, 1909(45), specified the use of oxides, peroxides, or salts of metals capable of acting as oxygen-carriers, in the decomposition of petroleum or hydrocarbon vapors.

Planes, Ltd., and Thompson, 1913(68), proposed to crack petroleum or other heavy hydrocarbons by heating in a cracking still with a catalyst such as finely-divided nickel, and hydrogen or purified water-gas, and with violent agitation during the operation. The distillation is effected at about 300° C., and under a pressure of 5 to 100 lbs. per sq. in. It is mentioned that the heavy hydrocarbon is first purified from asphalt, sulfur, and other catalytic poisons.

Franke, 1913(73), also specified the use of pyrophoric metals such as iron, nickel, chromium, and platinum, together with hydrogen given off from the oil during cracking.

Gross, 1913(75), proposed the use of metallic oxides, hydroxides or basic salts in the preparation of isoprene by the pyrogenetic decomposition of turpentine, copper oxide being instanced as suitable.

Hall, 1913(78), took out a patent for the production of motor-spirit from heavy hydrocarbons by heating the vapors under pressure in the presence of a catalyst capable of affixing hydrogen, allowing the vapors to expand and deposit carbon, and then condensing them. The temperature specified is 600° C. and upwards, pressure 5 atmospheres and the catalysts, metals such as nickel, cobalt, silver, palladium, chromium or manganese, or their oxides.

Holcgreber(79), in a patent of 1913, stated that benzene is obtained from the vapors of petroleum or its distillates by passing them, together with hydrogen, through a tube containing catalytic materials heated to 180 to 300° C. Acetylene is said to be first formed and then polymerized to benzene. Suitable catalysts are iron, copper, zinc, aluminum, nickel, cobalt, silver and platinum or mixtures thereof.

The use of hydrogen and nickel as a catalyst for converting

the unsaturated products from the cracking of oils into saturated aliphatic hydrocarbons was claimed in 1913 by Sommer(82) and also by the Steaua Romana Petroleum-Ges.(84). Valpy and Lucas, in 1913(86), patented a process in which a mixture of oil and steam is brought into contact with a heated catalyst, such as nickel or other metal or metallic oxide. The production of the catalysts was the subject of a further patent in 1914(99), these being made by heating a powdered metallic oxide or mixture of oxides with organic compounds of the metal. In a later specification the uses of permanent gas partly saturated with ammonia gas are covered. The oil to be cracked is distilled in a separate still, and the vapors are passed through a cracking tube, packed with the catalyst, and heated to 550 to 600° C. The cracked vapors pass through fractionating, condensing and stripping plant. Part of the uncondensed gas now passes through an ammonia saturator under a slight pressure to the still, where it is sprayed over the surface of the oil. This helps to carry the oil vapor as fast as it is formed to the cracking tube, and incidentally reduces the temperature of distillation of the oil. It is claimed that a portion of the ammonia is dissociated, forming nascent hydrogen, which in the presence of the catalyst hydrogenizes a portion of the unsaturated hydrocarbons formed, and appears also to arrest the separation of carbon. The ammonia has yet a further action in that it tends to produce a sulfur-free spirit, even when an oil containing 5 to 6% of sulfur, such as Mexican oil, is employed. A commercial unit erected at Dagenham has been in intermittent use for the past two years, about 50 tons of oil having been run through it. The authors have had the pleasure of examining a sample of refined spirit produced in this plant which had been made about eighteen months, and found it completely free from the usual obnoxious polymerization products. It had a smell which was not so pronouncedly cracked as some of these spirits, a comparatively low unsaturated content, and was quite "water-white." The plant is very simple in action and is very easily controlled. A cracking plant to produce 2,000,000 gallons of spirit per year, including "crackers," distilling and refining plant, and gas producer plant for heating stills, crackers, etc., would cost about £50,000.

Sabatier and Mailhe, 1914(93), decomposed heavy hydrocarbons by passing them over a network of wires heated electrically from 500° C. to red heat, and subsequently converted the unsaturated compounds produced into saturated hydrocarbons by hydrogenation over finely-divided metals at 200 to 300° C.

Hirschberg, 1914(96), proposed to use the voluminous chromium oxide obtained by calcining the chromium salts of volatile bases, such as ammonium chromate, as a catalyst for the conversion of heavy hydrocarbons into lighter hydrocarbons.

White, 1914(98), obtains light spirit from mineral oils and residues by bringing them in the liquid state, without steam or water, onto quicklime or quicklime containing carbon, at 400 to 650° C. Herber, 1914(111), proposed distilling oil mixed with lime in the presence of water or steam to produce lighter hydrocarbons. Porges and others, 1914(103), used iron oxide or the oxide of another metal capable of forming several oxides as catalyst, passing over it oil-vapors and steam at 500 to 600° C., the catalyst when exhausted being regenerated by heating in a current of air or oxygen.

Sabatier and Mailhe, 1914(109), converted crude petroleum into volatile hydrocarbons boiling below 150° C., by passing it over a heated catalyst composed of finely-divided metals, or metallic oxides (iron oxide) or salts capable of reduction to metals, mixed with a neutral refractory substance free from silica (magnesia, alumina, graphite), and an agglutinant free from silica (glue, dextrine, starch). When the catalyst became coated with carbon, it was regenerated by a current of steam, and then reduced by hydrogen. In a further patent(116) the catalytic agent is maintained at a temperature of 300° C. by an electric current.

Higgins and Preston, 1914(115), heat heavy hydrocarbons under a pressure, to such a temperature that the least volatile constituent is vaporized, and then the vapor, either alone or mixed with hydrogen, is passed through a catalytic medium, such as a mixture of nickel oxide and pumice stone, and condensed in contact with the medium.

Low, 1916(132), converts high-boiling oils into low-boiling ones by spraying them by means of hydrogen against a heated plate, having a surface of catalytic material.

ACTION OF METALLIC HALIDES

The well-known reaction of Friedel and Crafts has formed the basis for a number of experiments on the decomposition of hydrocarbons. In 1877, Abel(8) patented a process in which hydrocarbons are treated with aluminum chloride (anhydrous) or other metallic chlorides at 100 to 600° C., whereby petroleum is converted into light oils, and naphthalene into benzene and toluene.

In 1881, Gustavson(31a) treated hydrocarbons obtained by

fractionating American lignoïn or Caucasian kerosene by dissolving in them aluminum bromide, and then passing a stream of hydrobromic acid through. The liquid separates into two layers; the lower, being always approximately the same, points to the formula $\text{AlBr}_3 \cdot \text{C}_8\text{H}_{18}$. This layer is decomposed at 120°C ., giving gaseous hydrocarbons. The upper layer consists of unsaturated hydrocarbons and simple homologs.

Heusler (51a), in 1896, stated that unsaturated hydrocarbons are polymerized to saturated hydrocarbons by aluminum chloride, and at the same time sulfur is removed; in 1902, Aschan (64a) showed that at low temperatures olefines are polymerized to naphthenes in the presence of anhydrous aluminum chloride.

Engler (85a), in 1910, in his researches on the composition of lubricating oils, states that amylene heated under pressure gives methane and hydrogen, but with anhydrous aluminum chloride it gives a natural lubricating oil, which on further heating gives paraffins, naphthenes and olefines, while solid paraffins give liquid paraffins and olefines under heat and pressure.

Ipatiev and Routala, in 1913 (98a), showed that if ethylene is heated with anhydrous zinc chloride under a pressure of 20 atmospheres polymerization takes place at 275°C ., olefines, paraffins and naphthenes being formed. In the presence of anhydrous aluminum chloride, polymerization takes place at a lower temperature, but less naphthenes are formed.

In the same year a patent was taken out by the Continental Caoutchouc and Gutta Percha Co. (69) for the production of mineral oils of low boiling point from those of high boiling point

ethylene he obtained saturated paraffins ranging from isopentane to nonane, amylene and hexylene; and naphthenes from nononaphthene to pentadecanaphthene. The fractions boiling above 250°C . were poorer in hydrogen than polymethylene compounds. In the case of isobutylene, hydrocarbons were formed which reacted with nitric acid and potassium permanganate, but were insoluble in concentrated sulfuric acid (sp. gr. 1.84), and were probably aromatic hydrocarbons. Ethylene does not polymerize at 600°C . under atmospheric pressure. He suggests that the ethylene hydrocarbons are probably produced by polymerization of ethylene itself or from polymethylene compounds by fission of the ring; and saturated hydrocarbons by the hydrogenation of closed-chain hydrocarbons with fission of the ring, or by fission of the side chain from polymethylene nuclei.

Meyer and Tanzen, in 1912 (95a), passed equal volumes of acetylene and hydrogen through two tubes consecutively, the first heated to 640 to 650°C . and the second to about 800°C . In the tar formed, they identified phenanthrene, acenaphthene, styrene and *n*-hexylene.

Staudinger, Endle and Herold, in 1913 (99a), by passing isoprene through a tube heated to 750°C ., obtained 50% of tar containing benzene, toluene, naphthalene, methylnaphthalene, anthracene, chrysene and also butadiene, methane and carbon; at 400°C ., the isoprene was mainly unattacked, but small quantities of terpenes and amylene were obtained; from 600 to 700°C . the product was mostly unsaturated hydrocarbons;

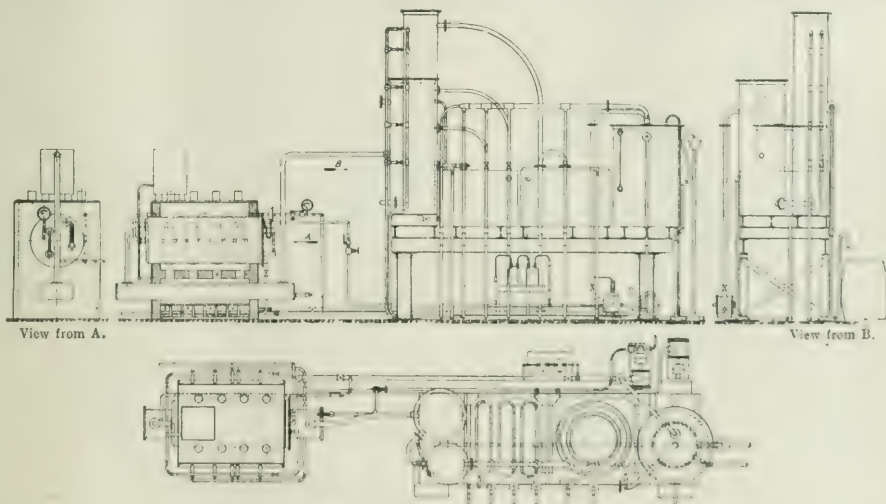


FIG. 2. LUCAS OIL CRACKING PLANT

by heating the high-boiling fraction with a catalyst such as aluminum chloride, with or without mercuric, ferric, vanadium, or other chloride or with aluminum in a stream of dry hydrochloric acid gas. In the same year a patent on similar lines was granted to Gray (66), who cracked oils by heating them with anhydrous aluminum chloride, ferric chloride or other metallic chloride at temperatures not higher than the final boiling point of the product desired. For naphtha the temperature was 325 to 350°F ., and for kerosene 500 to 600°F ., the cracking being effected in a still fitted with stirring blades.

In 1914 and 1915, McAlister (114, 118, 119a) took out several patents for the preparation of motor spirits from heavy oils, claiming large yields of water white, sweet smelling, saturated compounds of low boiling points. The dried heavy oil is distilled with anhydrous aluminum chloride in a still fitted with a stirrer, at a temperature of 300 to 350°F ., 1260 to 288°C .

It is difficult to see on what grounds these latter patents were obtained, as the process, chemical agent, and conditions had been specially and specifically mentioned in prior patents.

RECENT WORK ON THE THERMAL DECOMPOSITION OF HYDROCARBONS

Kharitshlow, in 1910 (87), subjected residues boiling above 270°C . from Baku and Grozni oil to cracking, and obtained, respectively, 25 and 18.9% of products boiling below 270°C ., in each case, together with a very fluid residue resembling solar oil. In 1911, Ipatiev (88c) showed that by heating ethylene and isobutylene in an iron tube under a pressure of 20 atmospheres, rapid polymerization took place at 380 to 400°C . From

from 700 to 750°C ., aromatic hydrocarbons began to be formed, and above 800°C . the product consisted mainly of aromatic hydrocarbons.

Jones and Wheeler, in 1914 (103a), by distilling bituminous coal at 20 atmos at temperatures up to 450°C ., obtained about 6.5% of tar, which consisted of about 40% volatile below 250°C ., and a pitch boiling above 300°C . The oils volatile below 300°C . consisted of ethylenic hydrocarbons of indeterminate composition, for the most part richer in carbon than the known olefins (C_2H_4 equal to 95 to 97% naphthalene and liquid benzolene, the former in excess, about 4 to 5% ethylidenehydride, about 7%, apparently homologs of naphthalene, naphthalene itself not being detected), and a small quantity of solid carbon. Benzene, anthracene, carbon, benzolene and solid aromatic hydrocarbons were absent.

Serretzoff, in the same year (104), by treating methyl alcohol with phosphorus pentachloride, obtained acetone and naphthenes; a gas composed of the general formula C_2H_4 , but no ethylene, which is strong evidence of the limited existence of nascent radicals (C_2H_3) as suggested by Hurd and Coward (75).

Rubinc, in 1915 (105), discussed the theory of reactions involved in the cracking of oils.

Peterson (111a) (112), subjected crude Russian petroleum and its products to destructive distillation obtaining aromatic hydrocarbons. In the same year, Meyer and Herold (110a) found *m*- and *p*-xylene, *o*- and *p*-methylnaphthalene and hydro-

rivatives of naphthalene in tar obtained from acetylene; in all, 23 compounds present in ordinary coal tar were detected.

In 1915, a large amount of experimental work was carried out, but it is worthy of note that the source of the large portion of it was the United States, for obvious reasons, the investigations of European workers having been directed into other channels. This work of the American investigators, although of great interest from a technical standpoint, has not advanced the real knowledge of pyrogenesis to any great extent, being too empirical.

Whitaker and Alexander(112a) showed that temperature and rate of flow determine the properties of oil-gas made from kerosene, higher temperatures and lower rates of flow increasing the rate of decomposition, and that proportion of free hydrogen formed.

Brooks and others(114a, 119a) showed that the olefine content of gasoline prepared from heavy hydrocarbons decreased as pressure of preparation increased, up to a maximum of 200 lbs. per sq. in., and then remained constant; and that the percentage of gasoline increased to 280 lbs. per sq. in. and then decreased. The temperature of working was 600 to 700° C. Working at 100 lbs. pressure, aromatic hydrocarbons were formed which they suggested were derived from petroleum hydrocarbons containing the phenyl group.

Bjerregaard(115a) passed crude petroleum and kerosene through an iron coil at pressures ranging from 275 to 1400 lbs. per sq. in. and temperatures from 340 to 440° C. and then expanded into vessels kept at 20 to 30 lbs. per sq. in. Yields of low-boiling oils depended on rate of feed and pressure. At these low temperatures no aromatic hydrocarbons were found.

Rittman, Twomey and Egloff(116a) stated that the percentage of aromatic hydrocarbons in cracked oil could be estimated from the specific gravity of the fractions obtained when following specified directions.

Sterne(118a) examined the condensate from carbureted water-gas, finding it to consist of 75.9% paraffins, 1.6% olefines and 22.5% aromatic hydrocarbons.

Ellis and Wells(120a), in discussing the properties of gasoline made by cracking kerosene, pay attention to the high specific gravity, iodine absorption and refractive index and find that the polymer deposited on standing decomposes on distillation, even under a vacuum of 6 to 10 mm., stating also that the polymerized products react with sulfur and sulfur chlorides, and that the gas produced gives with chlorine a liquid product.

Rittman, Byron and Egloff(121a) subjected aromatic hydrocarbons to cracking in the vapor phase under various conditions and found that general reaction may be indicated as follows: higher benzene homologues → lower homologues → benzene → (diphenyl → naphthalene → anthracene, the reverse reactions being negligible.

Ostromislenski(123a) stated that the pyrogenetic decomposition of homoligues of d-pentane at 500 to 600° C. yields homologues of isoprene, and that of saturated hydrocarbons and such as contain one double linking, yields erythrene, but not its homologues. Erythrene may be obtained from almost any hydrocarbon containing not fewer than four carbon atoms in the molecule.

In 1916, Friedmann(143a) showed that very pure normal octane heated in a sealed tube at 280° C. gives fractions boiling at 118 to 127° C. Whitaker and Leslie(134a), following up Whitaker and Alexander's work(112a), studied the effect of the addition of hydrogen in making oil-gas, the concentrations being approximately $\text{H}_2 : 1$ oil-gas, and, $2\text{H}_2 : 1$ oil-gas. The absorption of hydrogen is greater the higher the concentration, the higher the temperature, and the lower the rate of oil feed. The formation of methane is greater the higher the temperature.

Davies(133a) obtains gasoline practically free from unsaturated hydrocarbons from high-boiling petroleum oil by mixing the vaporized oil with superheated steam, and passing the mixture under pressure through tubular cracking apparatus packed with iron or steel shavings. The best conditions for experiment were found to be: 100 lbs. pressure per sq. in., 10 lbs. steam per gallon of oil, steam superheated to at least 600° C. and cracking temperature 650 to 675° C.

Zanetti(135a) subjected the propane (97%) butane (3%) fraction from natural gas to cracking. At atmospheric pressure and up to 750° C., no aromatic hydrocarbons were obtained, but ethylene, butylene, etc., and hydrogen, the percentage of hydrogen being greater the higher the temperature. The unsaturated bodies rose to a maximum at 750° C. and then decreased, benzene and toluene being found in the tar produced. Above 750° C., nickel and iron gauze inhibited the production of aromatic hydrocarbons, and favored the production of carbon and hydrogen.

Brooks and Humphrey(142a) stated that benzene homologues are present in the high-boiling distillates of petroleum, basing their conclusions on cracking experiments carried out on Jena-

nings and Oklahoma residues at temperatures not exceeding 420° C. and pressures not exceeding 100 lbs. per sq. in., in which they obtained small quantities of benzene homologues, also on the fact that Oklahoma oil heated with aluminum chloride gave the same results, as did a synthetic phenyl-paraffin, made by condensing pure benzene with chlorinated paraffin wax in presence of aluminum chloride; this on cracking gave benzene homologues, whereas paraffin itself did not give them. They claim that the temperatures used were too low to admit of the decomposition of hydrocarbons to acetylene with subsequent polymerization.

The work of Rittman, Twomey and Egloff(132a, 136a, 137a, 138a, 139a, 140a, 141a, 144a, 145a) may be here conveniently classed together as having a bearing on the much-lauded Rittman vapor-phase cracking-process. Most of this work is relative to the conditions governing the production of aromatic hydrocarbons from petroleum. They show that the maximum production of benzene takes place when the production of toluene and xylene have decreased, i. e., at higher temperatures, and that at the same time naphthalene begins to be produced, arguing from this that naphthalene is formed by the decomposition of monocyclic bodies. At ordinary pressures, higher temperatures were required for the production of aromatic hydrocarbons than when under increased pressure, but even at low temperatures, i. e., 450 to 600° C., some aromatic hydrocarbons are produced. Under pressures of 11 to 14 atmospheres, and temperatures from 600 to 650° C., alkyl and alkylene derivatives of naphthalene give benzene and toluene, their formation being assumed to take place: (1) by direct decomposition of methyl naphthalene; (2) by formation and subsequent decomposition of xylenes; (3) by synthesis from acetylene and allylene, the three reactions occurring either successively or simultaneously. Paraffin wax at atmospheric pressure and a temperature of 500° C. gave no aromatic hydrocarbons, but at 150 lbs. per sq. in. and a temperature of 600° C., appreciable yields of benzene, toluene and xylene were obtained, as well as liquid paraffins. Kerosene was subjected to the action of various catalysts in the liquid-vapor phase, yields of cracked oils from the various catalysts being given.

Vignon(148a) distilled coal at 400, 600, 850, 1000 and 1200° C., and analyzed the gases produced. Unsaturated hydrocarbons (ethylene, acetylene, etc.) are all distilled below 600° C., and are absent above this temperature. Methane and paraffins are very abundant up to 800° C., but then disappear; from 800 to 1000° C., hydrogen predominates, but then falls off, and at the highest temperature carbon monoxide is found.

De Montmolin(147a) examined the "ethylene-petrol" formed by the action of phosphoric acid on ethylene, finding it to be a complex mixture of hydrocarbons, mainly polymethylene (cyclohexane homologues), together with unsaturated and saturated aliphatic hydrocarbons and aromatic hydrocarbons. Di-isopropyl (b. p. 58 to 59° C.), di-methyl di-ethyl methane (b. p. 86 to 87° C.), hexahydrometaxylene, and hexahydrometaxylene were isolated in a state of purity, and hexahydrometaxylene, hexahydrometaxylene, decanaphthene, dodecanaphthene and tetradecanaphthene were identified.

Oil-gas produced in cracking solar oil for motor-spirit, when passed through sulfuric or phosphoric acids, is polymerized, giving a mixture of liquid hydrocarbons; this product was examined by one of the authors in 1913 and found to consist of a mixture of polymethylene hydrocarbons, together with unsaturated hydrocarbons of the terpene or polyterpene series, which had pronounced siccative properties. It is hoped that an opportunity will arise for a further examination of this product.

Fischer(146a) treated naphthalene with 4% powdered aluminum chloride in a sealed tube for 3 hours at 330° C. About 40% was converted into liquid hydrocarbons which analysis showed to have a composition intermediate between naphthalene and dihydronaphthalene.

Gurvitch(149a) treated freshly rectified amylene with floridin, the amylene being polymerized to di-amylene; carbon and alumina also affected the polymerization.

RECENT PATENTS ON OIL CRACKING

The demand for volatile hydrocarbons for use as fuel in internal-combustion engines in late years, and the question of obtaining an increased production by the utilization of fractions from crude petroleum of otherwise less value, has undoubtedly stimulated the activities of engineers and chemists in finding a solution of the problem, and over 60 patents with this end in view have been taken out since 1906.

Cowper-Coles, in 1906(35), was apparently the first inventor who worked specially for a product adapted for use in internal-combustion engines, the method of production being to pass paraffin oil vapors through a series of small tubes heated to about 1700° F. (926° C.).

In 1908, Noad and Townsend(40) proposed to decompose oil and water in liquid form in the presence of each other and of highly heated iron in the form of scrap or the like, claim being

Von Groeling(71) distilled and cracked hydrocarbons by passing the vapors from a still through externally-heated cracking tubes, where they meet a descending stream of hydrocarbons. The operation is conducted under slight pressure and at temperatures from 350 to 650° C.

Moeller and Wolterick(77) converted crude or heavy oils into light oils by mixing their vapors with highly superheated steam (at 700 to 800° C.) of substantially atmospheric pressure and passing the mixture over coke at dull red heat (600 to 800° C.).

Hall(78, 87, 89, 92, 102, 105, 119, 123) has been one of our most prolific inventors in the line with which we are dealing, and his process, modified from time to time as experience has been gained, is one, probably the most successful, of those being worked. It is hardly necessary for me to describe this process fully, as less than two years ago the inventor himself gave you a full description. Briefly, however, in the process as at present worked, the oil to be treated is passed through a continuous coil of about 600 ft. of cold-drawn tubing of 1 in. internal diameter, at temperatures and pressures which vary according to the desired product. The oil fed in at the cooler end of the retort is gradually heated and vaporized, the speed of the vapors being about 5000 to 6000 ft. in the latter portion of the coil, and where the temperature is highest. At the exit, the vapors are suddenly expanded into a tube of much larger diameter, down to atmospheric pressure. Here, an appreciable rise in temperature is experienced without external aid, due partly to transformation of the kinetic energy of the high velocity of the gases into heat, and partly to the disruption of the molecules of the oil. It is at this point that most of the cracking takes place, and a little graphitic carbon is formed. The vapors now pass through a series of dephlegmators, built on the Raschig principle. In the first of these, a little soft spongy carbon and pitch separate out, in the second a heavy residue free from pitch, and in the third a very light mobile residue. The vapors, cooled now to about 100° C., pass to compressors, which having already expanded the gas on exit from the converter tubes down to atmospheric pressure, now compress the wet vapors, which are cooled and stored under a pressure of 50 to 75 lbs. per sq. in.

A peculiar reaction has been noticed in these compressors when working for motor-spirit. As a rule, when gases are compressed, the temperature rises, but in the case of these gases, the temperature falls slightly after compression, which fall can be caused only by chemical combination, or polymerization of some of the lighter hydrocarbons, as it is well known that some of the hydrocarbons produced in cracking oil polymerize very readily even at ordinary temperatures and pressures. By returning the residues from the second and third dephlegmators, yields of 70% motor-spirit from the original oil used have been obtained. In working for motor-spirit, the temperature at the exit of the tubes is about 550 to 600° C., a temperature which requires varying between these limits according to the oil being cracked, but when once the optimum temperature for any particular oil has been decided, this temperature can be most rigidly adhered to, variations of $\pm 5^\circ$ C. being the extremes over periods of several hours working. This complete control of the temperature is a very important consideration in a process of thermal decomposition, as, at the temperatures employed, the thermal coefficient is very high, and comparatively small variations give rise to very divergent results. This is a point, by the way, to which many inventors have failed to pay sufficient attention. The rate of feed of oil to the tubes is also very carefully regulated by means of meters, being checked to $\pm 5\%$ of the feed per hour.

Hall's plant, with very small alterations, is eminently adapted for the production of aromatic hydrocarbons from petroleum, an installation consisting of eight converters with the necessary complement of dephlegmators, compressors, condensers and tanks having worked on these lines daily for about eleven months with complete success, a spirit having been produced in good yields containing up to 18.5% benzene, 17.5% toluene and 6.0% xylenes, which is very easily refined, the refined products containing only traces of paraffin or naphthenes, *e. g.*, from 1 to 2% on the finished product. When working for aromatic hydrocarbons, the temperatures and pressures employed are necessarily higher than when working for motor-spirit, being, respectively, 750° C. and 105 to 110 lbs. per sq. in., but these temperatures and pressures are as easily controlled as when working at the lower ones. It might be argued that when working with tubes of this diameter and under these severe conditions of cracking, there is a liability of the tubes becoming choked with carbon. This difficulty was certainly encountered at first, but has been overcome, and it is now quite common for a nest of tubes to run over 250 hours without cleaning, and then only a few of the tubes require to be replaced by clean ones, and the nest can be restarted immediately. The high speed at which the vapors pass through the tubes causes a scouring action, which carries any carbon formed through to the expansion tubes and dephlegmators, whence it is very easily removed. A fairly large amount of gas of high calorific value (1350 B. t. u.),

and having a distinct commercial value, is necessarily formed when cracking for aromatic hydrocarbons. Incidentally it may be mentioned that the aromatic hydrocarbons contained in the spirit produced can be very easily estimated by simple modifications of the James and Coleman tests, determinations by which agree very closely with the results obtained by fractionation to pure products. In the higher boiling portions of the spirit, *i. e.*, those boiling between 150 and 250° C., naphthalene is formed and has been isolated in a pure state and identified, while it is very probable that its derivatives are also present. Graefe and Walther(88) transformed heavy hydrocarbons into lighter ones by distilling under a pressure of 20 to 30 atmospheres in an autoclave. This, however, hardly seems to have much prospect of success on a large scale.

Shedlock and The Optime Motor Spirit Syndicate(91), for the production of motor-spirit from heavy oils, emulsify the heavy oils with water by means of resin, soap or other emulsifying agent, and then heat the emulsion under pressure at about 500 to 900° F. in presence of iron or steel shavings or other catalyst. The oil before emulsification is treated to remove sulfur and pitch. We understand that this process is being worked in this country, but do not know with what success.

Gray(94) passes oil through a bath of molten metal kept at a high enough temperature to cause cracking.

Fenchelle and Perkin(100) have patented a process in which heavy hydrocarbons are converted into lighter hydrocarbons, by heating them in the liquid state to 500 to 600° C. under a pressure of 50 to 60 atmospheres. The liquid, still under pressure, is then cooled to about 150° C., and allowed to escape at a lower pressure into a chamber, in which the lower hydrocarbons vaporize simultaneously. The invention is applicable to liquefied hydrocarbons such as naphthalene and paraffin wax. In this process it is claimed that by treating in the liquid phase in this manner very little carbon is deposited, and from all accounts a very fair amount of success has been met with in the experimental stage.

By Bacon and Clark(108), petroleum hydrocarbons having a boiling point of about 250° C. and upwards are decomposed and distilled under a pressure of 100 to 300 lbs. per sq. in., the heat being applied at such rate as to give a minimum yield of 18% gasoline boiling below 150° C.

Snelling(110, 128a) states that by heating low-grade crude oils, aliphatic oils, paraffin wax, rod wax, kerosene, lubricating oils, fuel oils, tarry still residues, etc., in a closed vessel to such a temperature that the vapors evolved produce an added pressure of preferably 600 to 800 lbs. per sq. in., a product resembling high-grade Oklahoma crude oil is obtained, which on distillation yields gasoline up to 20% and kerosene up to 40%. The still is preferably filled between one-fifth and one-half its cubic capacity.

Marks and Iroline Co.(120) use the same process as Snelling, reference being directed to his patent.

Bacon, Brooks and Clarke(121) convert petroleum oils boiling above 250° C. into products boiling below 200° C., by submitting them to a combined distilling and cracking operation, in a vertical tubular retort at a temperature of 350 to 500° C. and pressure of 60 to 300 lbs. per sq. in. The particles of tar and coke produced sink to the bottom of the retort and are removed.

Dubbs(122) mixes petroleum with water under pressure and then vaporizes the mixture under pressure. The pressure is then relieved, and the vaporized mixture discharged into a heated chamber in the form of fine spray. The resulting vapors are subsequently condensed.

Washburn and New Process Oil Co.(124) transform petroleum products of specific gravity 0.794 to 0.901 into products of specific gravity not exceeding 0.777, by heating with water in a retort at 340 to 510° C., and condensing the vapors under a pressure of 3 to 5 atmospheres, which is maintained both within the retort and condenser. In this case also it is difficult to understand how a patent has been obtained in face of the prior patents of Young(3), Redwood and Dewar(20) and the numerous patents of the Standard Oil Co.

Hall(125, 126) obtains lower boiling distillates from heavy oils, oil residues and bitumens by distillation at 475 to 490° C. in vertical retorts, mixed with equal or larger quantities of coke.

Palmer(130) increases the yield of volatile hydrocarbons from petroleum residues, by digesting them under pressure of the evolved vapor (60 to 400 lbs. per sq. in.) at a temperature above 200° C., but below that at which substantial carbonization takes place, and without the addition of steam, the heating being continued until the greater portion of the residue is converted into more volatile compounds, which are separated when the pressure is relieved.

Wells(131) decomposes heavy oil vapors by conducting them into a bath of molten lead, which is heated to about 480 to 540° C., and is violently agitated by mechanical means.

The Rittman process for the manufacture of gasoline and benzene-toluene from petroleum and other hydrocarbons, which has been so largely boomed in America, has been recently granted

letters patent in England (133). The investigations which led to this discovery, and its large-scale development were under the direct auspices of the U. S. Bureau of Mines, which tends to show how much importance is attached to this subject in that country. It was no doubt also influenced by the abnormal price which had to be paid for toluene about 12 months ago. As finally adapted for commercial purposes, the benzene-toluene plant consists of six furnaces, each heated by 22 gas burners and containing 2 rows of 5 vertical cracking tubes (11½ ft. long and 8 in. in diameter). To each tube is fitted a separate condenser and the oil supply for each tube is separate. Carbon deposited on the walls of the converter tubes is removed by wiping-chains attached spirally to a rotating rod passing up the center of the tube, and is collected in special carbon pots by means of scrapers at the bottom. The cleaning device requires to be removed and cleaned every few days.

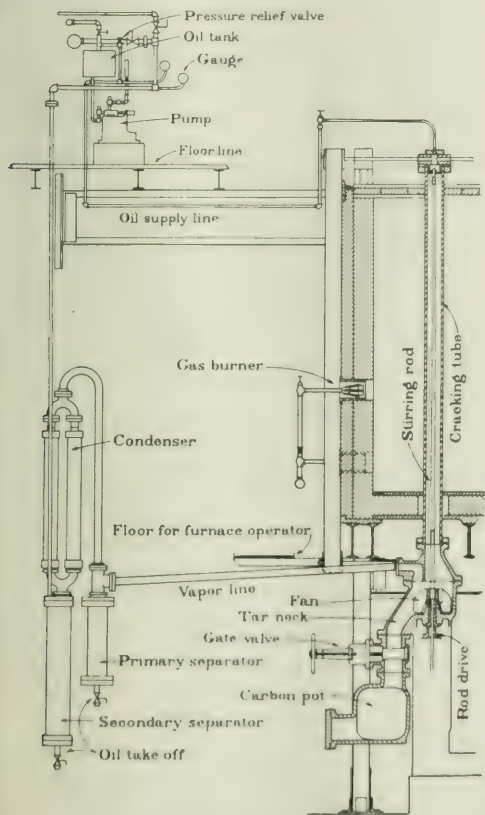


FIG. 5.—RITTMAN CRACKING PROCESS.

For the preparation of benzene-toluene the rate of feed to each tube is 15 gallons per hour and for gasoline 30 gallons per hour. Temperatures of about 700° C. and pressures of about 150 lbs. per sq. in. are employed. The reactions are found to be practically independent of the kind of oil used, although solvent naphthenes and light oil distillates from coal tar and water-gas tars give greater yields of benzene-toluene than is obtained from petroleum products, and are easier to handle.

A large amount of gas of high calorific value (1000 to 1200 B. t. u. per cu. ft.) is obtained, more than sufficient as fuel when the plant is run for benzene-toluene, but not sufficient for this purpose when running for gasoline.

The following yields from petroleum are claimed in the benzene-toluene process: 6 to 8% benzene, 6 to 8% toluene, 4 to 6% xylene, 6 to 15% gasoline, 25 to 30% creosote oil and pitch (including higher aromatic hydrocarbons and lubricating oil), 4 to 5% carbon and 15 to 60% gas of the original oil and when working for gasoline 25 to 30% gasoline with 20 to 75% residuum above 150° C. which is available for re-running.

The cost of installation based on a unit of 4 tubes is £1,146 per tube, which includes building and equipment, but not the cost of storage-tanks or apparatus for treatment of products.

It has long been known that aromatic hydrocarbons can be produced from certain types of petroleum, a process having been patented as early as 1860 for their recovery from oil-gas made from petroleum, but Rittman claims that it has never before been demonstrated that they can be produced in considerable quantities from any type of oil. In the early part of 1915, however, they were being produced in this country by the Hall process, which, if not prior to the Rittman process (which is very probable), was at least abreast with it, for it was not until much later that in this country at least we began to hear so much of the "new" discovery emanating from America. Studying the plant itself from the published photographs and sketches, it appears to be rather a cumbersome affair, several of the details striking one as not being quite sound. The tubes used in the process are most unwieldy, and it is difficult to understand how the vapors passing through can be at all evenly heated, in spite of the central cleaning rod which gives the retort an annular form. Oil-vapors are bad conductors of heat, and tubes of an inch diameter are more correct theoretically from this standpoint at least.

It is claimed that absolute command over the operating conditions is possible by causing the reactions to take place in the gaseous or vapor-phase. This term gaseous or vapor-phase has been used as a hook upon which to hang a whole series of claims, whereas numerous prior inventors have worked on, and specifically mentioned that condition. One fails to see how "absolute command over the operating conditions" can be claimed, when such crude methods of temperature-measurements as the naked eye, supplemented by periodic checks by pyrometers, are employed. It is well known that temperature-variations of an amount impossible to recognize by the naked eye, cause enormous differences in the character of the products evolved at these high temperatures, and these variations cannot be averaged up as to their effects. No cracking process can be completely successful, unless equable temperature conditions are maintained. The design of the furnace containing the retorts can hardly be conceived to aid in this matter, since wide differences must necessarily exist in different parts of it. The operation of changing the cleaning rods must take some time, as this portion of the apparatus cannot be easily handled while hot, and thus the operations cannot be nearly continuous. Intermittent cooling and heating of the brickwork and tubes must also be detrimental to them. It might be mentioned here that in the New Oil Refining Process particular attention was paid to the question of cleaning the tubes, which were arranged in such a way that a whole battery of 9 tubes could be cleaned while hot, the entire operation from shutting off of oil and water to starting again taking about 20 minutes. Another point which strikes one is: how is the stuffing-box of the stirrer rod kept tight at 700° C. and 150 lbs. pressure?

The cost of the installation appears almost prohibitive. Taking a unit plant consisting of 60 tubes, the cost would be £68,760 and this on the benzene-toluene process would handle about 18,000 American gallons of oil per day. With the Hall process a plant capable of handling 10,000 American gallons of oil per day would cost about £12,000.

The analysis of the spirits produced in the Rittman process as to aromatic hydrocarbon content is carried out in a most empirical manner, and depends on the specific gravity of fractions obtained by two fractionations through a 3-in. Hempel column, the second series on which the determination is made being cut at 95, 120 and 180° C. These fractions assumed that other bodies present with the aromatic hydrocarbons possessed an approximative value as below:

Temperature per cent	SPECIFIC GRAVITY AT Aromatic Hydrocarbon	
95° C.	0.87	0.87
120° C.	0.87	0.87
180° C.	0.87	0.87

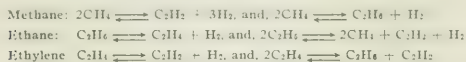
and a calculation from the determined specific gravities taking the above figure as a basis. In the assumption that the separation at varying temperature, if it will be known that the proportions of constituents in the products vary very considerably and if more than two classes of bodies are present, the assumption as to the gravity of the non-aromatics is entirely arbitrary and holds good, being used to validate a system of tests. The benzene-toluene spirit produced in the Rittman process contains considerable quantities of non-aromatic bodies produced by strong sulfates, and, and for the purpose of further refining from the benzene fractions, special methods have to be devised. The spirit produced by the Hall process is not so free from non-aromatics, only minute traces of non-aromatic bodies introduced by strong sulfates used, and the toluene produced is so easily nitrated as to need no treatment.

PART II—GENERAL CONSIDERATIONS

By A. E. DUNSTAN AND F. B. THOLE

Although the origin of the term cracking is due to petroleum practice, yet the investigation of the pyro-analysis and pyro-synthesis of hydrocarbons goes back to the days of the great chemist, John Dalton(1a), who, in 1809, decomposed methane and ethylene by means of electric sparks. It might possibly be urged that this decomposition is scarcely analogous to the cracking of a heavy hydrocarbon, but in point of fact the complexity of this latter process is so great and the multiplicity of its products are so confusing that the study of the subject must necessarily proceed from the starting point of the simplest possible reactions. Only in this way can one throw light on one of the most intricate problems that ever confronted the chemist.

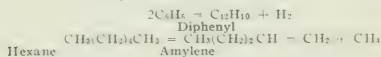
To the mind of Berthelot(13a, 14a, 15a) the pyrogenetic decomposition of hydrocarbons resolved itself into simple polymerization or else condensation with loss of hydrogen. Moreover, he contended that each change was reversible, so that at any particular temperature an equilibrium could be established between a complex series of decomposing, polymerizing or condensing hydrocarbons, together with free hydrogen and carbon. In the case of the four simple hydrocarbons Berthelot considered that the following reactions took place:



It will be seen that Berthelot ascribed to acetylene a most important rôle in the pyrogenetic phenomena as it always appears either as an intermediate or a final product. It is a well-known precursor of the aromatic hydrocarbons, and its chemically reactive nature fits it to be the "générateur fondamental des carbonures pyrogénés." When acetylene was heated to a dull red heat, Berthelot obtained from it benzene, styrolene, naphthalene and retene: $3\text{C}_2\text{H}_2 = \text{C}_6\text{H}_6$ (benzene), $4\text{C}_2\text{H}_2 = \text{C}_8\text{H}_8$ (styrolene), $9\text{C}_2\text{H}_2 = \text{C}_{10}\text{H}_8$ (retene).^{*} At a bright red heat it was decomposed into its elements.

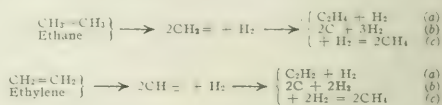
While Berthelot's views must be regarded as crude and insufficiently based on experimental evidence, yet the credit of putting forward for the first time a well-articulated theory of pyrogenesis is undoubtedly his.

Work on the lines laid down by Berthelot was vigorously pursued. The acetylene theory was violently attacked on the ground that it was difficult or impossible to isolate that hydrocarbon in the products of pyrogenesis. Thorpe and Young(21a), Armstrong and Miller(35a), and Haber(53a) considered that the first steps were the elimination of hydrogen and the production of olefines and methane, without any intermediate production of acetylene:

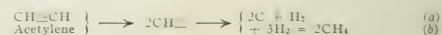


A paper of capital importance was contributed in 1908 by Bone and Coward(78a) on the thermal decomposition of methane,

moderate temperatures. (2) The thermal decomposition of the other three hydrocarbons is not so obviously a surface effect; it originates and is propagated in the body of the gas. (3) Acetylene is produced when ethylene suffers decomposition, but is not formed during the heating of ethane or methane. (4) At comparatively low temperatures acetylene polymerizes quite easily, yielding cyclic hydrocarbons, mainly of the aromatic type; consequently whenever ethylene is a primary product of pyrogenesis, acetylene will appear intermediately, polymerizing at once into benzene and its congeners; the optimum temperature for this polymerization is between 600 and 700°; at 1000° there is little evidence of this phenomenon. (5) Acetylene and ethylene combine with hydrogen at moderate temperatures yielding ethane; this reaction, however, ceases to be effective at 1000°. (6) One of the principal factors in operation at temperatures of 800° and higher is the direct hydrogenation of "nascent radicals" such as $\text{CH}=\cdot$, $\text{CH}_2=\cdot$, $\text{CH}_3=\cdot$, for which molecular fragments must be postulated a free although momentary existence during the dissolution process; this assumption undoubtedly accounts for the presence of the large amounts of methane which are always produced during any cracking operation.^{*} (7) In the cases of ethane and ethylene, it may be supposed that the primary effect of high temperature is to bring about an elimination of hydrogen, with a simultaneous loosening of the linkings between the carbon atoms, giving rise to the residues $\text{CH}_2=\cdot$ and $\text{CH}=\cdot$. These residues can have only a fugitive existence and may (a) unite to form $\text{CH}_2=\text{CH}_2$ or $\text{CH}=\text{CH}$; (b) decompose yielding carbon and hydrogen; or (c) be reduced to methane; thus:



(8) In the case of acetylene, the main primary effect is probably polymerization, but the possibilities of dissolution must also be borne in mind:



(9) Berthelot's theory of the attainment of equilibrium between dissolution and recombination is not borne out by experimental evidence.

THE THERMOCHEMISTRY OF SOME PYROGENIC REACTIONS

It will readily be appreciated that the majority of the reactions which proceed during pyrogenesis are either unknown or else complicated by side and consecutive changes. It is, therefore, very difficult to trace the distribution of energy during cracking. Taking some of the simplest operations described by Bone and Coward, it is possible to discover, by means of well-recognized thermochemical data, the concomitant energy-relationships:

REACTION	INTRINSIC ENERGY	VALUE OF x CALORIES	CONCLUSION AS TO REACTION
$\text{C}_2 + 2\text{H}_2 = \text{CH}_4 + x \text{ cal.}$	$0 - 0 = -21,750 + x \text{ cal.}$	+ 21,750	Exothermic
$3\text{C}_2\text{H}_2 = \text{C}_6\text{H}_6 + x \text{ cal.}$	$3(+47,770) = 12,510 + x \text{ cal.}$	+130,800	Exothermic
$\text{C}_2\text{H}_6 = \text{C}_2\text{H}_4 + \text{H}_2 + x \text{ cal.}$	$(-28,560) = 2710 + 0 + x \text{ cal.}$	- 31,270	Endothermic
$\text{C}_2\text{H}_6 = 2\text{C} + 3\text{H}_2 + x \text{ cal.}$	$(-28,560) = 0 + 0 + x \text{ cal.}$	- 28,560	Endothermic
$\text{C}_2\text{H}_4 + \text{H}_2 = 2\text{CH}_3 + x \text{ cal.}$	$(-28,560) + 0 = 2(-21,750) + x \text{ cal.}$	+ 14,940	Exothermic
$\text{C}_2\text{H}_4 = \text{C}_2\text{H}_2 + \text{CH}_4 + x \text{ cal.}$	$(-35,110) = 2710 + (-21,750) + x \text{ cal.}$	- 16,070	Endothermic
Propane			
$\text{C}_3\text{H}_8 + 3\text{H}_2 = 2\text{CH}_4 + x \text{ cal.}$	$47,770 + 0 = 2(-21,750) + x \text{ cal.}$	+ 91,270	Exothermic
$\text{C}_3\text{H}_8 = \text{C}_3\text{H}_4 + \text{H}_2 + x \text{ cal.}$	$2,710 = 47,770 + 0 + x \text{ cal.}$	- 45,860	Endothermic
$\text{C}_3\text{H}_8 + 2\text{H}_2 = 2\text{C}_2\text{H}_4 + x \text{ cal.}$	$2,710 + 0 = 2(-21,750) + x \text{ cal.}$	+ 46,210	Exothermic
$\text{C}_3\text{H}_8 = 2\text{C} + 2\text{H}_2 + x \text{ cal.}$	$2,710 = 0 + 0 + x \text{ cal.}$	+ 2,710	Exothermic
$\text{C}_3\text{H}_8 = \text{C}_3\text{H}_6 + \text{CH}_4 + x \text{ cal.}$	$(-57,600) = (-12,500) + (-18,900) + x \text{ cal.}$	- 27,200*	Endothermic
Hexane Amylene			
$\text{C}_6\text{H}_{14} = \text{C}_6\text{H}_8 + \text{H}_2 + x \text{ cal.}$	$2(11,300) = 33,500 + 0 + x \text{ cal.}$	- 10,900	Endothermic
Diphenyl			
$\text{C}_{10}\text{H}_8 = \text{C}_{10}\text{H}_6 + 3\text{H}_2 + x \text{ cal.}$	$(-46,600) = 4,100 + 0 + x \text{ cal.}$	- 50,700	Endothermic

* A typical "cracking" reaction.

ethane, ethylene and acetylene. Their main conclusions may be briefly summarized as follows: (1) Methane is exceedingly stable; it decomposes almost exclusively into its elements, and this decomposition is in all probability reversible at all temperatures; the dissociation is in the main a surface phenomenon at

* It requires a profound application of scientific imagination to visualize this non-molecular reaction.

It will be noticed that those reactions which proceed by absorption of hydrogen are in the main exothermic, i. e., the products formed have a less content of intrinsic energy than their generators; in other words, they are relatively more stable.

* Bone's theory is of interest in considering the possibilities of hydrogenation during cracking. Apparently much of the hydrogen would be utilized in the generation of methane.

A genuine cracking process such as is exemplified in the equation



is endothermic, seeing that, in part, relatively unstable molecules (the olefines) are being formed. It must be borne in mind also that these unsaturated products have a proportionally greater heat of combustion, *e. g.*,

Ethane, C_2H_6 , possesses heat of combustion = 370,440 cal.
 Ethene, C_2H_4 , possesses heat of combustion = 68,357 cal.

Ethylene C_2H_4 possesses heat of combustion = 302,183 cal.
 = 383,350 cal.

i. e., Excess over $(C_2H_6 - H_2)$ = 31,167 cal.

From the Nerst quotation $Q = RT \frac{d}{dt} \log K$, where Q is the heat of reaction, R the gas constant, T the absolute temperature and K the equilibrium constant, it is possible to calculate the temperature-coefficient ($\frac{d}{dt} \log K$) of the velocity of reaction.

In general the temperature-coefficient is surprisingly constant, for it has been found that for most chemical reactions the velocity is very approximately doubled for a rise of $10^\circ C$. To quote a few examples:

REACTION	VELOCITY CONSTANTS	Coefficient for 10°
$As_2H_3 = As + 3H$	$K_{250} = 0.00035; K_{307} = 0.0034$	1.23
$H_2O = H_2 + O$	$K_0 = 0.0120; K_{10} = 0.0180$	1.5
$2NO = N_2 + O_2$	$K_{250} = 19.6; K_{307} = 191800$	1.7
Inversion of Cane Sugar	$K_{25} = 0.765; K_{35} = 35.5$	3.6

There are certain consequences of changes of temperature and pressure on equilibrium which must be borne in mind.

Le Chatelier has enunciated a general law which may be stated as follows: When one or more of the factors determining an equilibrium is altered, the equilibrium becomes displaced in such a way as to neutralize, as far as may be, the effect of the change.

Thus, consider the change $C + 2H_2 = CH_4 + 21,750$ cal. Heat is set free during the synthesis of methane, consequently if heat is admitted to the system, the equilibrium is displaced in such a direction that heat is absorbed, *i. e.*, the dissociation of methane sets in. Similar considerations from the point of view of pressure change will be discussed later.

THE INFLUENCE OF TEMPERATURE ON CRACKING

It is evident from the work of Bone and Coward in particular, and of all previous workers in general, that at the highest possible temperatures there is complete dissolution of a hydrocarbon into its elements. In other words, chemical affinity ceases to act when the atomic vibrations reach a certain limiting value. This phenomenon holds good in some cases at quite low temperatures, as witness the dissociation of arsenic hydride and hydroiodic acid.

The temperature at which cracking begins depends mainly on the molecular weight and the constitution of the oil; speaking broadly, the more complicated the molecule, the more readily it undergoes dissolution, and further, the more unsaturated and labile the compound, the more easily it disintegrates. It has been shown above that the velocities of chemical changes are profoundly affected by changes in temperature. It is, therefore, easily credible that the most extraordinary differences in the nature of the products may be observed if the working temperature is even slightly altered, for one particular reaction may be so damped or accelerated as to mask entirely the progress of other parallel or simultaneous changes.

The theorem of Berthelot and Thomson that a chemical reaction tends to proceed, giving rise to products that occasion the greatest development of heat, must always be borne in mind. This theorem means that reactions are propagated of themselves if more stable bodies are formed under the conditions of temperature and pressure which obtain during the experiment. But it should be remembered that the changes which go on during cracking are not necessarily those which would spontaneously go forward to completion. Many exothermic reactions doubtless do go on to the end, but the endothermic processes, such as the pyroanalysis of ethane $C_2H_6 = CH_4 + H_2$ (31,200 calories), can be maintained only by the absorption of a large supply of energy.

Not only does alteration in temperature affect the speed of the various reactions, but also most profoundly does it alter the nature of the products. In the majority of commercial cracking systems it has been found that whereas at moderate temperatures (400-500°) the tendency is for the formation of a mixture of paraffins and olefins, at higher temperatures (over 700°) the effect is the generation of aromatic compounds.

From the large number of experiments recorded in the tabular matter on pp. 886 to 892, inclusive, it will be of interest to study a few examples.

The effect of temperature changes on the velocity of the decomposition of ethane may be briefly summarized thus: Up to 675° decomposition is slow, 6 hours being needed to eliminate 98% of the hydrocarbon. At 800° the reaction was so rapid

that 5 minutes sufficed to transform the same percentage. At 1000° still less time was required, while at 1140 to 1145° the gas barely survived a single passage through the tube.

Vignon (148a) distilled coal at various temperatures and analyzed the gases produced: at 400 to 600° there were formed acetylene and ethylene; at 600 to 800°, methane and other paraffins; at 800 to 1000°, much hydrogen.

Staudinger (99a) and his co-workers heated isoprene to a variety of temperatures: at 400°, the products were amylene, terpenes and unattacked isoprene; at 600 to 700°, the products were unsaturated hydrocarbons; at 700 to 750°, aromatic hydrocarbons appeared; at 750°, the tar contained benzene, toluene, naphthalene, methyl naphthalene, anthracene and chrysene, while hydrogen, butadiene, methane and carbon were also produced; at 800°, the products were entirely aromatic. Staudinger considers that the isoprene condenses to form hydroaromatic compounds, which ultimately at high temperature lose hydrogen, generating benzenoid hydrocarbons.

Zanetti (135a) cracked a mixture of 97% propane and 3% butane, derived from natural gas: at 750°, there were formed in the main ethylene, butylene and hydrogen: $C_3H_8 = C_2H_4 + [CH_3]$; $CH_4 = C_2H_2$; $C_3H_8 = C_2H_4 + H_2$. Above 750°, benzene, toluene, and other aromatic bodies were found to be present. The higher the temperature, the greater was the proportion of free hydrogen. It is noteworthy that as Zanetti's material was low in molecular weight and high in stability a greater degree of temperature was needed for this cracking.

Rittman (121a, 132a, 136a, 137a, 139a, 140a, 141a, 143a, 148a), to whose credit much interesting work must be put, considers that "gasoline" formation begins at about 400°, and approaches a maximum at 500 to 550°. The greatest content of aromatic hydrocarbons occurs between 650 and 700°. These optimum temperatures are naturally functions of the nature of the oil, the pressure, the size and shape of the reactive space and the rate of feed.

Rittman uses the Nerst formula to calculate the reaction velocities of a large number of possible and impossible changes at various temperatures. For example:

	K_{500}	K_{700}	K_{1000}
$C + 2H_2 = CH_4$	0.007	0.012	0.003
$C + H_2 = C_2H_2 + H_2$	0.027	0.094	1.28

Against this result must be urged the objection that Bone and Coward found that ethylene is produced to a less and less extent as the temperature rises, the percentage of this gas after one minute being at 675° 24, at 810° 11, at 1000° 7, and at 1140° nil.

Such reactions as $7C_6H_{14} = 10C_2H_6 + 9H_2$, $6C_7H_8 = 3C_8H_{10} + 3H_2$, and $7C_8H_{10} = 8C_7H_8 + 3H_2$, which are quoted by Rittman, are frankly impossible from molecular kinetic considerations, for the last case presupposes that collision between seven similar molecules are occurring simultaneously. It is possible that Rittman is writing this equation as the sum total of a number of consecutive reactions, in which case the velocity constants calculated by him represent only the slowest in a series of several superimposed rates.

Ipatiev (88a, 89a) finds that cyclo-hexane is much more resistant to heat than the open-chain hexane. The increased stability of ring systems is, of course, well known, and in this connection it is interesting to note that the cracking process which is worked at the highest temperature, *vis.*, cracking coal into coal gas, produces a tar which is prolific in compounds which contain complicated condensed rings. At 600 to 700°, Ipatiev found that both hexane and its cyclic analogs yield olefinic, but no aromatic compounds. In the presence of alumina and under high pressures, cyclo-hexane at 400° gives rise to olefins, polymethylenes, benzene and saturated polymethylenes and naphthalenes. Some methyl cyclo-pentane is also formed—an interesting example of the great stability of the five-membered ring. The same author found that ethylene and acetylene were capable of polymerizing at quite low temperatures (100 to 200°) when at 70 atmospheres pressure produced polymers of high molecular weight, together with high-boiling products of an unsaturated nature.

R. Meyer (92a, 111a) repeated some of Berthelot's work, and in particular showed that a mixture of gas obtained with hydrogen, gave a tar rich in high-boiling compounds of moderate weight, one abundant in hydrocarbons of very high molecular weight. The obtained product was soluble in benzene, toluene and chrysene.

The cracking of petroleum with the object of producing aromatic hydrocarbons has been generally the least successful, and in particular in those countries where petroleum and coal are both available relatively easily. In some cases, as in the case of coal tar, rather easily obtainable aromatic compounds are obtained, but the fact is that in practice it is very difficult to secure the necessary possible source of energy for the maintenance of such expensive plants by cracking.

CHRONOLOGICAL RESUME OF LITERATURE OF PYROGENESIS

OBSERVER	MATERIAL	TEMPERATURE	PRESSURE	CATALYST	PRODUCTS	REMARKS
Dumas	ethylene	v. high	not stated	..	$C + CH_4$	
Marchand	..	bright red heat	$C + CH_4$	
Buff and Hotmann	..	dull red	$C + CH_4$	
Magnus	..	not stated	liquid products	
De Wildt	..	electric spark	$C_2H_2 + H_2$	questionable.
Berthelot	acetylene	dull red	C_2H_2, C_2H_4, C_2H_6	
..	free hydrogen almost entirely	at higher temp. CH_4 would be formed
..	acetylene + hydrogen and other diluents	none	H_2, C_2H_2 , and tar	slower decomposition
..	acetylene + hydrogen	ethylene	
..	styrolene	C_2H_2, C_2H_4 , and tar with naphthalene	
..	ethylene	not stated	C_2H_2, C_2H_4 and tar	exceeds capacity
..	ethane	C_2H_2	equilibrium set up.
..	ethylene + hydrogen	dull red	C_2H_2 (divinyl)	60% yield
..	acetylene + ethylene	H_2, C_2H_2, C_2H_4 and naphthalene	
..	acetylene + benzene	H_2, C_2H_2, C_2H_4 and naphthalene	only 2% of original gas remained
..	acetylene + naphthalene	diphenyl + H_2 , chrysene and osin, no naphthalene or anthracene	
..	benzene	bright red	C_2H_2, C_2H_4 , naphthalene and possibly chrysene	
..	toluene	styrolene, anthracene and naphthalene	
..	benzene + ethylene	bright red	not stated	none	$C_2H_2 + C_2H_4$	
..	styrolene	$C_2H_2 + C_2H_4$	
..	styrolene + hydrogen	$C_2H_2 + C_2H_4$	
..	styrolene + ethylene	$C_2H_2 +$ naphthalene	
..	styrolene + benzene	anthracene, naphthalene and diphenyl	
..	benzene + naphthalene	anthracene + hydrogen	
..	anthracene	benzene and chrysene	
..	toluene	benzene, toluene (80%), naphthalene, diphenyl, anthracene and chrysene	1 gram per minute through 35 cm. porcelain tube.
..	xylene	chiefly toluene, benzene, xylene, naphthalene and anthracene	
..	cumene	benzene (small amount), toluene, xylene, cumene, naphthalene, anthracene and chrysene	
Faraday	liquid from compressed oil gas	chiefly benzene	
Armstrong and Miller	divinyl, olefines, acetylenes, benzene, "hexylene" (hexine C_6H_{10}), no paraffins	
..	tar and liquid due to compression of gas from above experiment	bright red	not stated	none	polymerizable hydrocarbons, benzenes, toluene, xylene, mesitylene, pseudo-cumene and naphthalene, crotonylene, olefines up to n-heptylene. Traces of paraffins and naphthalene	
Thorp and Young	repeated distillation of paraffin wax (45 M.P.)	B.P. of the wax	15-30 lb.	..	olefines and small amount of paraffins, in fractions up to 100°, no benzene	Simplest cases of cracking. No carbon or hydrogen set free.
Prunier	paraffin oils	"strong heat"	not stated	..	100°-200° fraction gave olefines and paraffins to nonene and nonylene	
Prunier	paraffin oils	$C_2H_2, C_2H_4, C_2H_6, C_2H_8$ and C_2H_{10} , styrolene, naphthalene	decent saturation of products varies with temperature, pressure and time
Grover-Williams	heavy petroleum	bright red	aromatic hydrocarbons	products in oil from compressed Paraffin gas.
Pilling and Hutton	carbon and hydrogen	1850°	CH_4 and C_2H_2	acetylene ionized by Bone.

CHRONOLOGICAL RESUME OF LITERATURE OF PYROGENESIS (Continued)

OBSERVER	MATERIAL	TEMPERATURE	PRESSURE	CATALYST	PRODUCTS	REMARKS
Tring	"	1100° 1550°	"	"	Proportion of methane rises. Acetylene decomposes to ethylene and methane	—
Torcher	paraffin oils	500°-600°	"	"	C ₂ H ₄ , CH ₄ , H ₂ and olefines	—
	turpentine	800	"	"	aromatic hydrocarbons and tar	—
Lewis	ethylene	800°-900°	not stated	none	CH ₄ and C ₂ H ₂ which polymerized to C ₂ H ₄	See Bone and Coward
"	"	1000°	"	"	naphthalene	"
"	"	1100	"	"	C ₂ H ₄ and C and H ₂ by decomposition of naphthalene	"
"	"	900°	"	"	H + C ₂ H ₄	See Bone and Coward.
"	Russian oil	oil gas making	"	"	aromatic hydrocarbons in the tar and possibly hexane and heptane, heptane and heptylene and naphthalene	—
Noyes, Blinks & Mory	oil gas	750-1,000°	"	"	C ₂ H ₄ , C ₂ H ₂ and propylene in gas products (chiefly naphthalene, also anthracene and ethylene in tar	"
Ipatiev	ethylene	400-450	"	iron and copper	polymers	"
"	"	high temperature	—	"	C ₂ H ₄ , CH ₄ , H ₂ and polymers	—
"	C ₂ H ₄ + H ₂ (excess)	"	—	"	CH ₄ and polymers	—
"	C ₂ H ₄ + H ₂ (excess)	"	—	nickel powder	CH ₄ , C ₂ H ₄	—
"	C ₂ H ₄ + H	400-450	220 atmosph	iron, copper or aluminum	product contains no cyclohexane	—
"	"	"	"	nickel	cyclohexane (quantitative yield)	—
"	cyclohexane	"	150 atmosph.	none	C ₂ H ₄ , H ₂ , paraffin and olefines	reversibility.
Engler and Lehmann	fish oil	distilled under pressure	150 atmos ph.	none	solid paraffin, M.P. 30-51, olefines, benzene and its homologues, monaphthalene, pyrene	"
Engler	animal fat	"	"	"	C ₂ H ₄ hydrocarbon produced into benzene and olefines	"
"	residue from petroleum B.P. + 200	"	with or without pressure	"	olefines, naphthenes and aromatic hydrocarbons. To oxidize the residue becomes poorer in hydrogen	"
Engler and Goring	petroleum	cracked for burning oils	"	"	olefines and paraffin from C ₂ to C ₁₀ , benzene and its homologues	"
Engler and Schneider	"	distilled	6 atmosph.	"	similar results to above	"
Ipatiev	ethylene	380-400	70 atmosph	"	Below 250° C. rapid polymerization to paraffins, olefines and evaporates above 500° C. then a formed a large quantity of paraffin in by design Ipatiev obtained paraffin from pentane to naphthalene, amylene and hexylene, cycloparaffin from C ₂ to C ₁₀	"
"	acetylene	"	"	"	aromatic hydrocarbons	"
"	ethylene	"	"	Al ₂ O ₃	better yield of aromatic hydrocarbons	"
"	"	600	atmosph	none	does not polymerize	"
Ostrom Lenck	dipentene	400-450°	atmospheric	none	complex hydrocarbons (benzene)	"
"	acetylene (solid)	"	"	"	acetylene (solid) 41.3% (solid)	"
"	benzene and naphthalene	500-700	"	nickel	oils and gas products (acetylene)	"
"	naphthalene	"	"	"	C ₂ H ₄ and paraffins (by benzene)	"
Meyer and Fink	acetylene	acetylene	"	"	—	"

CHRONOLOGICAL RESUME OF LITERATURE OF PYROGENESIS (Continued)

OBSERVER	MATERIAL	TEMPERATURE	PRESSURE	CATALYST	PRODUCTS	REMARKS
Whitaker and Alexander	kerosene (150°-290 B.P.)	1,600°	"	"	gas contained 96% H ₂ at feed of 30 cc. per minute. Carbon and H ₂ only at feed of 10 cc. per minute.	—
"	"	800°	"	"	gas contained 52% illuminants	—
Brooks	Texas solar oil (sp. gr. .8462)	100°-600°	"	various contact substances	8 to 20% yield of highly unsaturated acroleins, absorbed by sulphuric acid	—
"	Oklahoma reduced oil (sp. gr. .875)	not stated	450 lbs.	none	yield of gasoline increased with pressure up to 250 lbs. and then decreased. Unsaturation decreased as pressure increased up to 250 lbs.	production of aromatic hydrocarbons is ascribed to the fission of high-boiling phenylated compounds and not to polymerization of acetylene.
Rittman and Egloff	middle tar oils	not stated	not stated	none	yield of benzene and toluene depends on the proportion of the oil cooling below 200°. The heavier oils are unsuitable for cracking	—
Brooks and Humphrey	Jennings and Oklahoma oil B.P. above 275°	420°	100 lbs.	"	small amounts of benzene and toluene and <i>n</i> -xylene	—
"	"	not stated	not stated	aluminium chloride	"	heavy petroleum contains phenylated compounds causing e.g. fluorescence.
"	paraffin wax	"	"	none	no aromatic hydrocarbons	—
"	synthetic "phenyl paraffin"	"	"	aluminium chloride	benzene and toluene	—
Davies	high boiling petroleum mixed with superheated steam	650°-675°	100 lbs.	iron shavings	gasoline almost free from unsaturated compounds	—
Egloff & Twomey	paraffin wax, M.P. 47°	500°	atmospheric	not stated	no aromatic hydrocarbons	Rittman plant.
"	"	600°	"	"	aromatic hydrocarbons	—
"	"	500°-600°	150 lbs.	"	"	causes for benzene and toluene formation:
Egloff	neutral tar oil, 150°-325°	650°	14 atmosp.	"	4.2% benzene	(1) direct decomposition of methyl naphthalene.
"	"	600°	14 "	"	2% toluene	(2) formation and decomposition of xylene.
"	petroleum	650°	11 "	"	degree of unsaturation increased to 700 and then declined	(3) polymerization of acetylene and methylacetylene.
"	"	600°-700°	atmospheric	"	"	—
Egloff & Twomey	gas oil	450°-600°	"	"	benzene, toluene and xylene	—
"	gas oil	750°	atmospheric	not stated	naphthalene	—
"	"	800°	"	"	anthracene	—
Whitaker and Leslie	kerosene mixed with hydrogen	621°	"	"	absorption of H ₂ is greater as the temperature and concentration increases; methane is formed more readily at higher temperatures	—
"	"	723°	"	"	"	—
"	"	825°	"	"	"	—
Anschütz	—	—	—	—	—	formation of complex hydrocarbons is due to condensation and elimination of H ₂
Ipatiev and Dowgelevitch	hexane	650°-700°	atmospheric	aluminum	paraffins, olefines and hydrogen, no aromatics	—
"	"	"	high pressure	"	explosion occurs	—
"	cyclo-hexane	500°	"	"	olefines, cyclo-paraffins and benzene	—
Norton and Andrews	n-hexane	bright red	not stated	not stated	olefine to hexylene, benzene and butin; small amount of paraffins	—
"	"	550°	"	"	no action	—
"	"	600°	"	"	no gas; traces of unsaturated bodies	—
"	"	700°	"	"	olefine to hexylene, butin small; no benzene	—
"	n-hexane	bright red	"	"	olefine to hexylene and butin	—
"	n-pentane	bright red	not stated	not stated	ethylene, propylene and erythrene	—
Day	ethylene	350°	"	"	trace of decomposition	—
"	"	400°	"	"	methane, ethane and liquid products	—

CHRONOLOGICAL RESUME OF LITERATURE OF PYROGENESIS (Continued)

OBSERVER	MATERIAL	TEMPERATURE	PRESSURE	CATALYST	PRODUCTS	REMARKS
Letny	residues from Baku petroleum	red heat	..	wood charcoal	benzene and hydrogen, naphthalene, phenanthrene and anthracene	—
Gustavson	American lignin, Caucasian kerosene	1,200°	..	aluminum bromide	methane and impurities	—
Lisenko	residues from petroleum	434°-501°	..	not stated	increased yield of benzene	—
Engler and Rosner	Baku crude oil gas	not stated	mainly olefines, hydrogen, methane and ethane	—
Nikiforoff	double cracking of heavy oil (Baku)	325-350 700°-1,200°	atmospheric 2 atmospheres	..	12% yield of benzol	Ogloblin by same methods obtained 3% benzene, 1% toluene, 2% xylene
Zelinski	cyclo-hexane	170	not stated	palladium	begins to decompose	active,
"	"	200°-300°	benzene and hydrogen	reversible at 100-110°.
"	methyl cyclo-hexane	toluene and hydrogen, in place of di- or tetrahydro-derivatives of cyclo-hexane	no reaction with the cyclo-pentane derivatives below 300°.
"	cyclo-hexene (ex cyclo-hexanol)	benzene and hydrogen	—
"	cyclo-hexene (ex cyclo-cyclo-hexane)	benzene and a new cyclo-hexene	—
Zelinski and Herzenstein	cyclo-hexane and methyl cyclo-pentane	300	not stated	palladium	H ₂ , benzene and unchanged methyl-cyclopentane	Illustration of the stability of the cyclopentane ring.
"	Baku naphtha (102°-104°)	toluene and methyl cyclo-hexane, probably cyclo-pentane derivative	—
Dobrochotov	Baku naphtha (103-105°)	toluene and product similar to standard material of previous experiment (Baku naphtha)	—
Jones	cyclo-hexane	495°-500°	atmospheric	porous porcelain	hydrogen, methane, ethane, acetylene, benzene	—
"	methyl cyclo-hexane	500°-510 530	benzene, toluene, and similar products to that from cyclo-hexane	—
"	1-4 di-hydro-naphthalene	420	hydrogen, methane, naphthalene, anthracene, olefines	—
"	1, 2, 3, 4, tetrahydro-naphthalene	530	hydrogen, methane, ethane, acetylene, benzene and naphthalene	—
Bossieu	mazout	dry distillation	not stated	—	10-12% aromatic hydrocarbons	—
Drunkovitz	oil vapour from heavy oil	704-871	..	hot iron plates	aromatic hydrocarbons	—
Edeleanu	superheated petroleum	not stated	..	not stated	aromatic hydrocarbons	—
Pamphilov Redwood	petroleum vapour (osutki)	dull red Nobel's regenerative furnace	..	not stated	15% benzene in the benzene, anthracene and naphthalene	—
Vaith	residues	700-800	..	—	concrete hydrocarbons	could depend on temperature and rate of feed.
Hone & Coward	methane	1000	atmospheric	not stated	carbon, hydrogen and methane, change of activity at 1000°	—
"	"	700°	no detectable products	entirely inactive at 700°
"	"	785	hydrogen, methane and acetylene	—
"	"	1150	hydrogen, methane and acetylene	—
"	ethane	675	hydrogen, methane and ethane, in place of benzene, toluene, and trace of naphthalene	—
"	"	800	C ₂ H ₄ , C ₂ H ₆ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , and C ₂ H ₂	—
"	"	1000	C ₂ H ₄ , C ₂ H ₆ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , and C ₂ H ₂	—
"	"	1140°-1185	C ₂ H ₄ , C ₂ H ₆ , C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , and C ₂ H ₂	—
"	ethylene	570-600	C ₂ H ₄ , C ₂ H ₆ , C ₂ H ₂ , and C ₂ H ₄	—

CHRONOLOGICAL RESUME OF LITERATURE OF PYROGENESIS (Continued)

OBSERVER	MATERIAL	TEMPERATURE	PRESSURE	CATALYST	PRODUCTS	REMARKS
Jones & Conrad	—	700-750	..	—	less C, H ₂ main products are C ₂ H ₄ , CH ₄ , H ₂	—
..	—	800	..	—	main products CH ₄ , C ₂ H ₄ , traces of C ₂ H ₂ (at early stages C ₂ H ₄ and C ₂ H ₂)	—
..	—	950°	..	—	CH ₄ , C and H ₂ (at early stages C ₂ H ₄ and C ₂ H ₂)	—
..	—	1180	atmospheric	—	mainly C and H ₂ and little CH ₄ (at early stages C ₂ H ₄ and C ₂ H ₂)	—
..	acetylene	180°-500	..	potassium persulfate	C ₂ H ₂ , C ₂ H ₄ , C ₂ H ₆ , C & H ₂ , and aromatic hydrocarbons, main products were polymerized	—
..	..	650	50% polymerized, 30% carbon & hydrogen	—
..	..	800	..	not stated	10% C ₂ H ₂ , C ₂ H ₄ , CH ₄ , monosubstituted C ₂ H ₃ and CH ₃ (at early stages C ₂ H ₄ and C ₂ H ₂)	—
..	..	1000	CH ₄ , H ₂ and C (at early stages C ₂ H ₄ and C ₂ H ₂)	—
..	..	1120-1150	C and H ₂ , trace of CH ₄ (at early stages C ₂ H ₄ and C ₂ H ₂)	—
McKee	benzene	700	100% to decompose	—
Meyer and Tausen	acetylene and hydrogen	610-600-800	n-hexylene and aromatic tar obtained, containing phenanthrene, acenaphthenes and styrene	—
Routala	amylene	heat under pressure	..	not stated	naphthenes	—
Aschan	olefine	low temperature	not stated	aluminium chloride	polymerization to cycloparaffins	—
Ipatiev and Routala	C ₂ H ₄	275° C.	70 atmosp.	zinc chloride	polymerization	naphthenes.
..	—	—	—	aluminium chloride	polymerization at lower temperatures	increase with temperature.
Kuznetsov	$\left\{ \begin{array}{l} \text{CH}_4 \\ \text{C}_2\text{H}_2 \\ \text{C}_2\text{H}_4 \\ \text{C}_2\text{H}_6 \end{array} \right\}$	650	..	aluminium	decomposition to elements	same result by Lidov and Kuznetsov, using magnesium.
Smith and Lewcock	benzene	795	atmospheric	carbon deposited acts as catalyst	53% yield of diphenyl; also carbon and hydrogen	condensation with elimination of hydrogen.
Worstell and Barwell	n-heptane n-octane	900 in Pintsch gas-retorts	not stated	not stated	coke, tar (25%), spirit (4.0%) and gas: methane, heptane, octane and ethylene; no acetylene or naphthene, benzene and its homologues; naphthalene, anthracene, phenanthrene and chrysene	these products are precisely similar to those found in coal-gas and coal-tar.
Hider	n-hexane	600-800	acetylene and methane	this type of decomposition appears to be a general reaction in the first stage of pyrogenesis.
..	benzene	not stated	tend to form diphenyl and hydrogen	greater stability of the ring compound.
..	n-hexane	900-1000	coke, tar, hydrogen, methane, ethylene and aromatic hydrocarbons	the formation of benzene from hexane is not direct.
Fischer and	n-octane	750	under pressure	..	slight production of lower-boiling products	the higher the molecular weight of a paraffin, the more easily it decomposes
Zanetti	propane (97%), butane (3%) mixture	750	atmospheric	..	acetylene and hydrogen; no aromatic hydrocarbons; unsaturated hydrocarbons are at a maximum	—
..	propane (97%), butane (3%) mixture	above 750	atmospheric	not stated	benzene and toluene are produced	—
..	nickel and iron	these catalysts inhibit the formation of aromatics and promote decomposition to carbon and hydrogen	—
Zelinski	—	—	—	—	—	aluminum and titanium oxide promote the formation of aromatic hydrocarbons.

CHRONOLOGICAL RESUME OF LITERATURE OF PYROGENESIS (Continued)

OBSERVER	MATERIAL	TEMPERATURE	PRESSURE	CATALYST	PRODUCTS	REMARKS
Tchitchibabin	acetylene	not stated	not stated	various	(a) decomposition into (b) polymerization to benzene (c) condensation to solid hydrocarbon (d) hydrogenation to paraffins, olefines and naphthenes	—
Jackson and Lawrie	—	high frequency discharge	—	not stated	a solid polymer (C ₂ H ₂) _n which on heating pro- duces methane and liquid hydrocarbons	—
Sernagiotto	—	—	—	—	transitory existence of C ₂ H ₂ radical shown by formation of (CH ₂) _n , cyclic and un- saturated hydro- carbons by action of phosphoric oxide on methyl alcohol	—
Standinger	isoprene	400°	not stated	not stated	a little "amylenes" and terpenes	—
"	"	600°-700°	—	—	unsaturated hydrocar- bons	—
"	"	700°-750°	—	—	aromatics in small amount	—
"	"	800°	—	—	aromatics only	—
Engler	amylene	not stated	not stated	not stated	methane and hydrogen	—
"	"	atmospheric	"	aluminum chloride	"lubricating oil"	—
Rittman and Twomey	gas oil	not stated	"	not stated	benzene formation needs rigorous cracking. Tol- uene and xylene both yield benzene. Naph- thalene is formed by the cracking of mono- cyclic aromatic hydro- carbons	—
Slater	methane	"	"	various sur- face agents - lime, charcoal, graphite, iron, car- borundum, etc.	all increase velocity of decomposition	reverse action is found by Ipatiev to be accelerated by presence of metallic oxides.
"	—	—	—	silica	the action is retarded	—
Rottman, Byron and Egloff	—	—	—	—	progress of formation of aromatic hydrocarbons is in this order— cymene → xylene → toluene → benzene → naphthalene → anthracene → carbon and gas	irreversible.
Butcher and Reid	ethylene	180°	atmospheric	nickel on Kieselguhr	ethane	—
Garvitch	amylene	atmospheric	—	nickel on Kieselguhr	mostly isoprene	—
Lassmann	acetylene	about 1000° discharge	—	—	—	—
"	acetylene and carbon monoxide	—	—	—	—	—
Edlett & Moore	acetylene	not stated	—	—	—	—
Montmolieu	acetylene and phos- phoric acid	500°	—	—	—	—
F. Fischer	naphthalene	700°	—	AlCl ₃	—	—
Lackmann & Berg	acetylene and potassium	red heat	—	—	—	—
Matzner & Wichelhaus	hydrocarbons	—	—	—	—	—

The thermal decomposition of petroleum into aromatic compounds occurs at temperatures considerably in excess of those needed for simple cracking, and in consequence much more serious losses occur in the shape of carbon and fixed gases. Paraffin hydrocarbons at these temperatures are almost completely decomposed. The desired products are not the primary results of cracking; they are obtained from them by further decompositions and syntheses. Accompanying them are other characteristic bodies, usually classed under the heading of unsaturated hydrocarbons, but which are far more reactive than the simple olefines. Butadiene is a typical example of the compound, and it was identified by Berthelot, Armstrong and Miller, and Thorpe and Young. The presence of these highly active products renders the working up of the aromatic hydrocarbons a little difficult until experience shows how they may best be eliminated.

Summing up, therefore, the effects of temperature on petroleum distillates of the nature of solar oil it may be said that (1) temperatures up to 500 to 600° yield in the main a mixture of olefines and paraffins; (2) temperatures *circa* 700° yield a mixture of olefines, diolefines and aromatic hydrocarbons, with little paraffins; (3) temperatures *circa* 1000° yield mainly permanent gases (much methane) and a tar similar to coal-tar, in that both contain aromatic hydrocarbons.

THE EFFECT OF PRESSURE ON CRACKING

Considering any reversible reaction, it is found that on increasing the pressure at constant temperature, the equilibrium is displaced in the direction in which the volume diminishes. This is but a special case of Le Chatelier's law, that when one or other of the factors which determine an equilibrium is altered, this equilibrium is displaced in such a way as to neutralize, as far as possible, the effect of the change. This law must be borne in mind whenever any change in temperature or pressure is contemplated.

Again taking as an example the reaction $C + 2H_2 = CH_4 + 18,900$ calories, it is obvious that since this change proceeds from left to right with a diminution of volume, the formation of methane will be accelerated by increase in pressure. Similarly, since this same reaction is exothermic, increase of temperature will retard the formation of methane.

In general terms, it will be seen that increased pressure favors synthesis or combination, while diminished pressure promotes analysis or dissociation. If cracking were merely a gas proposition, one would undoubtedly crack under a lowered pressure, and at high temperature—in other words, adopt gas works practice.

A further point that must be borne in mind depends on the effect of pressure on concentration, for a reaction proceeds with a velocity depending on the concentration of the reacting substances and their products.

Consider the reaction $C_2H_6 = C_2H_4 + H_2$. If the hydrogen is maintained within the sphere of operation, the reaction will attain a position of equilibrium when certain limiting concentrations of the gases are reached; addition of more hydrogen will bring about reduction of the ethylene until the balance is readjusted. Removal of hydrogen will cause the complete dissolution of the ethane.

The two equilibria discussed in this section are interesting in that they show how irreconcilable are the demands made by the chemist who desires to produce the maximum yield of light spirit, and the minimum of carbon, from a given oil. On the one hand, increasing pressure promotes the hydrogenation of carbon and other unsaturated compounds, while on the other hand, the primary dissolution of a paraffin into the lower olefine is inhibited.

On surveying the literature, it is found that the general effect of excessively high pressures is to bring about reactions at low temperatures, which otherwise would require much more drastic heating. These reactions are mainly in the nature of polymerizations, for Ipatiev obtained from ethylene at 400° and 70 atmospheres pressure a very wide range of complex hydrocarbons and Egloff and Twomey^(141a) similarly obtained aromatic compounds from paraffin wax at a lower temperature by employing a higher pressure.

It may, therefore, be concluded that high pressure favors complex-building and reduction. Some technical processes of the two-phase type make use of high pressure to maintain the necessary cracking temperature.

CATALYSIS

Moissan first noticed that when acetylene is brought into contact with a variety of freshly reduced metals, it decomposes with incandescence producing liquid hydrocarbons, among which is benzene. In 1899, Sabatier^(61a) passed a mixture of acetylene and hydrogen over reduced nickel, and obtained a

complete reduction to ethane. This reaction was considered by its eminent discoverer to be explicable on the ground that reduced nickel formed an unstable hydride, and this substance yields atomic or nascent hydrogen to the acetylene. The nickel can be regarded as a catalyst of hydrogenation, but it would be anticipated that this metal should be capable of combining with hydrogen already in a state of combination; in other words it should react as a catalyst of dehydrogenation, and in point of fact it does so. Many examples have already been given which show that at sufficiently high temperatures all hydrocarbons are decomposable into products of lower molecular weight. In the presence of catalysts this change can be accomplished at a lower temperature, and, therefore, with a greater degree of ease and less loss.

When acetylene is passed over reduced nickel at 250° C., carbon, hydrogen and liquid hydrocarbon result. These latter bodies on being hydrogenated over nickel at 200 to 300° yield saturated paraffinoid and cyclo-paraffinoid products. Sabatier actually obtained from acetylene replicas of Pennsylvanian, Baku and Galician petroleum, and somewhat boldly endeavored to explain from his results the occurrence of natural oil on the assumption that beds of reduced metal exist in the terrestrial stratification.

While the hydrogenation of such unsaturated hydrocarbons as are present in cracked oils offers the most attractive prospects, it must be borne in mind that: (1) catalysts are very readily poisoned by traces of sulfur compounds, arsenic and the halogens; (2) excess of free hydrogen must be employed; (3) relatively low temperatures are needed—the activity of the catalysts is greatly reduced or even entirely inhibited at temperatures higher than 400°; (4) the best catalyst is nickel; cobalt and iron are much inferior, while copper begins to be effective at about 400°; and (5) a catalyst accelerates a reversible change in either sense of the reaction.

VARIOUS CATALYSTS—In most cracking processes there will be some deposition of carbon. It is, therefore, of interest to observe any specific instance where carbon has been found beneficial catalytically.

COKE—Bone and Coward point out that sugar charcoal promotes the reaction $C + 2H_2 = CH_4$. Smith and Lewcock^(94a) find that coke accelerates the formation of diphenyl, and Slater similarly agrees that this catalyst is effective in the decomposition of methane.

REDUCED NICKEL—Zanetti finds that this substance at high temperature inhibits the formation of aromatic hydrocarbons, but obviously the specific catalytic action of this element is inoperative, except possibly as a catalyst of dehydrogenation. A similar result was observed by Ostromilenski^(82a). Ipatiev reduced benzene to cyclo-hexane, and showed the reversibility of the reaction. He also reduced ethylene to ethane, while, of course, Sabatier has accomplished a great number of such reactions.

ALUMINA AND FLORIDIN—These compounds have been used by Gurrvitch^(149a), and even at atmospheric temperature and pressure they possess the power of polymerizing amylene into diamylene. Ipatiev has also used alumina in the polymerization of ethylene to aromatic compounds.

ALUMINUM CHLORIDE AND OTHER ANHYDROUS METALLIC HALOIDS—Humphrey^(142a) converted various heavy petroleum residues into aromatic compounds, using aluminum chloride, and McAfee has patented a cracking process which depends on the same catalyst. Aluminum bromide has been used by Gustavson^(31a). Both Aschan^(64a) and Ipatiev^(98a) have polymerized olefines at relatively low temperatures in the same way. It should be borne in mind, however, that the free hydrogen haloids are quite energetic in polymerizing unsaturated hydrocarbons, so that it is not impossible that at least some of the activity of these metallic chlorides is due to hydrolytic formation of hydrogen chloride. This is borne out by the work of Egloff and Moore^(144a). Most chemists appear to regard the reactivity of aluminum chloride as being due to the formation of intermediate additive compounds, followed by their scission and the building up therefrom of new compounds.

OTHER MATERIALS—The iron tubes and retorts in which cracking proceeds, masses of metallic substance, shavings, blocks of metallic oxides, and the like have been used as catalysts. It is a very moot point whether any of these bodies exerts a specific action. In all probability their application depends on this general advantage of surface. Too much importance can hardly be assigned to these quasi-catalytic effects due to surface-action. To quote only a few: there are the Welsbach mantle, the Bone-Coward furnace, the contact process for sulfuric acid, and colloidal palladium hydrosols. Whether the surface

acts purely physically as an adsorptive medium, or whether there are formed loosely-held complexes, is entirely a matter of opinion.

It must always be remembered that a catalyst in a reversible reaction equally catalyzes the reverse change. For example, consider the formation of methane from its elements $C + 2H_2 = CH_4$. Whatever catalyzes the synthesis of methane will also catalyze its analysis. At any given temperature, a condition of equilibrium tends to obtain, and the catalyst simply accelerates the establishment of this condition.

THE MECHANISM OF PYROGENESIS—The opinion that Berthelot so ably sets forth relating to the formation of condensation or polymerization products appears diametrically opposed to any final views of the mechanism of cracking, since simplification and dissolution are the objects of this operation. Yet the opposition is of degree rather than of kind, for Berthelot made use of temperatures and conditions which lead to pyrosynthesis following upon pyroanalysis.

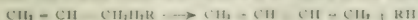
The swing of the pendulum led to the theory of nascent radicles, which was handled so skillfully by Bone and Coward, and which from the point of view of the coal-traffic chemist appears so inevitable. But is it necessary to postulate so profound a dissolution in the customary cracking operation? Without doubt at temperatures approaching 1000° C. such a radical break-up of organic molecules is possible and probable, but are we to contemplate this inter-atomic disruption at temperatures so low as 500°?

The answer to this question is both in the negative and the affirmative. Given a definite hydrocarbon with which to start, and conditions of temperature and pressure not drastic, there is no reason to go further than the views of Thorpe and Young and of Haber, who suggest that a simple scission takes place: $C_6H_{14} = C_3H_8 + CH_4$. This theory is supported by the work of Ipatiev, Norton and Andrews (37a) and Zanetti. It must be recognized, however, that to accomplish this step in a heterogeneous mixture would be impossible, since each compound needs an optimum temperature for this simple cleavage.

Consider the next step, predicating that the chosen paraffin has split into olefine and simple paraffin. The latter will probably not crack further, since its stability is greater than that of its generator. What will be the fate of the olefine? A diligent search among the literature will show that at quite moderate temperatures and in the presence of all sorts of catalysts and quasi-catalysts, olefines are extremely reactive. For example, from isobutylene, Ipatiev obtained paraffins, olefines and cycloparaffins. Aschan found that at low temperature, polymerization to cycloparaffins took place, while Gurrich obtained di-amylenes from the simple olefine. On the other hand, Engler discovered profound decomposition into carbon, hydrogen and methanes. Quite a number of recent patents propose to make isoprene and erythrene by the thermal decomposition of unsaturated hydrocarbons, and here we have yet another possibility of pyrosynthesis. What is the mechanism of this variety of reactions? Engler (85a) considers that the olefines condense with elimination of hydrogen, to form an artificial lubricating oil.

Heating this body, there result paraffins, naphthenes and unsaturated compounds. Further, that olefines yield polyolefines, which are degraded in quite a similar manner by the effect of heat. It is a well-known fact that most simple olefines, even with sulfuric acid treatment, yield the bi-molecular polymer, e. g., amylenes produces di-amylenes.

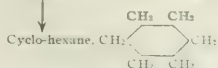
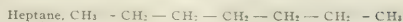
Assume then that the olefines as a preliminary stage polymerize or condense with elimination of hydrogen. The next step in the argument is due to Ostromislenski, who last year showed that dipentene yields isoprene when heated to 400 to 600° ($C_{10}H_{16} = 2C_5H_8$) and dibuxene produces dimethyl erythrene. Further, the higher olefines break down, as shown in the equation:



ERYTHRENE APPEARS TO BE AN ALMOST UNIVERSAL PRODUCT IN THE CRACKING OF PETROLEUM

Erythrene was isolated by Berthelot, Armstrong and Miller, Noyes and Morley (39a), Norton and Andrews, and has been observed by the present authors in an investigation dealing with the compounds present in spirit produced by the Hall process. Curiously enough isoprene itself has never been identified in the products from petroleum. Apparently one must have a complex olefine as a primary product.

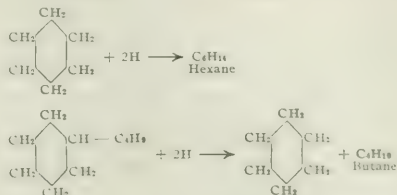
A slight variation from the above theory is due to Ipatiev, who suggests that erythene itself may be a starting point for the formation of higher olefines by a process of polymerization. It is unlikely, however, that this is more than a contributory factor to the main primary reaction at low temperatures. More plausible is the same author's view that polymethylenes are a primary product after the preliminary break up. Thus,



In this case it must be borne in mind that ring formation is unlikely unless five or more carbon atoms are present in the homocatenary hydrocarbon, which is the starting out material.

Ipatiev's view, therefore, is by no means incompatible with the theory outlined above, and it leads to interesting consequences.

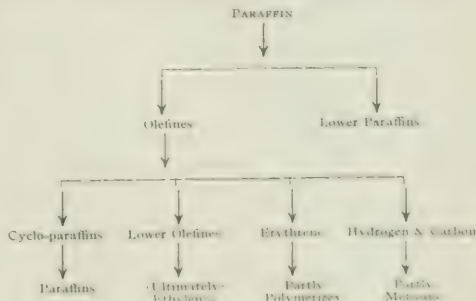
Given the presence of free hydrogen, the scission of this cycloparaffin ring would lead to the production of saturated homocatenary hydrocarbons, and further, the side chains of cycloparaffin might well split off, yielding paraffin:



What a large range of polymerization is possible may be gathered from the summary given by Lebedev (150a). This chemist recognizes five types of product:

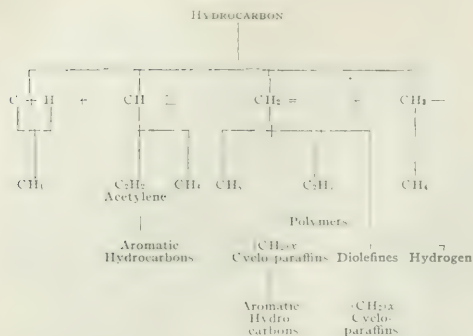
- (1) Via ethylene, to styrolene, $R-CH=CH_2$
- (2) " " " " to stilbene, $R-CH=CH-R$
- (3) Via acetylene to benzene and its homologues
- (4) Via allene to cyclobutene
- (5) Via erythrene to cyclohexane

The following scheme will serve roughly to illustrate the behavior of a paraffin cracked at the lowest possible temperature.



The effects of a rise in temperature on the primary products must now be considerable. The acetylene theory of Berthelot, although it has been widely accepted in the past as the most likely explanation of the formation of aromatic hydrocarbons, appears, in the light of Bone's work, to play only a subsidiary part, as indeed Armstrong and Miller contended in 1886. Assuming that the primary products are paraffin and olefine, it is necessary to trace out the ultimate fate of each. Obviously, given a sufficiently high temperature, both will come into the sphere of reaction. The paraffins will first enter into simpler paraffins and olefins, therefore the behavior of olefins only needs to be considered. At some point or other, cracking will be encountered as the ultimate olefine. Methylenes then may have a transitory existence. Ethylene, given the 10,000° pressure as a main product at temperatures exceeding 1000° (85). At higher temperatures, cracking is progressively more and more noticeable. The acetylene product will not come either from olefins or be reduced by free hydrogen to ethylene and ethane. It thus appears that the role of acetylene is subordinate. (How then is the occurrence of aromatic hydrocarbons to be explained?) In the last place, the theory of the transitory existence of nascent radicals becomes more and more important as the cracking temperature rises.

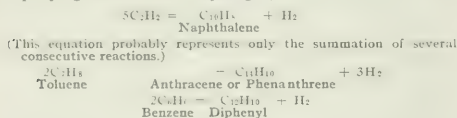
The following scheme (p. 885) shows some of the possibilities.



In the presence of an appropriate catalyst, reduced nickel in particular, Sabatier considers that the molecular scission into nascent radicals goes on at much lower temperatures, such as 350°. If hydrogen be present in excess, then these molecular fragments will tend to be reduced, and consequently paraffin will be produced. On the other hand, at higher temperatures, and in the absence of hydrogen, he finds that carbon and hydrogen are the end-products. Even the more stable cyclic hydrocarbons behave in a similar manner, benzene as an example mainly being degraded to methane.

Now it has been pointed out that the rôle of the catalyst is not to initiate a reaction, but to hasten the final equilibrium, and hence what happens at a low temperature with the aid of reduced nickel may well proceed at higher temperatures in its absence.

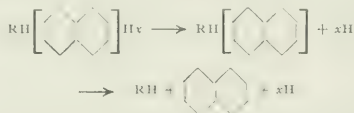
Yet another well-defined reaction undoubtedly comes into play in pyrosynthesis, more particularly at high temperatures, and that is the condensation of two or more molecules, with accompanying elimination of hydrogen, thus:



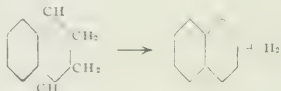
This point is borne out by the experiments of Jones and Wheeler (193a), who assume in coal the existence of hydrogenated aromatic nuclei, such as



This "compound" at temperatures *circa* 400° loses hydrogen:



n point of fact at this temperature dihydronaphthalene does lose hydrogen:



An interesting side issue is that Jones and Wheeler isolated heptacosane, $C_{27}H_{56}$, in coal substance, so that from this standpoint the destructive distillation of coal for coal-gas is a cracking operation.

A final point on the mechanism of cracking may here be emphasized. Starting on the one hand with acetylene at a moderate temperature, and using reduced nickel, Sabatier has synthesized fair imitations of American, Caucasian and Galician oils. On the other hand, by employing higher temperatures, a number of chemists have obtained from the same gas, compounds identical with those occurring in coal tar and of the highest complexity. Does it not appear that the nature of the material

to be cracked has little influence on the final products? Taking a concrete case, naphthalene has been identified from the following sources:

SOURCE	OBSERVER
Acetylene, C_2H_2	Berthelot, Meyer & Fricke, Bone & Coward
Benzene, C_6H_6	Berthelot
Oil-Gas Tar.....	Armstrong & Müller
Cracked Paraffin Oil.....	Prunier
Cracked Turpentine.....	Tocher
Ethylene, C_2H_4	Lewis, Bone & Coward, Norton & Noyes
Oil-Gas Tar.....	Noyes & Mory
Cracked Petroleum Residues.....	Engler
Cracked Petroleum Residues.....	Rittman
Cracked Baku Petroleum.....	Staudinger
Cracked Baku Ostaki.....	Redwood
Ethane, C_2H_6	Bone & Coward
Acetylene, C_2H_2 + Hydrogen.....	Meyer & Tanzen
Isoprene.....	Salzmänn & Wichelhaus
Cracked Lignite Oils.....	Salzmänn & Wichelhaus
Cracked Coal-Tar Oils and Petroleum.....	Liebermann & Burg
Any Paraffin Hydrocarbons.....	Worstell & Burwell

THE CHEMICAL NATURE OF THE PRODUCTS FROM CRACKED OILS

As has been indicated in the preceding pages, cracked oil will contain paraffins, cyclo-paraffins, olefines, diolefines and aromatic hydrocarbons, the relative amounts of these depending on the experimental conditions under which the oil has been cracked. A detailed investigation of the products obtained under varying conditions is in progress by Mr. Lomax and ourselves, but some of the preliminary results obtained may be briefly mentioned.

GASEOUS PRODUCTS—The gas produced by cracking oil contains hydrogen, gaseous paraffins, olefines, and diolefines, together with small amounts of the vapors of volatile liquid products. Mr. Lomax has examined the gas produced by a comparatively low temperature process, cooled by passage through tubes surrounded by ice and salt, then through solar oil cooled by the same means, and finally passed into cooled bromine. The unsaturated components of the gas were absorbed with avidity, and the resulting bromides submitted to fractional distillation in a vacuum. A liquid fraction of comparatively low boiling point was obtained which, on redistillation at ordinary pressure, was found to consist mainly of ethylene dibromide mixed with smaller amounts of propylene and butylene dibromides. A well-defined portion of high boiling point was also obtained, which solidified on cooling, and on recrystallization from alcohol gave white leaflets melting at 114° C., whose analytical figures corresponded with the formula $C_4H_5Br_2$, indicating the presence of erythrene.

LIQUID PRODUCTS—The liquid products obtained by cracking oil are usually produced with one of two objects: either as a source of motor-spirit, or as a source of aromatic hydrocarbons such as benzol and toluol. In the first case the cracked oil is distilled at a suitable temperature, the entire distillate being used as motor-spirit after suitable refining. In the second case suitable fractionation is employed in order to obtain (a) a light motor-spirit nearly free from aromatic hydrocarbons; (b) an "aromatic fraction" boiling approximately between 70 and 170° C., and, therefore, consisting largely of benzol, toluol and solvent naphtha; and (c) a heavy residue containing no hydrocarbons which it would be worth while to isolate.

The distillate in either of these cases is conveniently referred to as "cracked spirit," and its composition varies in the proportion though not in the nature of its constituents.

The properties of a cracked spirit are familiar to most of the members of this Institution. The spirit is usually yellow, the color developing on keeping, and the odor most characteristic, resembling somewhat that of coal-gas (since this consists partly of water-gas carburized by cracked oil). The large proportion of olefines and diolefines present render difficult the refining of the spirit by sulfuric acid since these combine with approximately their own weight of acid, great heat and discoloration also resulting. As the pronounced odor of the spirit is the intrinsic odor of the mono- and diolefines (especially of the latter), a product as sweet-smelling as natural petrol cannot be obtained without complete removal of these substances. Apart from the odor, the diolefines possess the curious and, from the motor-spirit point of view, highly undesirable property of yielding in storage a viscous yellow liquid which is sparingly soluble in the light spirit, and partly separates as a heavy oil. On heating, this thick oil decomposes with almost explosive violence, yielding a hard resinous residue. The supernatant spirit also produces an explosion when distilled, owing to the decomposition of this oil. It is uncertain at present whether this viscous oil is a polymeric or an ozonide derived from the diolefine; it is probably a mixture of several substances of different chemical natures.

The diolefines appear to be produced to a greater extent in cracked spirits made at a fairly high temperature than in those obtained by low-temperature cracking, and moreover predominate in the low-boiling fractions of the cracked oil. Fractions rich in diolefines are converted almost entirely on keeping into explosive resinous products. The lower boiling fractions of cracked spirit are polymerized with evolution of heat by sulfuric and hydrochloric acids and by anhydrous aluminum and ferric chlorides, products of a terpene-like odor and character being produced. Sodium also induces slow polymerization to an oil of high boiling point and not unpleasant odor.

Several cracked spirits have been fractionally distilled, and the fractions boiling up to 80° shaken with bromine water till this was no longer decolorized. The bromine derivatives have been purified by distillation and analyzed, and prove the presence of erythrene, amylene, hexylene, and heptylene.

The portion of a cracked spirit boiling between 70 and 170° always contains benzol, toluol, and xylol. After removal of olefines and diolefines by means of sulfuric acid, these hydrocarbons can be isolated in the form of nitro-derivatives.

The composition of a cracked spirit can be most readily determined by shaking a known volume with excess of cold concentrated sulfuric acid which dissolves olefines and diolefines. If the proportion of diolefines is considerable, the violence of the action may be moderated by shaking first with 80% acid, which removes most of the diolefines, but only a small part of the olefines.

The residue, after measuring, is then shaken with cold, slightly fuming sulfuric acid till no further absorption results. The operations are conveniently carried out in a stoppered burette, and the two absorptions indicate olefines (with diolefines) and aromatic hydrocarbons respectively. The residual spirit is a mixture of paraffins and cyclo-paraffins. If fractions of fairly definite boiling point are so analyzed, the nature of the paraffins in this residue will be known, and a specific gravity determination will thus indicate the relative proportions of paraffin and cyclo-paraffin. A few series of such analyses may be of interest:

A—Fraction (B. P. 80 to 138°) of "Cracked Spirit" intended as a Source of Benzol and Toluol.
B—Fraction (B. P. 85 to 87°) of "Cracked Spirit" for Motor Fuel.
C—"Cracked Spirit" for Motor Fuel.

PERCENTAGES:	A	B	C
Loss to Concentrated Sulfuric Acid (Olefines and Diolefines)	17	46.5	18
Loss to Fuming Sulfuric Acid (Aromatic Hydrocarbons)	83	29.5	7
Residue (Paraffins and Cyclo-paraffins)	0	24.0	75

Under existing conditions, the bibliography of pyrogenesis, while too extensive for publication with full titles, etc., in these pages is so important and essential to the foregoing text, that we have as a compromise reduced it to the subjoined index of the literature of the subject.

CHRONOLOGICAL INDEX OF PATENTS

- 1 Suedic, Parisienne pour Leclairage au Gaz. E.P. 1860, 1267.
- 2 Brouillonnet, L. L. 1883.
- 3 Young, J. E.P. 1865, 3345.
- 4 Vincent, Richards, and Others. E.P. 1866, 616.
- 5 McKenzie, E. P. 1866, 769.
- 6 Young and Brink. E.P. 1866, 1278.
- 7 Stoll and MacIvor. E.P. 1869, 3088.
- 8 Abbe, E.P. 1877, 4769.
- 9 Robert, E.P. 1881, 301.
- 10 Williams, E.P. 1881, 1603.
- 11 Stoll, E.P. 1881, 1925.
- 12 Ball, E.P. 1881, 9510.
- 13 Ball, E.P. 1884, 12681.
- 14 Hurl, Ger. P. 3134, 1885, and 4769, 1888.
- 15 Alexow, Ger. P. 39919, 1886.
- 16 Radecke-Motzmann, Ger. P. 37728, 1886.
- 17 Nikoloff, E. P. 1886, 10957.
- 18 Ger. P. 85881, 1895, and 14543, 1901; Russ. P. 290, 1894.
- 19 Borne, E.P. 1890, 11908.
- 20 Borden, E.P. 1887, 1922, and Russ. P. 312504, 112505, 1886.
- 21 Dwan and Redwood, E.P. 1889, 10277, 1890, 13016, 1891, 1571, Ger. P. 31552, 1889, U.S.P. 41994, 126175, 1890.
- 22 Hissatz, E.P. 1890, 2442, Ger. P. 31607, 1888.
- 23 Lamp, E.P. 1890, 1120, 11035, and 11757.
- 24 Yachon and Algie, E.P. 1892, 3216.
- 25 Doodhett, E.P. 1892, 1983, 1964, 2161.
- 26 Young, E.P. 1893, 35.
- 27 Smith, E.P. 1893, 3097.
- 28 Young, E.P. 1893, 12593.
- 29 Doodhett, E.P. 1894, 24674.
- 30 Houten, E.P. 1896, 5888.
- 31 Ger. Pat. 16954, 4th. Dec. 1896, 2d. E.P. 1896, 10078.
- 32 Scott, U.S.P. 667,333, 1892, 1896.
- 33 Mehl, E.P. 1896, 15613.
- 34 Houten, Ger. P. 36644, 1895.
- 35 Doodhett, E.P. 1898, 1111.
- 36 Gossard, Ger. P. 1899, 13949.
- 37 D. E.P. 1899, 6969.
- 38 Ger. P. 1899, 13975, 1906, 1908, 1909.
- 39 Nelson, Ger. P. 190, 13119, E.P. 1903, 13119, U.S.P. 1,222,979, 1904, Ger. P. 1,240,616, 1906.
- 40 Gossard, Ger. P. 1904, 11968.
- 41 Scott, Ger. Pat. 1904, 11968.
- 42 Houten, Ger. Pat. 1904, 11968.
- 43 Houten, Ger. Pat. 1904, 11968.
- 44 Houten, Ger. Pat. 1904, 11968.
- 45 Houten, Ger. Pat. 1904, 11968.
- 46 Houten, Ger. Pat. 1904, 11968.
- 47 Houten, Ger. Pat. 1904, 11968.
- 48 Houten, Ger. Pat. 1904, 11968.
- 49 Houten, Ger. Pat. 1904, 11968.
- 50 Houten, Ger. Pat. 1904, 11968.
- 51 Houten, Ger. Pat. 1904, 11968.
- 52 Houten, Ger. Pat. 1904, 11968.
- 53 Houten, Ger. Pat. 1904, 11968.
- 54 Houten, Ger. Pat. 1904, 11968.
- 55 Houten, Ger. Pat. 1904, 11968.
- 56 Houten, Ger. Pat. 1904, 11968.
- 57 Houten, Ger. Pat. 1904, 11968.
- 58 Houten, Ger. Pat. 1904, 11968.
- 59 Houten, Ger. Pat. 1904, 11968.
- 60 Houten, Ger. Pat. 1904, 11968.
- 61 Houten, Ger. Pat. 1904, 11968.
- 62 Houten, Ger. Pat. 1904, 11968.
- 63 Houten, Ger. Pat. 1904, 11968.
- 64 Houten, Ger. Pat. 1904, 11968.
- 65 Houten, Ger. Pat. 1904, 11968.
- 66 Houten, Ger. Pat. 1904, 11968.
- 67 Houten, Ger. Pat. 1904, 11968.
- 68 Houten, Ger. Pat. 1904, 11968.
- 69 Houten, Ger. Pat. 1904, 11968.
- 70 Houten, Ger. Pat. 1904, 11968.
- 71 Houten, Ger. Pat. 1904, 11968.
- 72 Houten, Ger. Pat. 1904, 11968.
- 73 Houten, Ger. Pat. 1904, 11968.
- 74 Houten, Ger. Pat. 1904, 11968.
- 75 Houten, Ger. Pat. 1904, 11968.
- 76 Houten, Ger. Pat. 1904, 11968.
- 77 Houten, Ger. Pat. 1904, 11968.
- 78 Houten, Ger. Pat. 1904, 11968.
- 79 Houten, Ger. Pat. 1904, 11968.
- 80 Houten, Ger. Pat. 1904, 11968.
- 81 Houten, Ger. Pat. 1904, 11968.
- 82 Houten, Ger. Pat. 1904, 11968.
- 83 Houten, Ger. Pat. 1904, 11968.
- 84 Houten, Ger. Pat. 1904, 11968.
- 85 Houten, Ger. Pat. 1904, 11968.
- 86 Houten, Ger. Pat. 1904, 11968.
- 87 Houten, Ger. Pat. 1904, 11968.
- 88 Houten, Ger. Pat. 1904, 11968.
- 89 Houten, Ger. Pat. 1904, 11968.
- 90 Houten, Ger. Pat. 1904, 11968.
- 91 Houten, Ger. Pat. 1904, 11968.
- 92 Houten, Ger. Pat. 1904, 11968.
- 93 Houten, Ger. Pat. 1904, 11968.
- 94 Houten, Ger. Pat. 1904, 11968.
- 95 Houten, Ger. Pat. 1904, 11968.
- 96 Houten, Ger. Pat. 1904, 11968.
- 97 Houten, Ger. Pat. 1904, 11968.
- 98 Houten, Ger. Pat. 1904, 11968.
- 99 Houten, Ger. Pat. 1904, 11968.
- 100 Houten, Ger. Pat. 1904, 11968.

DISCUSSION

SIR BOVERTON REDWOOD said that, in view of the amount of attention devoted at the present time to the subject, it would be safe to predict that a large number of investigators would owe a deep debt of gratitude to the talented and industrious authors of the paper to which the members had just listened. Further, it might be said that the Institution of Petroleum Technologists had taken important action, entitling it to credit, by arranging for the placing on record of so comprehensive an account of the evolution of the process of cracking, and of the principles underlying it. The subject was, all would agree, one of entrancing interest, as well as of great industrial importance, and he thought that a careful study of the paper might lead to further developments of an entirely unsuspected nature. This paper would, therefore, form a most valuable permanent record of an authoritative character for future study. The speaker was precluded from discussing the relative merits of the process with which his name was associated and of other methods of achieving the same results. He thought also, that as a measure of precaution he ought to disclaim acquiescence even in the views of the authors on that particular point, however much he might or might not agree with them. At any rate he could safely say that his old friend, Professor Dewar, and himself had been born too soon. No one was in a better position than Mr. Lomax and his associates authoritatively to speak of the results obtained by the working of the Hall process "somewhere in England," for a period of nearly a year, on a practical scale, for the manufacture of toluene. He would, however, like to add his own personal testimony to what had been so well said as to the efficiency of that method of obtaining aromatic hydrocarbons from petroleum. Although the inventor of the process was an American citizen, a subject of the United States, the speaker nevertheless felt proud that his process was practically worked out and brought to a success in this country; and that it was being most successfully worked, and was giving admirable results at a time when, according to published statements, the workers at the Rittman process, under the aegis of the United States Bureau of Mines, were still grappling with difficulties which in this country had been encountered at an earlier stage, and had already been successfully overcome.

DR. M. B. BLACKLER said that a monumental work had been produced by the authors on a subject which, to his mind, would become of great economic importance in the near future. Cracking could be considered from two points of view: (1) the production of aromatic hydrocarbons, and (2) the production of motor-fuel for internal-combustion engines. He did not believe that when aromatic hydrocarbons became the servants of peace, the production of these bodies from petroleum by the cracking process would have an economic value, but he was certain that this process was going to be of great assistance in the production of fuel for the future requirements of the high-speed internal-combustion engine. In a process of this description, where molecules of a complex nature were subjected to high pressure, and passed through heated tubes at the velocity of an express train, it was necessary to choose conditions which offered the maximum results for the purpose in view, namely to produce a spirit which could be placed on the market at an economic price. So far as the speaker's experience carried him he could agree with Dr. Dunstan's view that in the action described the heavier hydrocarbons were broken down mainly into three distinct classes—paraffins, olefines, diolefines, with smaller quantities of aromatic hydrocarbons and heterocyclic hydrocarbons, and varying quantities of gas. From the economic point of view it was the diolefines which affected the utility of the fuels produced. Crude cracked spirits possessed an atrocious odor, and in a longer or shorter time, deposited heavy material of a gummy consistency, which was detrimental to its use in the ordinary carburetor. Before placing cracked spirits on the market, it would, therefore, be necessary to develop a process which would economically eliminate the diolefines, which were prone to polymerization, while still leaving the whole of the olefines present in the crude spirit. The usual method of purification was to use some strong chemical, like sulfure acid, which acted not only on the diolefines but on the olefines also, and it was impossible to restrain it in such a way that it would act on the diolefines only. In addition to the unnecessary loss caused by this method of purification, a certain residuum of diolefines was always left behind, which changed after the material had been standing some time, and the spirit then deposited "gum," and developed an objectionable odor. It was thought that if some definite chemical or chemicals, not necessarily strong, could be discovered, which would have a selective action on the bodies that were slightly more unsaturated (the diolefines), than on the other unsaturated bodies present (olefines and aromatics), it might be possible to develop a process which would

rid the cracked spirit of the undesirable diolefines, and leave behind olefines and saturated bodies which would not undergo change. He was not in a position to give details, but that process had been worked out, and it had been found that it was possible to eliminate the whole of the diolefines from the crude spirit, leaving behind a colorless, odorless product, containing olefines and paraffins, together with small quantities of aromatic hydrocarbons and polymethylenes; then, no matter how long this product was kept, it would not undergo any change. If, however, the process were not conducted with sufficient care, and small quantities of diolefines remained in the finished product, a change did take place after four or five months' standing and there was a gradual deposition of gummy matter, and an objectionable odor developed in the spirit. In a complex process such as that under review, no matter how temperature and pressure were controlled, it was impossible to guarantee that a certain percentage of the obnoxious diolefines would not be obtained, and in the majority of cases 6 to 8% would be present.

A peculiar property of the spirit obtained by the cracking process, which would, in the speaker's opinion, influence the fuel question, was that these spirits, unlike petrol, mixed with alcohol. It had been previously determined that alcohol mixed with a certain quantity of benzene was an excellent fuel for a petrol engine. The speaker felt sure, therefore, that in the future, when the supply of petrol became insufficient for the world's demand, cracked spirit obtained from heavy hydrocarbons would be mixed with alcohol in proportions up to 50%, and used as fuel for high-speed internal-combustion engines. An interesting point is the boiling-point of such a mixture. When purified cracked spirit boiling from 35 to 220° C. was mixed with an equal quantity of alcohol, 90% of the mixture boiled below 100° C.

DR. F. M. PERKIN remarked that the question of cracked spirit was, as Dr. Blackler had stated, one of an economic character entirely. If at the present time oil could be cracked in such a way as to produce hydrocarbons of the benzene series, such as benzol, toluol, etc., this would be better than cracking it in any other way. It was known that cracking at such very high temperatures as would be necessary caused very much larger quantities of gas to be produced, and there was also the great difficulty of the deposit of carbon. Personally, he was not a believer in the Rittman process, where a chain had to be kept constantly swirling round in order to remove the carbon into receiving pots below, and where the working pressure was something like 150 lbs. In the Hall process, the principle was quite different; there it was a question of expanding into a chamber to get rid of the carbon, and in that case there was no great difficulty in getting up high temperatures. He had had no experience in trying to crack mineral oils to get the hydrocarbon aromatic series; in fact, he had never attempted to do it. But as the process by Fenchelle and himself had been mentioned, he would say that in that case the conditions of working were such as to give a less proportion of carbon than probably any other process—simply for the reason that the oil, during the whole time that it was passing through the process, was kept in a liquid condition. The pressure upon the oil, no matter what the temperature might be, was always so high that the oil never reached its critical temperature, and never, therefore, passed into the form of vapor. Under these conditions there was, of course, less possibility of complete decomposition into carbon and hydrogen than happened in other cases. He might say, from an experience ranging over about eighteen months on a hot steel plant, dealing with about 150 gallons per hour, the tubes employed, which were moderately narrow, had been choked with carbon on only two or three occasions, and in these instances largely by trying experiments for which the plant was not intended. For example, an attempt had been made to crack green oil of the gas works, which, of course, contained hydrocarbons of the benzene series, and large quantities of naphthalene and anthracene, which immediately wanted to break up into carbon and other undesired products. In dealing with ordinary fuel oil, containing practically no aromatic hydrocarbons, there was no great difficulty in obtaining petrol. But this was the same difficulty as obtained in other processes, no matter what the process was, the gummy dimer and trimer, and the like were produced. The next problem was in what proportion were they going to be formed? Was it possible to remove them with 1% of sulfure acid, or would it be necessary to add 5% in order to get rid of them? Further, when it was supposed that they had been removed, were they going to reform again in about a year's time? That was the difficulty. There might be only 5 or 10% of these gummy aromatic hydrocarbons, which on complete or partial removal gave a beautiful, clear, white petrol. Frequently, however, if the material for a year or so was stored in the tank, the "gum" would have formed again. If the hydrocarbons were to be used immediately after their first purification, would the gummy substances actually be there and then the value

say in the ascent of a stiff hill, or other critical occasion, or were they formed again only by prolonged storage? As a matter of fact they formed very much more rapidly in sunlight than in the dark. He thought that the cracked petrol should be used within six weeks of its purification. That had been a difficulty in the case of a good many processes hitherto, and although the speaker, like Dr. Dunstan and his confrères, and Dr. Blackler and Mr. Lucas, had done a large amount of experimental work, the difficulty of keeping out the gummy products had not been overcome, though he was confident that it would be got over in due course. He did not, however, agree that the cracked oils had an unpleasant odor; he rather liked the smell of them. The public had to remember that when they were dealing with cracked oils, they were not dealing with petrol as obtained from the oilfields; it was not the same product; it had a different smell, just as an eau de Cologne varied in smell from oil of lavender. Undoubtedly, in due course the right process would be evolved for purifying these cracked oils, and the work of the authors would go a very long way to forward that achievement. The wonderful bibliography would form a standard in the annals of the Institution of Petroleum Technologists. Dr. Dunstan's equations were of inestimable value. It was only by combination, each student learning from others, and not being afraid to let others know what was being done, that the industry would go ahead.

MR. A. D. LUCAS, who spoke next, had little criticism to offer on what had been said. He could speak only as an engineer, and not as a chemist. The explanation of the processes of cracking had been extremely thorough and complete, and what he had to say related more to the practical side of the question than to the theory. One point in particular occurred to him. Dr. Perkin had referred to the formation of gummy products with time, due, he presumed, to some form of polymerization. Now, a point on which there had been very little literature and very little experimental work was the rate of cooling after the cracking temperature had been reached. The speaker believed that the particular atom of carbon appearing in a final radicle like CH_2 or CH_3 , as the case might be, was not in that radicle from the moment it was formed up to the time it was subsequently isolated. Probably it took several forms, at one time CH_2 and at another time CH_3 , until it finally settled down. The first time an olefine was formed in the process of cracking from paraffin, it repeatedly broke up and re-formed again before it took its final form. If that were so, the rate at which it was cooled after breaking up the original oil, whatever that was, must have a great influence on the final product. He had found by actual experiment that if gases were allowed to remain at a certain temperature for a considerable period, and cooled slowly, the products were quite different in many respects from those which would be obtained with sudden cooling; in other words, sudden expansion after heating would give totally different results from those obtainable by cooling at the same pressure as the vapor issued from the cracking tube.

In regard to the effect of catalysis, the speaker quite agreed with what the authors had said, and in all probability the term "catalysis" was a convenient one for covering a multitude of sins; in nine cases out of ten the catalyst did not act as a catalyst at all. It might possibly, however, have a selective occlusion effect. A particular catalyst might pick up and hold dissociated vapors, and bring them under such conditions that they reconstituted themselves into more or less saturated or semi-saturated bodies. Having been so formed, these were removed mechanically from the surface, which thus became available for occluding further radicles, which again associated together, and were in turn removed mechanically from the surface of the catalyzer. The reason the speaker considered that there must be some such effect as he had described was that he had used a catalyzer made in a somewhat peculiar way, mechanically. This catalyzer was not in the true sense spongy, but it was mechanically spongy, and had the property of absorbing petrol like cotton wool. It consisted, however, of such hard material that it might be cut with a knife, and show an absolutely metallic section. It was not a catalyzer like finely-divided nickel: it was much coarser, but was extremely efficient as a catalyzer. Its catalyzing properties decreased when it was first used, but after a time they began to rise until they reached the top of the curve where they were most efficient, and from that they descended very slowly and steadily. There was no evidence of deterioration, mechanical or otherwise, but after the catalyzer had been in use some time it was found that on heating it certain compounds issued from the catalyzer body. He was not sufficient of a chemist to say what those compounds were, but there was distinct evidence of some modification of the nature of the catalyzer, and these compounds apparently entered into its reactivities. He had in his laboratory samples of oil-products carefully prepared, in 1912, both by the Lamplough process and the New Oil Company's process: the bottles could be turned upside down, open, and the oil products would not flow out.

MR. W. J. A. BUTTERFIELD wished to add his thanks to those already accorded to the authors, and in particular to Mr. Lomax for the magnificent and invaluable bibliography, in which he could see no omissions, unless at one point, *viz.*, about 1890, when the American gas engineers and chemists were doing a lot of work on the cracking of oils in connection with carbureted water-gas plant (see the *Progressive Age* and the *American Gaslight Journal* of that period). A. H. Elliott showed as early as 1885 (*Am. Chem. J.*, 6, 248) that carbureted water-gas tar, as then made, was largely composed of aromatic hydrocarbons, since he found 2.6 to 2.9% of anthracene in it. At a rather later date, when a carbureted water-gas plant was introduced into this country, opportunity was afforded of studying the cracking of heavy oils in that plant. It was easy to work such plant to produce liquid products consisting almost wholly of aromatic hydrocarbons. In "The Chemistry of Gas Manufacture," first published in 1895, he had described a liquid he had examined in 1893 as "a pale, clear liquid, obtained by vigorous scrubbing of carbureted water-gas after the grosser matters have been deposited in the purifiers and other apparatus. It had a specific gravity of about 0.89, and contained 30 to 35% by volume of benzene. This liquid only yielded about 5% of pitch, but much naphthalene." He thought a valuable lesson might be learned from some of the earlier experiences with a carbureted water-gas plant, in the cracking of oils, for present application in the cracking of them for the production in particular of aromatic hydrocarbons. If the United States authorities, instead of sticking to the advice of the academical staff of the Bureau of Mines, had gone to some of the highly experienced gas engineers, and chemists of the States for an opinion on the Rittman system, a great deal less money would have been wasted on it. In that method of cracking a wide tube was employed, 8 inches in diameter, and there was comparatively little surface-action. Radiation, of course, could have no effect on a real gas, but passing through that tube were particles of liquid in the form of spray, and undoubtedly the radiant heat from the sides of the tube acted on those particles in a totally different manner from the contact heat of a hot substance. A much larger proportion of carbon was produced in cracking liquid particles by radiation in that way. That had been the experience in coal-gas retorts, where the difference in the tarry products between retorts partially and fully filled was very noticeable. In conclusion, he would like to call attention to the question put by the authors towards the close of the paper: "Does it not appear that the nature of the material to be cracked has little influence on the final products?" In this connection he congratulated himself that some twenty years ago he had written to the same effect when referring to the composition of the oils deposited from oil-gas and carbureted water-gas, *viz.*, "The composition of the deposited oils is less dependent on the kind of oil used in the manufacture of the gas than on the heat employed in the production." The authors' work had led them to the same conclusion.

MR. E. H. CUNNINGHAM CRAIG wished to ask one question. These cracking processes had taken place with the idea of producing either a motor-spirit or the carbon-ring compounds. He would be glad to know what conditions the authors considered most favorable for the formation of the maximum of methane. He presumed that a high temperature would be best, with, probably, very little pressure. It was possible that some people might at some time want to obtain a maximum of methane as pure as possible, while not concerned in any way with the formation of motor-spirits, gummy or otherwise, or carbon-ring compounds.

DR. A. E. DUNSTAN then replied to the discussion. He had been much interested in hearing Dr. Blackler's account of the effect of alcohol in reducing the boiling point of cracked spirit mixtures. With regard to gumming, he wondered whether the various speakers on this point would incline to the view that ozonides were produced. The effect of sunlight rather suggested that this was the case, and if so, when the dienes and trienes were removed, further deposits of gummy matter were, as Dr. Blackler had pointed out, unlikely. He had no experience of any case where a simple olefine could be turned into a gummy body by the effect of light and oxygen; it might, of course, be possible, but he was not aware of it. With regard to the separation of diolefines and olefines in the laboratory, with the ordinary reagent, as Dr. Blackler would know, the reactivity of the two classes of compound was not so very different: whatever removed the diolefine would remove the olefine. He could only presume, therefore, that Dr. Blackler made use of some special method, possibly of the contact action type, which produced the effect. With regard to maximum methane production, the speaker would be inclined to heat the oil to about 1000° C. in the presence of ample hydrogen.

CURRENT INDUSTRIAL NEWS

COPPER, ALUMINUM, ZINC AND IRON WINDINGS FOR DYNAMOS

According to an article in *Engineering*, 103 (1917), 441, Prof. R. Richter has recently experimented on the comparative merits of the above metal windings for dynamos with these results. Taking copper-wire winding as a standard, the loss of efficiency to a dynamo with windings of aluminum is from 1.5 to 2 per cent, with zinc wire 3 to 6 per cent, and with iron wire 8 to 12 per cent. Against this, he finds that, at pre-war prices of metal, a dynamo with aluminum windings will be 3 per cent cheaper than one with copper windings, while those with zinc or iron windings would be, respectively, 50 and 62 per cent more expensive. He concluded by saying that this may lead to the more extensive use of aluminum in Germany for electro-motors, etc., as he expects that the production could be increased to any required extent. What justification he has for these last remarks is not stated.—A. MACMILLAN.

REMOVING RUST FROM IRON PLATES

As a result of experiments recently carried out at the Consolidated Gold Field Laboratory, South Africa, Mr. F. W. Watson has published an account of an easy, cheap and effective method of removing iron oxide from corroded and pitted iron plates. Previous practice on the Rand has been to remove this mechanically either by hammers, chisels or sand-blast. While largely efficient, each of these methods is liable to leave traces or nodules of rust, especially at the bottom of the pitting, and these nodules prevent the covering of paint adhering to the iron and form nuclei for further corrosion. The method evolved consists in applying to the surface of the iron a mixture of finely crushed sodium thiosulfate and sodium chloride in the proportions of two parts of the former to one of the latter. The mixture is prepared, then wetted (just sufficient to be cohesive) and applied to the iron plate. If time be no object, the moist mixture can be left till the plate is clean, but the action is much more rapid if the mixture is scraped off every 2 or 3 hrs. and the iron scrubbed thoroughly with a wire brush, applying water at the same time. The treatment is repeated till the plate is clean. Usually a period of 24 hrs. is sufficient for a badly corroded plate. The liberation of hydrochloric acid takes place slowly and its action on the metallic iron appears to be slight. When the plate is thoroughly clean, it is washed well and dried quickly. A coating of paraffin is at once applied to protect the surface against atmospheric action. The metal is then ready for the application of paint or other protective covering.—M.

SULFATE OF AMMONIA IN INDIA

According to *Gaz World*, 66 (1917), 9, Dr. H. H. Mann, Agricultural Chemist to the Government of Bombay, points out that sulfate of ammonia is one of the materials which has promise of very large development in India. The quantity available can be largely increased by establishing coke ovens in connection with the collection of iron works, and it is reported that the Tata Iron and Steel Works will be shortly a considerable source of supply. Even now, Bengal supplies itself with this material and exported about 800 tons in 1915. In Madras, the material has an established position, while in Bombay the future of no other artificial manure is so promising. It is being used chiefly in mixture with other manures for tea and other planting crops, and this use will probably extend considerably in the near future, especially in sugar-growing countries. Experiments have proved that in the black soil areas of India, sulfate of ammonia can be satisfactorily used as a top dressing for sugar cane, and, mixed with other artificial manures, it has given excellent results with many garden crops.—M.

ALCOHOL FROM ACETYLENE

Theoretically the preparation of alcohol from acetylene looks very easy. By hydrogenation the acetylene, C_2H_2 , can be converted into ethylene, C_2H_4 , which is transformed into ethyl sulfuric acid by means of sulfuric acid; hydrolysis then transforms the ethyl sulfuric acid into alcohol, C_2H_5OH . But neither this direct way nor various indirect processes appeared for a time to prove technically profitable and so the manufacture of alcohol from calcium carbide, which, on treatment with water, yields acetylene, seemed to remain a problem. Within the last few years, however, several German chemical works have taken patents on the preparation of alcohol from acetylene by means of acid mercury salts of aldehydes which differ from their alcohols by a deficiency of two atoms of hydrogen. Whether and how far, says *Engineering*, the preparation and hydrogenation of these aldehydes is at present being utilized in Germany, we do not know. The alcohol department of the Swiss Government, in March, granted a concession for the manufacture of 7,000 tons of alcohol (more later) per year from calcium carbide to the Elektrizitätswerk, Lonza, of Gampel and Basle, Switzerland. The works are to be opened within 18 months and are to supply at least 2,500 tons of alcohol to the Government. The new works are to be erected at Bisp, some miles up the Rhône east of Gampel. The process of the Lonza Company consists in passing vapors of acetaldehyde mixed with an excess of hydrogen over finely divided nickel (catalyst). Water and alcohol are formed, the former is frozen out and the excess of hydrogen gas reacts again with aldehyde vapor. The Swiss patent, on which the process is based, is not yet available in England.—M.

TAR VARNISH FOR IRON-WORK

The South African correspondent of the *Iron and Coal Trades Review* recommends from personal experience the following prescription for tar varnish for preserving iron-work: Heat about 100 gallons of tar to a low boiling point and add 100 lbs. of freshly slaked lime sifted over the top and then worked down. Boil the mixture until it becomes pasty. Let it settle for a few minutes and then add 20 lbs. of tallow and 5 lbs. of powdered resin. Stir until thoroughly mixed and all the ingredients are dissolved; then allow to cool. The mixture should not be raised to a higher temperature than 100° F. Should the preparation be too thick, it can be thinned down with paraffin or naphtha. This gives a beautiful finish like a stove enamel. The works in which this is used are situated right on the edge of the sea and the southeast winds eat away iron-work very quickly. All gasholders, galvanized iron roofs and galvanized sides of buildings are painted two coats with this tar varnish and then white-washed over this, which thoroughly protects them from the weather and salt air. The varnish is elastic and will stop corrosion. A similar mixture was used with excellent results for coating the girders of all the bridges on a railway in the north of England.—M.

PREVENTION OF LEAKAGE THROUGH CEMENT

To stop leakage through cement (such as tunnel walls, etc.) the walls thoroughly and paint with a solution consisting of 8½ lbs. of zinc sulfate dissolved in a gallon of water. The zinc sulfate will act on the base of the cement forming zinc zinc sulfate and zinc hydrate. Another method is to use one part water glass, sodium silicate, to five parts of water and apply a coat with a brush. This is allowed to dry for about an hour and another coat is applied. The second coat has about three times put on, with not over an hour between the applications of the separate coats.—M.

NATURAL GAS AS A BOILER FUEL

The outbreak some years ago, says *Engineering*, 103 (1917), 428, of a gas jet at Neungamme, near Hamburg, caused a temporary stir. We thought that the gas had afterwards exhausted itself, but we find that the gas has been caught, and, being mainly methane and not suitable for being mixed with illuminating gas in percentages exceeding 15 per cent, has been used as a fuel in the Hamburg Waterworks at Rothenburgot. Twenty-four of the boilers there are fired with the gas which is introduced under a head of from 10 to 40 cm. of water. The gas supply being unreliable, the grates were not interfered with, so that, in emergency cases, a return to coal fuel could be effected. To check the air supply through the grate, the latter is kept covered with a layer of slag. In three years, August 1913 to August 1916, the pumping works used 18,800,000 cu. m. of this gas, the gas consumption being 0.66 cu. m. per horse power hour, and 15 cu. m. of gas for raising 100 cu. m. of water to a height of 53 meters. It is estimated that the use of the gas saved 22,400 tons of coal. In Torda, Hungary, natural gas was adopted as domestic fuel last autumn after having been utilized in four factories, the municipality and the natural gas company having entered into a contract under which the company supplied the apparatus and connections.—M.

BEET SUGAR MANUFACTURE IN JAPAN

The British Attaché at Yokohama reports that a company with a capital of 5,000,000 yen (\$2,500,000) has been formed to manufacture beet sugar in Corea. The Company intends to erect a mill at Kokai-do or Hsian-do at a cost of 1,800,000 yen (\$900,000). It is estimated that the mill will consume 90,000,000 kin (69,230,770 lbs.) of beets per year, and will produce 12 per cent of sugar. A second factory will be built later. Relative to the application made by a sugar manufacturing company in Pyongyang, it is reported that official permission has been granted and that, to begin with, a sugar refinery will be set up at Pyongyang at a cost of 1,800,000 yen (\$900,000).—M.

THE FRENCH SAFFRON MARKET

At Marseilles, says the *Oil and Color Trades Journal*, 51 (1917), 1871, this industry enjoys considerable prosperity and comprises ten large factories doing good business with the south of France. Saffron is obtained from Gatinais, the French colonies, Spain and the Levant. The latter origin, being stronger, is very popular. At present, however, it is not to be got. Saffron is sold in leaves and in powder form. Leaves are most preferred as they do not lend themselves to adulteration. Morocco, however, supplies a similar product which has both the taste and perfume of saffron. At present, the factories are provided with fairly satisfactory stocks of the raw material, but a deficit is feared for the coming season as the cultivation has been greatly neglected since the outbreak of hostilities.—M.

THE WORLD'S CENTRE FOR PAPER AND PULP

That Canada is rapidly becoming the world's centre for the manufacture of pulp and paper is indicated by recent figures. For the year ended July 1916, the exports of paper amounted to \$21,678,868 in value, of which 88 per cent went to the United States and 5.2 per cent to the United Kingdom. The total is an increase of 31 per cent over the figures for the previous year. Taking the situation as a whole, the total exports of paper and pulpwood for the fiscal year ended July 1916, were valued at \$40,865,266, of which the United States received 87 per cent and the United Kingdom 5 per cent. The increase over the previous year was 27 per cent. The exports of pulpwood from the Province of Quebec alone for the past year exceeded \$4,000,000 in value.—M.

THE DYE INDUSTRY

The rapidity with which the dye industry, says the *Chemical Trade Journal*, 60 (1917), 528, has been developed in England and in America has been something of a surprise to the Swiss makers and doubtless to the Germans as well. It is recognized that the former monopolists will have a formidable competition to face when the war is over, and money is being set aside with the hope of meeting it with a prospect of success.

A report just issued by the Basel Chamber of Commerce and quoted in the *Manchester Guardian* mentions that the recently formed German cartel, which includes not only the two old main groups but also the more important of the other firms, has a capital which the stock market values at \$200,000,000, and that it is likely to fight hard to regain its position in neutral markets.

In the meantime, both Entente and German makers have made amalgamation offers to Swiss firms, but it has been decided that none of these will be accepted during the war, if at all. Swiss makers have found it difficult to increase their comparatively small production of synthetic indigo owing to difficulties in obtaining the requisite raw materials, but they state that a Manchester company is putting a good quality on the market and another English concern is making large quantities of commoner qualities and selling them cheap. The Basel Chamber considers that the days of very high prices for dyes are gone.

The British Government has established a special temporary department of the Board of Trade to deal particularly with matters relating to the encouragement, organization and, so far as necessary, the regulation of the dye industry. Sir Ewan Jones has been appointed Commissioner and will act in close consultation with the various dye-making and dye-using interests concerned.—M.

EFFECT OF AMMONIACAL LIQUOR ON CONCRETE

A gas liquor tank, says the *Journal of Chemical Industry*, quoting from *Zeit. Chem.*, showed signs of leaking. The liquid which escaped contained ammonia, free and fixed, much calcium and, as acid radical, thiosulfuric and thiocyanic acids. The ammonium salts in the liquor had attacked the lime in the concrete, forming soluble calcium salts. Coating the inside of the tank with materials such as tar is only partly effective, as it is difficult to avoid the development of cracks. A suitable lining to the tank is to be preferred—lead, iron, or glass being suggested. Zinc is not a suitable material. Where iron is used it is recommended to keep the atmosphere of the tank free from air and so avoid rusting. For this purpose coal gas is recommended.—M.

MOTOR SPIRIT FROM KEROSENE

According to a contemporary, demonstration of the Freeman process of transforming illuminating oil into motor spirit was given recently at Chesham, England, by the inventor, W. N. Freeman. The process, it is claimed, is exceedingly simple, being accomplished in a series of stills without the aid of chemicals or of resorting to the usual destructive cracking process.

From ordinary lamp oil, the inventor produces a motor spirit described as of exceptional purity and homogeneity, as may be judged by the fact that between the first and last fractions distilled there is a difference of only 5.4° Baumé as compared with a difference of over 25° Baumé in the highest quality motor spirits in the English market.

The percentages of motor spirit produced by the Freeman process vary with the quality of the kerosene treated, but the maximum limits are stated to be approximately 60 per cent in volume. By this new method, it is claimed that as many as 24 different petroleum products can be produced at the same time, the cost of transformation being insignificant.—M.

SWEDISH SUBSTITUTE FOR BENZOL

The difficulty of obtaining benzene, says *Oil and Color Trade Journal*, 51 (1917), 2043, has been spurring on inventors to find some good substitute in all parts of the world. In Sweden, where benzene has been very scarce for the past twelve months, use is being made of sulfite alcohol (to which benzol has been added) as a carbureting material for explosion motors. Benzol, in turn, having become scarce (in fact, it can hardly be obtained), Mr. Rustiger, a Swedish engineer, thought of adding to the sulfite alcohol some substitute of benzol, which he has now found in acetylene; 5 to 6 kilos of carbide of calcium are added to 100 kilos of sulfite alcohol in which the carbide is then dissolved at 92°. The mixture seems to have given excellent results, and the carbureting medium can be used in motor cars without any alteration being made in the driving mechanism. Mr. Rustiger, who has patented his invention, is convinced that, in normal times, sulfite alcohol could even compete with benzene.—M.

MINERAL OUTPUT IN CANADA

From the report on the mineral resources and statistics of Canada drawn up for the Department of Mines, we see that the war has stimulated the production of nickel, copper, zinc, iron and steel, molybdenum and also of chromite and magnesite, while the dearth of skilled labor has impeded progress.

The gold production for 1916 was 926,963 oz., valued at \$19,162,025, showing an increase on 1915.

The output of silver was 25,669,172 oz. against 26,625,950 oz. for 1915.

The production of copper has increased during the last three years, the figures for 1915 and 1916 being 100,785,150 lbs. and 119,770,414 lbs. respectively.

The output of nickel was 82,953,640 lbs. as compared with 68,308,657 lbs. for the previous year.

The ores from the Cobalt and Temiskaming district in northern Ontario contain 4 to 10 per cent cobalt, 2 to 8 per cent nickel, 15 to 40 per cent arsenic and from 500 to 5000 oz. silver to the ton. Sulfur and lead in these ores are absent. The production of cobalt (metal, oxide, etc.) amounted to 841,839 lbs. in 1916.

The amount of pig iron produced was 1,169,257 short tons; to this must be added 28,625 tons of ferro-metals made in electric furnaces.

The value of asbestos produced stands highest, although in bulk the year 1913 gives higher figures; from 1,822,461 tons of asbestos rock sent to the mills, 112,832 tons (6.3 per cent) of asbestos fibers were recovered.

Other mineral products in 1916 were:

	Tons		Tons
Coal	14,461,638	Pyrites	309,411
Gypsum	311,648	Quartz	135,803
Magnesite	55,413	Salt	134,000
		Natural gas	28,058,680 cu. ft.
		Petroleum	198,114 bbls.
		Zinc	2,515,000 lbs.

—M

GELATINE

As is well known, says the *Monthly Trade Review*, the manufacture of glue is one of the oldest industries in Japan. A development in this industry is now reported: the production of gelatine. When the war broke out and the importation of this article was made impossible or very difficult, export were sent abroad to study the matter with the result that a home industry has now been established turning out a gelatine product equal to the foreign one. It is believed that, in a few years, the Japanese gelatine industry will have expanded to such a degree as to make further imports unnecessary and it is maintained that in 5 or 6 years a considerable export of gelatine can be expected.—M.

GLYCERINE SUBSTITUTES IN GERMANY

As German pharmacists have been prohibited from selling glycerine except when ordered by a physician, numerous formulae for substitutes have from time to time been published. The following information regarding certain German substitutes (some of which are proprietary preparations) is taken from *Pharm. Ztg.*, 62 (1917), 105:

- (1) A 2 per cent solution of gelatine mixed with an equal volume of glycerine.
- (2) Mucilage of quince seed to which boric acid and alcohol are added.
- (3) Salep mucilage.
- (4) Algin, a mucilage made by macerating laminaria stalks with solution of sodium carbonate.
- (5) Carvien, a proprietary preparation of unknown composition.
- (6) An aqueous solution containing 21 per cent magnesium chloride and 40 to 50 per cent glucose. It does not dry but is used for certain technical purposes.
- (7) A concentrated solution of a potassium salt of a glycosaccharic acid or lactic acid or an acid allied to one of these.
- (8) A solution consisting of calcium chloride, potassium lactate and mucilage.
- (9) A 5 per cent quince seed mucilage to which 10 per cent of glycerine is added.
- (10) Glycol.
- (11) Lempellin, a carrageen mucilage with borax and formaldehyde.
- (12) Mollphoras, a concentrated solution of sucrose and invert sugar it is said to be an efficient substitute.
- (13) Novo-glycerine, a gelatine solution.
- (14) Perglycerin.
- (15) Protol, a glycerine prepared biologically.

—M

CAMPHOR REFINING AT FORMOSA

The British Attaché at Yokohama has forwarded an extract from the local press from which it appears that with a view to exporting camphor in a finished state, it is proposed to erect a camphor refinery in Formosa to treat the whole of the output of the island, and that a company with a capital of \$1,000,000 is to be formed in Formosa with this object. The camphor produced in Formosa has hitherto been shipped to foreign countries in its raw state with the exception of a portion which was refined at Kobé. The output in Formosa this year was 11,616,000 lbs., and the receipts accruing therefrom valued at \$3,165,000.

Indications are evident that the price of camphor is gradually showing an upward tendency on the international market, and the receipts may even amount to \$3,400,000. The demand for camphor is increasing both on the Japanese and the foreign market with the progress of the war.

In Formosa all possible measures are being taken to encourage the planting of camphor trees. In recent years, many young trees have been planted, but during the next 30 years it will be impossible to utilize these for industrial purposes. On the other hand, old trees are gradually diminishing and some anxiety is manifested as to the welfare of the industry. The shipments to the United States last year amounted to 465,000 lbs. each month, and under a new contract the monthly shipments after April 1 will be increased to 600,000 lbs.—M.

ALIZARINE DEIPHINOL

British Dye, Ltd., were recently able to produce the introduction to the color market of British-made indigo dyes under the name of "color synthesis". They are now in a position to announce the introduction of "color synthesis," a blue acid dye which has been developed by the same chemical group as alizarine, but which lacks the usual distinctive quality.

It is interesting to note, says *Monthly Trade Review*, 60 (1917), p. 14, that a product of this type has previously been manufactured by one German firm only, although the factory had been liquidated some years ago.—M.

ALCOHOL FROM WOOD-PULP LYES

An account of a discovery in Königsberg, Germany, was recently published, dealing with a method for the production of alcohol from the lyes of the wood pulp industry. The discovery, it is stated, has been tested with excellent results. To produce the pulp the wood is treated with sulfite of soda. This gives lyes which have hitherto not been utilized.

The removal of these lyes was both troublesome and expensive, as they could not be let off into the rivers without previous purification. Their saccharic acid content was found to pollute the water and poison the fish during the summer months when the water was low. Pulp and paper factories had therefore to erect great purifying plants or at least collecting basins in which lyes could first be purified before being let off. The sugar-containing sulfite lyes—so much waste—are now by the new process converted into industrial alcohol.

The Government, recognizing the immense economic importance of the discovery, has taken the matter in hand and quite a number of works are to be established in the vicinity of wood pulp factories. In this way it is hoped to obtain 400,000 or 500,000 h. liters of alcohol for industrial purposes. The results already obtained at Königsberg have given indications that these figures may be even exceeded. The state possesses the patent and will probably monopolize the alcohol manufacture with a view to securing a good and constantly increasing source of revenue.—M.

CHEMICAL MANUFACTURE IN FRANCE

As regards dichromate, France had, before the war, been dependent on England and Germany; some 3,000 tons of dichromate were imported annually. The new works at Pontthierry compete with England and make 500 kg. sodium dichromate per day. This sodium salt does not crystallize well, being more soluble than the potassium salt, and was first used as a concentrated solution, but a crystalline product is now obtained.

According to the *Industrie Chimique*, potassium permanganate is made at Château-Ponsue at the rate of 100 kg. per day, and the output is to be much increased. The same works also manufacture golden sulfide of antimony which had been prepared in a small scale in the north of France. Another chemical industry of northern France—that of potassium carbonate and other potassium salts from the residues of molasses distilleries, has been taken up at Choisy.—M.

A NEW REAGENT FOR ALDEHYDES

Fazi, in an Italian contemporary, gives the details of a new reagent for aldehydes, which allows the detection of the most minute quantities of a number of these compounds. It will detect 0.0078 mg. of benzaldehyde, 0.019 mg. of vanillin, or 0.006 mg. of furfural. It will not, however, effect more than a group separation so that it can hardly be said to detect given aldehydes.

The reaction is as follows: To the aldehyde in chloroform solution, two or three drops of a chloroformic solution of acenaphthene are added and then with care 1 cc. of concentrated sulfuric acid. A green ring changing to red-violet is formed in the presence of the aldehyde. If the tube is shaken, the sulfuric acid is colored green and then red-violet.

This reaction is sufficient to discriminate between aromatic and aliphatic aldehydes since the latter do not give any coloration. Formic and acetic aldehydes, for example, give white precipitates which consist of condensation products. Aldoses and carbohydrates containing an aldehyde group which yield furfural or aromatic aldehydes on treatment with cold concentrated sulfuric acid also yield the reaction. In the case of lactose (sugar of milk) the green color appears at the end of a few minutes and passes to violet in about 40 minutes. Maltose reacts more slowly than lactose.—M.

PRODUCTION OF PLATINUM

The British Consul at Ekaterinburg reports that notwithstanding the high price of platinum, the production of the metal on the Urals during 1916 showed a further decrease. The total output amounted to 86,508 oz. as compared with 118,709 oz. in 1915. The production in 1913 and 1914 was 158,084 oz. and 156,755 oz., respectively, while in 1909 no less than 214,042 oz. were produced.

The chief causes of the decline are the shortage of labor, the difficulty of obtaining spare parts for dredgers and the exhaustion of the richer alluvial deposits. The report goes on to say that no doubt new alluvia will be found when extensive prospecting is resumed, but there is nothing to indicate an improvement in the production of platinum in the near future, at any rate, during the war. It is highly probable the output for 1917 will be less than for 1916.—M.

OLIVE OIL PRODUCTION IN PORTUGAL

The *Diário do Governo*, Lisbon, of May 24, publishes a statement issued by the Portuguese Ministry of Finances from which it appears that the 1916-17 production of olive oil in Portugal amounted to 16,150,149 liters, and stocks of oil on March 30 amounted to 18,279,976 liters.—M.

EXPERIMENTS IN SUBSTITUTES

It is reported by a German contemporary that a use has been found for the troublesome weed couch-grass (*quecke*, *triticum repens*), which, it says, in the spring contains sugar, as well as elements of rubber, tritine (which resembles starch) and also mannin, a nutritive element in manna resembling sugar.

It is now recommended by scientists that couch-grass should be used for food after being dried, chopped and ground. It may be used for soups and for vegetable and flour dishes. An analysis shows the following results for couch-grass hay: 4.93 per cent digestible albumen, 1.33 per cent fat, 45.44 per cent carbohydrates, giving a fodder equal in value to the best clover hay.—M.

BRITISH BOARD OF TRADE

During the month of June the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.

- Arsenate of potash
- Ceiling and table-lamps, burning paraffin and petroleum oil
- Gas helmets for chemical works
- Gear wheels, up to 2 in. in diameter, in steel and gun metal for war purposes
- Ink powders, blue black, red, green
- Lubricating tins, split, 8½ in. inside, 1 in. wide
- Motor car engines, adapted to use paraffin
- PLANT for manufacture of artificial silk
 - for making alpagatas soles
 - for making carbon papers
 - automatic, for making vesta matches
 - for blowing large glass globes into moulds
 - for printing red charts
 - for manufacture of waterproof and other tubes (pumps, etc.) from wood pulp
- Marcasite frames for hand bags
- Metallic dust
- Photo-frames, electro-plated, to retail from 18 c.
- Portable clockwork fans
- Potassium permanganate
- Rubber sponges
- Spurred rye (ergot of rye)
- Silver mounts for purses
- Small steam turbines (less than 1 h. p.)
- Tags for boot and corset laces
- Tobacco pipes (meerschaum)

—M.

SCIENTIFIC SOCIETIES

CALENDAR OF MEETINGS

- American Chemical Society**—Annual Meeting, Boston, September 10 to 13, 1917.
- National Exposition of Chemical Industries (Third)**—Grand Central Palace, New York City, September 24 to 29, 1917.
- Technical Association of the Pulp and Paper Industry**—Joint Meeting with the Technical Section of the Canadian Pulp and Paper Association, Holyoke, Mass., September 27 to 29, 1917.
- National Wholesale Druggists Association**—Annual Convention, Chicago, October 1 to 4, 1917.
- American Electrochemical Society**—Autumn Meeting, Pittsburgh, October 3 to 6, 1917.
- National Paint, Oil and Varnish Association**—Annual Convention, Chicago, October 8 to 10, 1917.
- American Institute of Mining Engineers**—Annual Meeting, St. Louis, October 8 to 13, 1917.

THE CHEMICAL SOCIETIES IN NEW YORK CITY

1917-1918 SEASON—RUMFORD HALL, THE CHEMISTS' CLUB

- October 5—American Chemical Society.
- October 19—Society of Chemical Industry.
- November 9—American Chemical Society.
- November 23—Society of Chemical Industry.
- December 7—American Chemical Society. *Joint Meeting with Society of Chemical Industry and American Electrochemical Society.*
- January 18—Society of Chemical Industry. *Perkin Medal Award.*
- February 8—American Electrochemical Society. *Joint Meeting with American Chemical Society and Society of Chemical Industry.*
- March 8—American Chemical Society. *Nichols Medal Award.*
- March 22—Society of Chemical Industry.
- April 12—Society of Chemical Industry. *Joint Meeting with American Electrochemical Society and American Chemical Society.*
- May 10—American Chemical Society.
- May 24—Society of Chemical Industry.
- June 7—American Chemical Society.

DECENNIAL INDEX TO CHEMICAL ABSTRACTS

The first volume of the Decennial Index to Chemical Abstracts is ready for distribution and will be mailed with the September 20 issue of Chemical Abstracts to all subscribers whose remittance is received in the Secretary's office by September 10. A notice has been sent to all subscribers that it is important that prompt payment be made.

To members who subscribed before January 1, 1917, the price of the Index is \$2.0000. To members who subscribed after January 1, 1917, the price is \$2.5000. To all other subscribers after May 10, 1917, the price is \$3.0000 a volume, without discount of any kind. Additional postage of 50 cents to Canada and \$1.50 to foreign countries should accompany the remittance.

There will be an additional charge of 25 cents for postage to members whose remittances are not received by September 10, so that their first volume can be mailed with the September 20 issue. The three additional volumes will be mailed as received, the last one probably in the latter part of 1918.

CHAS. L. PARSONS, Secretary.

THIRD NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES, GRAND CENTRAL PALACE, NEW YORK WEEK OF SEPTEMBER 24, 1917

The Third National Exposition of Chemical Industries which opens on September 24th in the Grand Central Palace, New York, will be the largest exposition of its kind ever held at any place in the world. It will occupy three floors of the Grand Central Palace, and have about 350 exhibitors (for list see page 908).

PROGRAM OF ADDRESSES AND MOTION PICTURES

MONDAY, SEPTEMBER 24

Afternoon: OPENING ADDRESSES:

- Dr. C. H. Herty, Chairman Exposition Advisory Committee.
Dr. Julius Stieglitz, President American Chemical Society.
Dr. C. G. Fink, President American Electrochemical Society.
Dr. G. W. Thompson, President American Institute of Chemical Engineers.

Evening:

MOTION PICTURES

- Hydraulic Power Development.⁴
Making a Giant Steam Turbine (General Electric Company).
(a) Handling Pig Iron.
(b) Filling the Cupola and Pouring Castings.
(c) Machinery and Assembling the Castings.
Generation of Electric Power.²
Transmission of Electric Power.¹
The Fixation of Atmospheric Nitrogen by Electricity at Niagara Falls and Feeding the Soil with the Products.³ American Cyanamid Company.
The King of the Rails or The Evolution of Transportation⁵ (General Electric Company).

TUESDAY, SEPTEMBER 25

Afternoon:

MOTION PICTURES:

- Carpet Weaving.¹
Manufacture and Use of Wool and Its Products.²
Cotton as a Source of Wealth—Growing and Manufacturing Its Products.³
The Manufacture of Leather and Its Products.¹
(a) Tanning.
(b) Working up Leather.
(c) Manufacturing of Shoes.

The Manufacture of Glass.²

LECTURE:

- Dr. Alexander Silverman of the University of Pittsburgh "Glass Manufacture."

Evening:

ADDRESSES:

- Dr. M. T. Bogert, Chairman Chemical Committee, National Research Council.
"The Operation and Work of the National Research Council for the National Weal."
Dr. F. W. Lewis, Chairman U. S. Tariff Commission.
"The Tariff Commission and Its Operation."
Dr. Crammel Jones, Technical Expert to U. S. Tariff Commission.
"The Tariff Commission and Its Operation with Reference to the Chemical Schedule."
Motion Pictures:
Production of Spelter and Manufacture of Lead Business.
(a) Mining, ore and lead ore, concentrates.
(b) Smelting for Lead and Zinc at Joplin and Henrietta.
Production of Commercial Lead from the ore by the Picher Process.
(c) Manufacture of Carbonate of Lead for Paint Pigment.
(d) Manufacture of Lead Pigments.
John R. Macdonald, Assistant General Sales Manager, Eagle-Picher Lead Co.

Wednesday, September 26

Evening:

- Meeting of the Technical Association of Pulp and Paper Industry.

MOTION PICTURES:

- Manufacture and Use of Liquid Fuel.
The Cordage Industry.⁴
Manufacture of Soap.¹
The Soap Industry.²
The Manufacture of Soda Ash.³

Evening:

- Address:
Mr. W. A. Rife, President National Lead Company.
"The Lead Industry."
Dr. C. H. Fink, President American Electrochemical Society.
"The Electrochemical Industry."
Motion Pictures:
Manufacture of Soda Ash by the Lehigh Valley Process.
(a) Mining and Smelting of Soda Ash.
(b) Production of Soda Ash.
(c) Production of Soda Ash by the Lehigh Valley Process.
(d) Production of Soda Ash by the Lehigh Valley Process.
(e) Production of Soda Ash by the Lehigh Valley Process.
(f) Production of Soda Ash by the Lehigh Valley Process.
(g) Production of Soda Ash by the Lehigh Valley Process.
(h) Production of Soda Ash by the Lehigh Valley Process.
(i) Production of Soda Ash by the Lehigh Valley Process.
(j) Production of Soda Ash by the Lehigh Valley Process.
(k) Production of Soda Ash by the Lehigh Valley Process.
(l) Production of Soda Ash by the Lehigh Valley Process.
(m) Production of Soda Ash by the Lehigh Valley Process.
(n) Production of Soda Ash by the Lehigh Valley Process.
(o) Production of Soda Ash by the Lehigh Valley Process.
(p) Production of Soda Ash by the Lehigh Valley Process.
(q) Production of Soda Ash by the Lehigh Valley Process.
(r) Production of Soda Ash by the Lehigh Valley Process.
(s) Production of Soda Ash by the Lehigh Valley Process.
(t) Production of Soda Ash by the Lehigh Valley Process.
(u) Production of Soda Ash by the Lehigh Valley Process.
(v) Production of Soda Ash by the Lehigh Valley Process.
(w) Production of Soda Ash by the Lehigh Valley Process.
(x) Production of Soda Ash by the Lehigh Valley Process.
(y) Production of Soda Ash by the Lehigh Valley Process.
(z) Production of Soda Ash by the Lehigh Valley Process.

THURSDAY, SEPTEMBER 27

FRIDAY, SEPTEMBER 28

Afternoon Symposium on National Resources for Chemical and Allied Industries.
Mr. C. H. Crawford, Assistant to President, Nashville, Chattanooga & St. Louis Ry.
Mr. V. V. Kelsey, Chemist-Industrial Agent, Carolina, Clinchfield & Ohio Ry.
Dr. T. P. Maynard, Mineralogist-Geologist, Central of Georgia Railway.
Dr. B. A. Schubert, Mineralogist-Geologist, Norfolk & Western Railway.
Mr. J. H. Watkins, Geologist, Southern Railway.

Evening Meeting of the American Institute of Chemical Engineers.

MOTION PICTURES:
The Metal Industries:
1. Silver, "The Treasure of the Incas."
2. Gold, "The Basis of Business."

1 reel. 2 reels. 3 reels. 4 reels.

Afternoon **MOTION PICTURES:**
Asbestos as Fire Protection.¹
Building of Roads and Their Maintenance¹ (DuPont de Nemours Company).
Framing with Dynamite (DuPont de Nemours Company).
The Sugar Industry.²
The Flour Industry.³
Meeting New York Section, American Chemical Society.

SATURDAY, SEPTEMBER 29

Afternoon **MOTION PICTURES:**
The Manufacture of Portland Cement.¹
Triumph of the Ultramicroscope.¹ Seeing Invisible Colloid Particles.
The Milk Industry.²
Preparation of Condensed Milk.³

LIST OF EXHIBITORS AT THE THIRD NATIONAL EXPOSITION OF CHEMICAL INDUSTRIES

COMPLETE AS FURNISHED BY THE MANAGERS OF THE EXPOSITION ON AUGUST 27, 1917

Abbe Engineering Company
Abbe, Paul
Ackerberg Company, H. R., Inc.
Ainsworth & Sons, Wm.
Alberene Stone Company
American Aniline Products, Inc.
American Bitumatic Enamels Company
American Chemical Mfg. Company, Inc.
American Chemical Society—Alabama Section
American Coal & By-Products Coke Company
American Cyanamid Company
American LaFrance Fire Engine Company, Inc.
American Metal Company, Ltd.
American Synthetic Dyes, Inc.
American Synthetic Color Company
American Steel Package Company
American Transformer Company
Amalgamated Dye & Chemical Company
Anaconda Copper Mining Company
Angel, H. Reeve, & Company, Inc.
Anti-Hydro Waterproofing Company
Aqua Chemical Company, Inc.
Arkell Safety Company
Armstrong Cork Company
Arnold, Hoffman & Company
Badger, E. B., & Sons Company
Baker, J. T., Chemical Company
Barber Asphalt Paving Company, Inc.
Barrett Company
Bausch & Lomb Optical Company
Beach-Ruess Company
Beckers, Wm. Aniline & Chemical Company
Benzol Products Company
Bethlehem Foundry & Machine Company
Blaikiston's, P., Son & Company
Bloede Company, Victor G.
Boyer Oil Company
Brassard Company, Inc.
Bristol Company, The
Brown Instrument Company
Buffalo Foundry & Machine Company
Butterworth-Judson Corporation
Calco Chemical Company
Campbell, John, & Company
Canadian Chemical Journal
Carborundum Company, The
Carolina, Clinchfield & Ohio Railway
Carrier Engineering Corporation
Castner Electrolytic Alkali Works
Celite Company of America
Celluloid Zapon Company
Central Dyestuff & Chemical Company
Central of Georgia Railway
Central Scientific Company
Chemical Catalog Company
Chemical Company of America, Inc.
Chemical Construction Company
Chemical Pump & Valve Company
Chile Exploration Company
Chromos Chemical Company
Clark's Iron Foundry
Clenzall Machine Company of America
Condensate Company of America
Consolidated Gas, Electric Light & Power Company
Randall Pettet Company
Contact Process Company
Coors Chemical Porcelain Company
Corning Glass Works
Corn Products Refining Company
Crane Company
Crescent Color & Chemical Works, Inc.
Consolidated Color & Chemical Company
Day Company, J. H.
De Laval Separator Company
Denver Fire Clay Company
Detroit Chemical Works
Detroit Range Boiler Company
Devine Company, J. P.
Diamond State Fibre Company
Dorr Company, The
Dow Chemical Company, The
Downingtown Mfg. Company
Dräger Oxygen Apparatus Company
Draper Manufacturing Company, The
DuPont, E. I., de Nemours & Company
Dunlon, E. L., de Nemours & Company
Dye Products Chemical Company
Edison, Thomas A., Inc.
Eimer & Amend
Electro-Bleaching Gas Company
Electron Chemical Company
Electrolytic Zinc Company, Inc.
Elmore, G. H.
Elyria Enamelled Products Company
Empire Chemical Company
Equitherm Control Corporation
Everlasting Valve Company
Fleisher & Company, W. L., Inc.
Foote Mineral Company, Inc.
Foundation Company, The
Foxboro Company, The
Franco-Swiss Dyes, Inc.
Freeport Sulphur Company
Fuller Engineering Company
Garriges, Chas. B., Company
Geisenheimer & Company
General Bakelite Company
General Chemical Company
General Ceramic Company
General Electric Company
General Filtration Company, Inc.
Glens Falls Machine Works
Gordon Engineering Corporation
Goulds Manufacturing Company, The
Greiner, Emil, Company, The
Guernsey Earthenware Company
Hardinge-Conical Mill Company
Harrison Safety Boiler Works
Hayward & Company, S. F.
Hellenic Chemical & Color Company
Hemingway, Frank, Inc.
Hepworth Company, S. S.
Hercules Engineering Corporation
Herold China & Pottery Company
Hood, B. Mifflin Brick Company
Hooker Electrochemical Company
Hoskins Manufacturing Company
Houston Real Estate & Loan Company
Hull Electrostatic Separator Company
Hunt Dry Kiln Company
Huyck, F. C., & Sons
Imperial Color Works, Inc.
Imperial Dyeework Company, Inc.
Independent Chemical Company
Industrial Filtration Corporation
International Equipment Company
International Glass Company
Janney, Steinmetz & Company
Jewell Polar Company
Kalbfleisch Corporation
Kelly Filter Press Company
Kewanee Manufacturing Company
Keystone Fibre Products Company, Inc.
King Chemical Company
Klett Manufacturing Company, Inc.
Klipstein, A., & Company
Knoxville Board of Trade
Koppers Company, H.
Laboratory Supply Company, The
Lead Lined Iron Pipe Company
Leeds & Northrup Company
Lehigh Car Wheel & Axle Works
Lehigh Foundry Company, The
Lehigh Stoker Company, The
Life Saving Devices Company
Little, Arthur D., Inc.
Lummus, Walter E., Company, The
Lunenburg, Emil F.
Lunkenheimer Company
Luzerne Rubber Company
McCready Publishing Company
Macbeth-Evans Glass Company
Machinery Utilities Company
Madera Bros., Inc.
Manufacturers Record
Marden, Orth & Hastings Company, Inc.
Mattheson Alkali Works
Merck & Company
Metallurgical & Chemical Engineering
Metz, H. A., Laboratories
Metals Disintegrating Company, Inc.
Mine & Smelter Supply Company
Monarch Manufacturing Works
Monsanto Chemical Works
Moore & Simon
Mott J. L. Iron Works
Moulton Engineering Corporation
Multi-Metal Separator Screen Company
Nash Engineering Company
Nashville Chattanooga & St. Louis Railway
National Aniline & Chemical Company
National Gum & Mica Company
New Process Chemical Company
Newport Chemical Works, Inc.
New York Revolving Portable Elevator Company
Niagara Alkali Works
Nitrogen Products Company
Norfolk & Western Railway
Norton Company
Obex Company, The
Ohio Pottery Company
Oliver Continuous Filter Company
Palo Company, The
Paper, Inc.
Paper Mill & Wood Pulp News
Penn. Salt Manufacturing Company
Pfaudler Company, The
Philadelphia Quartz Company
Pneumator Company, Inc.
Pratt Engineering & Machine Company
Precision Instrument Company
Precision Thermometer & Instrument Company
Process Engineers, Ltd.
Product Sales Company, The
Prest-o-Lite Company
Provost Engineering Corporation
Pyroelectric Instrument Company
Quigley Furnace Specialties Company
Raritan Copper Works
Raymond Bros. Impact Pulverizer Company
Research Corporation
Research Laboratory of Chicago
Roessler & Hasselacher Chemical Company
Ruggles-Coles Engineering Company
Schaar & Company
Schaeffer & Budenberg Manufacturing Company
Schaum & Uhlinger, Inc.
Schutte & Koerting Company
Scientific Equipment Company
Scott & Company, Ernest
Semet-Solvay Company
Seydel Manufacturing Company, The
Sharpley Specialty Company, The
Shriver & Company
Sidio Company of America, The
Solvay Process Company
Southern Railway System
Sowers Manufacturing Company
Squibb, E. R., & Sons
Sparks, John C.
St. George Chemical Company
Stamford Manufacturing Company, The
Standard Aniline Products, Inc.
Standard Emarex Company
Stevens-Aylsworth Company
Stokes, F. J., Machine Company
Sturtevant Mill Company
Sweetland Filter Press Company
Swenson Evaporator Company
Tank Equipment Company
Takamine Laboratory
Taylor Instrument Companies
Tenn. Coal, Iron & Railroad Company
Textileather Company
Textile Color
Textile World Journal
Thermal Syndicate, Ltd., The
Thwing Instrument Company
Toch Bros.
Tolhurst Machine Works
Trade News Service
Uehling Instrument Company
United Filters Corporation
United Gas Improvement Company
United Lead Company
United States Cast Iron Pipe & Foundry Company
United States Magnesite Corporation
United States Smelting Company, Inc.
Van Dyk Company
Virginia Smelting Company
Wallace & Tiernan Company, Inc.
Warner Chemical Company
Warner Klipstein Chemical Company
Warner Webster & Company
Werner & Pfeleider Company
West Texas-Mex. Company
Westinghouse Electric & Manufacturing Company
Whitall Tatum Company
Williamsburg Chemical Company, Inc.
Zapon Leather Cloth Company
Zaremba Company

NOTES AND CORRESPONDENCE

TWO LETTERS ON FULLER'S EARTH AND ITS VALUATION FOR THE OIL INDUSTRY

Editor of the Journal of Industrial and Engineering Chemistry:

While the article entitled "Fuller's Earth and Its Valuation for the Oil Industry," which appeared in the June 1917 issue of *THIS JOURNAL*, contains some interesting information which is substantially correct as far as it goes, it appears to the writer that Mr. Richert has not given the American fuller's earth producers the consideration to which they are entitled.

A more liberal consideration of the subject would acknowledge the excellent results obtained by American producers from the systematic and scientific manner in which they have developed domestic fuller's earth resources.

The sample designated as "A" in Mr. Richert's article, being of unknown origin, no practical information can be derived from the data pertaining to it, except that this earth, as a type, could not be successfully utilized in operations on a commercial scale.

The importation of German earth has never acquired any commercial significance in this country, while on the other hand some of our domestic earth has been exported to Germany, where refiners of edible oils have used it with satisfactory results. From a practical point of view therefore, consideration of German earth is superfluous, and the subject may be confined to the investigation of the domestic and English earths. The English earth examined by Mr. Richert was apparently of standard quality, as the results obtained are normal. The domestic earth, judging from the results obtained, was not at all representative of the domestic product that is being offered by American producers at the present time. The impression created by Mr. Richert's article, namely, that the English earth is much superior to domestic earth, should therefore be corrected.

Since about 1880, when fuller's earth was first used in the refining of edible oils, its use has increased steadily. Earth imported from England, because of peculiar satisfactory properties, became accepted as the standard and a very large proportion of the earth used in the refining of edible oils has been of English origin. The importation of English earth reached its maximum in 1914, but has fallen off considerably since.

The high price, shortage and irregularity of the supply of English earth naturally stimulated American enterprise and the production of domestic earth has developed remarkably. For a number of years American deposits of fuller's earth have been known which furnished earth equal and in some cases, superior, in bleaching quality, to the finest English earth. The domestic earth, however, was objectionable on account of the high percentage of oil which was retained by the earth in the filter press and also on account of the tendency to heat and even ignite when compressed air was blown through the press in the process of emptying the press. The amount of oil retained by English earth in best commercial practice is frequently claimed to be as low as 8 per cent, but a more average figure would be 12 to 15 per cent. With domestic earth of the past, the retention has been as high as 30 per cent and generally not below 20. The greatest objection to the use of domestic earth, however, was its so-called "pyrophoric" nature or its tendency to fire when blown. There is no doubt of the fact that if the domestic earth could have been blown in the same manner as English earth, the percentage of oil retained would have been materially reduced.

In order to overcome these objectionable features, very thorough investigations have been made, and considerable experimental work has been done by both producers and users of fuller's earth. Some grades of earth which have failed to respond to treatment have been abandoned, while efforts have been concentrated upon those which have shown most promise.

Methods of milling, grinding and drying have been studied and varied with gratifying results. Methods of using the earth in actual practice have been investigated. Some domestic earths may now be treated in exactly the same manner as English earth with equally satisfactory results; others, under certain conditions, require special treatment. A large Texas producer has invented a process for washing the earth in the press with hot water, which is claimed to reduce the retention of oil several per cent below the best results obtained with English earth.

The American fuller's earth industry is passing through a period of transition and conditions have changed materially from what they were only a year ago. Domestic fuller's earth now being offered to the trade is the result of sound, scientific investigation; it is in many ways equal, if not superior, to the standard English earth and its use has become so firmly established that it is doubtful that English earth will ever resume the important position in the oil industry that it occupied previous to the war.

In making these remarks, it has been the aim of the writer not to direct unfriendly criticism to the article written by Mr. Richert, but merely to correct any erroneous impressions which may have been made by drawing general conclusions from the data presented by Mr. Richert.

WALL-BENNETT INSTITUTE
Chicago, July 16, 1917

R. J. QUINN

Editor of the Journal of Industrial and Engineering Chemistry:

In reply to Mr. Quinn's criticism, I wish to state that the article entitled "Fuller's Earth and Its Valuation for the Oil Industry," was written merely to describe a cheap and quick method of determining, in the laboratory, the efficiency and economy of fuller's earth. The data presented were selected out of a list of numerous earths with the point in view of showing that bleaching power and absorption value, considered with the price of the raw materials, fix the economical value of the earths.

At the time of writing the article, November 1916, the relative merits of English and American earths had not entered my mind; on the other hand, up to that time I had not found a single American earth that would economically compare with the standard English earth.

That the domestic product, offered by American producers at the present time, is in many ways equal if not superior to the standard English earth is pronounced evidence of the rapid progress of the American industry.

PORESMOUTH, N. S.
August 4, 1917

THEODORE C. RICHERT

REVISION OF COBALTI-NITRITE METHOD FOR DETERMINATION OF POTASH CORRECTION

The above mentioned article appeared in *THIS JOURNAL* 9 (1917) 785. Referring to page 786, first paragraph, and after the sentence beginning, "Transfer to a mortar, mix thoroughly and grind," the following should be inserted:

"Now add 4 g. calcium carbonate to content of mortar and further mix and grind."

R. C. HART AND E. H. SCHWENKE

A NEW FILTER FLASK CORRECTION

In my article printed under the above title, *THIS JOURNAL* 9 (1917) 104, the (1) in second column at the top of drawing should include some description being given that the 8" instead of extending 4" down from the end of that tube to W.

LEE A. SHAW

WASHINGTON LETTER

By PAUL WOOTON, Metropolitan Bank Building, Washington, D. C.

Events in which chemists are interested moved rapidly in Washington during the last month. The "Chemical Alliance" was incorporated. The ceramic industry received important recognition by the Bureau of Mines when one of the three experiment stations authorized for establishment this year was assigned exclusively to ceramic work. The government bureaus handling matters of interest to the chemical industries and the committees of the Council of National Defense and of the National Research Council have effected their evolution to a war footing and are progressing much more rapidly with their work. The pyrite and manganese situations reached critical stages, to say nothing of the many other interesting matters that developed during the month.

Dr. W. H. Nichols, chairman of the Committee on Chemicals, of the Council of National Defense, feels that he has taken one of the most important steps since he has been directing the affairs of the committee in perfecting the Chemical Alliance. The need for such an organization was accentuated by the policy of the Department of Commerce with regard to the allotment of the imports of certain minerals. The organization, which is constructed on the lines of the Textile Alliance, is incorporated under the laws of Connecticut. W. H. Nichols is president; Horace Bowker, vice-president; and J. D. Cameron Bradley, secretary and treasurer. The Executive Committee consists of Henry Howard, Horace Bowker, J. D. Pennock and E. R. Grasselli. The active members of the Alliance are limited to twenty-five, but ample latitude will be given for the affiliation of associate members. The Alliance is composed of sections corresponding to the organization of the Committee on Chemicals. It was necessary, however, to add a pyrite section which is composed of A. R. Ledoux, New York, *Chairman*; Horace Bowker, New York; C. F. Burroughs, Baltimore; Henry Howard, Boston; and F. H. Nichols, New York.

The object of the organization is stated to be: To promote in all lawful ways the common interest of its members and to secure the advantages to be obtained by mutual cooperation; to acquire and disseminate information concerning trade conditions at home and abroad credits and other matters of interest; and to promote the interests of the chemical industry in all its branches.

That the country be given the opportunity to use every chemist of military age in a capacity where he can give the maximum of service has called forth very active efforts during the past month on the part of the Chemistry Committee of the National Research Council, the Technological Division of the Bureau of Mines and the Secretary of the American Chemical Society. Despite the spirit of cooperation which is actuating War Department officials it is very evident that the draft machinery neither lends itself to an adjustment which will permit of high efficiency in differentiating between men (nor to rapidity of action in obtaining detail to positions adapted to their particular training). In order that drafted men may be certain of assignment to duties where they can be of greatest service will require constant vigilance on the part of outside agencies, as has been demonstrated. It is in this work that Dr. M. T. Bogert, chairman of the Chemistry Committee, and Dr. Charles L. Parsons, secretary of the American Chemical Society, have been particularly active during recent weeks. In their efforts in this connection they are being handicapped by an evident lack of compliance with the following course of procedure which was recommended by the American Chemical Society:

"If enlisted in any capacity, inform the Secretary of the Society by postal card of the company, regiment, and corps in which you are enrolled, in order that a record may be kept of the fact and the War Department advised from time to time of chemists in the army should their services as chemists be required."

The demand for chemists for military service is increasing rapidly. In order that the already overtaxed industry may be disturbed as little as possible it is the desire to fill these places with chemists of military age. It is apparent that this will require the cooperation of the individual chemist if the plan can be worked out as effectually as is the hope. Some chemists are not reporting or calling any attention to their profession, it is understood, because they believe their chance of obtaining commissions and advancement is greater in the line of the army than in the specialized service. It is believed by those in close touch with the War Department that this is a mistaken conclusion. There is going to be a good chance of securing commissions for chemists. In addition to this, however, there is

the more important duty that men with special qualifications serve where they can do greatest good. The gas work is being widened rapidly and chemists are needed urgently. Just at this time there is an urgent need for chemists to undertake important scientific work in France. This demand will continue to increase as the number of American soldiers at the front is augmented. The Ordnance Division of the War Department also is in need of chemists; the manufacture of a variety of chemical products, the testing and analysis of materials, and the general inspection and control of these products as well as foodstuffs will call for a very large number of men in the chemical profession.

When carefully collected information indicated to Van. H. Manning, the director of the Bureau of Mines, that the lack of progress in the ceramic industry is due almost entirely to lack of technical knowledge, he decided to give aid in the way of a government experiment station. Two years ago Congress authorized the establishment of ten mining experiment stations, three of which were to be established each year. The three first stations went to Butte, Tucson and Fairbanks. One of the second three has been awarded to the iron-mining district of Lake Superior, another will be assigned to the petroleum industry and the third goes to the ceramic industry. The fact that this latter industry should have received such prompt consideration, when the demand for the stations is so great, is regarded as the best indication that the importance of ceramic activities is at last being appreciated.

The ceramic station will be located at Columbus, Ohio. It will be in charge of R. T. Stull, who is a widely known ceramist. An agreement has been signed whereby the School of Ceramics of the Ohio State University will give valuable assistance to the station. This will enable Dr. Stull to have the advice and assistance of such well-known ceramists as Prof. Edward Orton and Prof. Arthur S. Watts. As 20 per cent of the value of ceramic ware is represented by the fuel consumed, one of the first problems that will be attacked at the new station will be the prevention of fuel waste.

Wide divergence of opinion as to the best policy to pursue with regard to the importation of iron pyrites and manganese has led to strenuous activities on the part of those interested. One group is anxious to secure a large allotment of tonnage so that imports may be increased decidedly and reserves built up. Those contrarily minded believe that as few vessels as possible should be kept in this trade so that the shipping may be released for more important uses and more encouragement can be extended to the domestic industries. The matter is being considered by the Shipping Board and other governmental agencies.

In the controversy which has been raging, it is pointed out, on the one hand, that the average delay to shipping that is diverted from Gibraltar to Huelva, Spain, to take on pyrites, is 10 days. With the establishment of a reserve of food and equipment for our armies and those of our allies being limited by the lack of shipping, it is argued that pyrite should be imported only for the needs that can not be met by local production. This is met by the contention that the delay to shipping is insignificant in comparison with the harm that would be done vital industries and retardation of crops that would result from an eleventh-hour attempt to stimulate mining enterprises that in themselves would call forth vast sums of capital and huge expenditures of labor that are much needed in other directions.

The same argument is applied to the manganese situation. The condition with regard to that valuable alloy metal, however, is more acute, as two months are required to make the round trip voyage to Brazil, and from the fact that it enters more immediately into materials needed for the prosecution of the war. In addition, it is declared that the prospect of securing within the United States supplies sufficient for domestic needs is not as good as is the case with pyrite.

It is admitted by all concerned that the controversy just at this time is most unfortunate as the prospect of securing more ships for these imports is discouraging the investment of capital in domestic development. It is believed that a medium course can be arrived at, which, by intelligent variation, will be for the best interest of the nation as a whole.

Commandeering by the government of three ships engaged in the sulfur trade between Louisiana and Atlantic coast points has brought forth a vigorous protest from Dr. Nichols of the Committee on Chemicals. While the matter is being considered by the proper authorities, Dr. Nichols is using every effort to in-

duce other vessels to enter the trade. It is feared that such action will tend to discourage Great Britain in her efforts to aid in supplying the deficiency in the pyrite supply.

The work of the Internal Revenue Bureau's laboratory, which has been described in an official announcement as a discovery of a process for securing glycerine from sugar, has been referred to the Food Administrator.

Dr. Nichols reports that decided progress is being made in the matter of stripping illuminating gas. The matter is also being urged by the War Industries board. Many municipal utilities commissions have consented to a change of standard which will permit the removal of the toluol from their illuminating gas.

War work, which now occupies practically all of the time of Dr. W. F. Hillebrand and his associates at the Bureau of Standards, is being accelerated by the fact that they are now occupying

the Chemistry Building. The new edifice is one of the best equipped for chemical research in the country.

Most of the work being done in the chemical division of the Bureau of Standards is of such a nature that comment on it would be of value to the enemy. While many additional members have been added to the chemical staff, it has become practically impossible to continue much of the regular work of the division. Time has been found, however, in which to take up the examination and analysis of reagents, which is to be conducted in cooperation with the American Chemical Society. An agent of the Bureau of Standards will pay a visit in the near future to all manufacturers of reagents to gather the data necessary to the conduct of the research.

The Bureau is about to take up a special study of platinum metals and their alloys with each other. The work on chemical glassware and porcelain has been completed. The conclusions reached will be presented at the Boston Meeting of the American Chemical Society.

PERSONAL NOTES

Dr. Charles K. Francis, for the past seven years chemist and professor of petroleum technology in the Oklahoma Agricultural and Mechanical College, has resigned to become chief chemist for the Cosden Oil Co., Tulsa, Okla.

Dr. Raymond Freas has been appointed adjunct professor of chemistry in the University of Virginia.

Dr. Hardee Chambliss, chemical director of the Commercial Acid Co., St. Louis, has been commissioned Major in the Ordnance Section of the Officers' Reserve Corps.

Mr. E. E. Fickett, of the department of chemistry of Washington University, has been with Hildreth & Co., engineers of New York City, for a part of the summer. His work has been the inspection of pig iron for one of the allied governments.

Mr. H. J. Brownlee, formerly with the Redman Chemical Products Co., has enlisted with the Engineers' Corps of Kansas City.

T. Dale Stewart, instructor in chemistry at the University of Chicago during the past year, goes to the University of California as instructor in organic chemistry.

Dr. G. O. Wendt, instructor in chemistry at Rice Institute during the past year, has been appointed instructor of quantitative analysis at the University of Chicago.

Wm. D. Turner, associate in chemistry at the University of Chicago, goes to the Missouri School of Mines, Rolla, as assistant professor of chemistry.

Prof. E. V. McCollum has resigned his position as professor of agricultural chemistry at the University of Wisconsin, to take charge of the department of chemistry of the new school of hygiene and public health established by the Rockefeller Foundation in connection with the medical school of Johns Hopkins University.

Prof. Edward G. Mohr, of Purdue University, has taken charge of metallographic work in the laboratory of Sears, Roebuck & Co., until school opens this fall.

Mr. Arthur L. Israel, of Chicago, is serving as Captain in the Quartermaster's Office, Southeastern Department, Charleston, S. C.

Mr. L. E. Warren, for eight years associate chemist in the chemical laboratory of the American Medical Association, has resigned his position to take charge of the research laboratories of the New York plant of Wm. R. Warner & Co.

Mr. George B. Houghston, formerly with the International Silver Co., Meriden, Conn., has joined the research forces of the Scovill Manufacturing Co., Waterbury, Conn.

Dr. H. B. North, associate professor of chemistry, Fitzer College, has recently resigned his position in order to become director of the Research Laboratories of the York Metal & Alloy Co., York, Pa.

Mr. Forest Rutherford, for many years superintendent of reduction works for the Copper Queen Consolidated Mining Company, Douglas, Ariz., severed his connections with the company on June 1 and will establish himself as a consulting metallurgical engineer.

Peter MacEwan, editor of the *Chemist and Druggist*, died suddenly at Highgate, England, on May 16, aged sixty. Mr. MacEwan joined the editorial staff of the *Chemist and Druggist* in 1885, becoming editor in 1899, a position he filled with conspicuous success.

Dr. Leon I. Shaw, of the department of chemistry of Northwestern University, has been advanced to the position of assistant professor of chemistry on leave of absence for one year for service with the United States Government. He has received the appointment of First Lieutenant in the Ordnance Officers' Reserve Corps.

Mr. J. C. Moar has been appointed acting manager of the Atlanta Sales Office of the Pratt Engineering & Machine Co., owing to the absence on account of illness of the manager of the office, Mr. J. B. Jacaway.

Dr. Carl L. Alsberg, Bureau of Chemistry, Washington, D. C., and Prof. E. F. Ladd, of North Dakota, have been elected to the Committee to Revise the Scope of the Association of American Dairy, Food and Drug Officials.

Edward M. Beck, vice-president and general manager of the Akron Varnish Company, and one of the best varnish research chemists in this country, died recently in a Cleveland hospital, at forty-four years of age. He had patented a number of processes for varnish manufacture, and had spent four years in the study of the chemistry of varnish in the largest plants of Germany.

Mr. Fred W. Padgett, research fellow in oil, gas and gasoline at the University of Pittsburgh for the past four years, has been appointed associate professor of chemistry in the University of Oklahoma, where he will develop a research department in oil, gas and gasoline.

The American Ceramic Society included Rochester, N. Y., in the itinerary of their Annual Science Meeting, and fifty or thirty-one members of the society visited the plant of The Fireclay Company in Lodi, Pa., and associated with them the works of Dr. W. F. C. Smith, chief chemist and technical officer of the company. The party was personally escorted to the visitors. The Fireclay Company is situated on a hill having a general strike of sandstone and shale, and their products are of the highest quality. The largest in the world devoted to the manufacture of fireclay bricks, a trip to the Lodi Fireclay Company was very interesting, after which they were taken to the plant of the Lodi Fireclay Company at Lodi, Pa., where they were met by Mr. C. M. Smith, president and general manager of the company, and after a short stay a visit to the plant of The Fireclay Company. The party departed.

Professor Abraham Henwood, presiding officer of the Philadelphia Section, A. C. S., has been granted the degree of Doctor of Science by Muhlenberg College.

Prof. Kristian Birkeland, of the University of Kristiania, the eminent Norwegian engineer, who, in conjunction with Dr. Sam Eyde, developed the well-known Birkeland-Eyde nitrogen fixation process, died in Tokyo on June 18, at 49 years of age.

A Committee on Industrial Fatigue has been organized under the Advisory Commission of the Council of National Defense, with the following membership: Dr. Thomas Darlington, New York, *Chairman*; Prof. Frederic S. Lee, Columbia University, *Executive Secretary*; Prof. R. E. Chaddock, Columbia University; Prof. Raymond Dodge, Wesleyan University; Dr. D. L. Edsall, Harvard Medical School; Mr. P. S. Florence, Columbia University; Miss Josephine Goldmark, National Consumers League; Prof. E. G. Martin, Leland Stanford University; Dr. J. W. Schereschewsky, Public Health Service; Dr. Ernest L. Scott, Columbia University. The committee is investigating munition factories and other industrial establishments that are manufacturing war supplies, with the view of showing how avoidable fatigue may be eliminated and how the greatest output of the necessities of war may be secured compatible with the maintenance of the working-power of the workers.

Mr. O. J. D. Thomas, for the last four years in charge of the technical work of the Canadian Brake Shoe Company, Sherbrooke, has been appointed chemist in charge of the new research laboratory of the E. B. Eddy Company, Hull, Que.

The Annual General Meeting of the Society of Chemical Industry was held in The University Buildings, Birmingham, England, July 18 to 20, 1917. The nominations to offices are: *President*, Prof. Henry Louis; *Vice-Presidents*, Dr. Charles Carpenter, Mr. John Gray, Mr. A. R. Ling, Prof. R. F. Rutman, and Mr. J. T. Wood; *Ordinary Members of Council*, Mr. A. G. Bloxam, Mr. W. J. Rees, Mr. Edwin Thompson and Prof. James Walker.

Dr. William Bullock Clark, eminent geologist, and professor of geology in Johns Hopkins University, died suddenly from apoplexy on July 27, at his summer home at North Haven, Maine, aged fifty-six years.

John W. Herbert, of New Jersey, has assumed his new duties as general manager of the Federal Dyestuff & Chemical Company's plant at Kingsport, Tenn. He is also chairman of the board of directors.

Dr. Martha Tracy, of the Philadelphia Section, A. C. S., has received, in course, the degree of Doctor of Public Hygiene from the University of Pennsylvania.

Dr. Henry Kraemer will succeed the late Dr. Julius O. Schlöterbeck as professor of pharmacognosy of the College of Pharmacy of the University of Michigan. Dr. Kraemer has been for twenty years professor of botany and pharmacognosy at the Philadelphia College of Pharmacy. He has been the editor of the *American Journal of Pharmacy* for nearly twenty years, and is the author of several standard text-books on botany and kindred subjects.

Mr. Albert F. Ganz, professor of electrical engineering at Stevens Institute of Technology, and a member of the American Electrochemical Society since November, 1908, died at his-home in Hoboken, N. J., on July 27, 1917. Prof. Ganz made many valuable scientific and commercial tests and investigations, and was well known in the electrical world.

Mr. A. W. Gauger has resigned as secretary of the Pittsburgh Section, A. C. S., and has been granted a leave of absence by the Bureau of Mines to accept a commission as first lieutenant in the Sanitary Engineering Corps of the U. S. military forces. Mr. Gauger has been connected with the Bureau of Mines in Pittsburgh as a gas chemist. He is the third officer of the Pittsburgh Section to receive a military commission.

The Informal Congress and Re-union of the American and Canadian Engineers and Architects of Norwegian birth or descent will be held at Chicago Norske Klub, September 27 to 29, 1917. Address correspondence to Joachim G. Glaver, chairman of Committee on Arrangements, Railway Exchange Building, 80 E. Jackson St., Chicago.

Mr. W. Rabak, formerly instructor in the chemical department of the University of Nebraska, has accepted a position in the laboratory of the American Medical Association.

Mr. A. W. Phillips, formerly superintendent of the Aetna Explosive Company's guncotton plant at Gary, Ind., and for the past year general superintendent of the Aetna Chemical Company's Canadian smokeless powder plant at Drummondville, P. Q., has resigned that position to accept the superintendency of the synthetic acetone plant of the Canadian Electro-Products Company at Shawinigan Falls, Quebec. R. A. Lockery, operating superintendent at the Drummondville plant, succeeds Mr. Phillips.

Thomas C. Craven, formerly of Madero Brothers Company, has been elected president of the Keystone Chemical Supply Company, of Philadelphia, to succeed C. H. Scarborough.

Mr. Leo P. Nemzek, chief chemist for several years at the plant of John Lucas & Co., Inc., Gibbsboro, N. J., has joined the staff of Harrisons, Inc., as paint expert.

As a war measure the new office of assistant director of the Bureau of Mines has been created. Mr. Frank de Wolf, director of the Geological Survey of Illinois, has been selected for this post and will assist Director Manning in the administration of the extensive mineral deposit survey of the Bureau of Mines, with especial supervision over mineral supplies for war needs. The Illinois Survey has loaned Mr. de Wolf's services to the government for a period of three months, with salary and expenses paid.

The largest Safety and Sanitation Congress and Exposition ever held will take place at the Grand Central Palace, New York City, September 10 to 15, 1917, under the auspices of the National Safety Council and the American Museum of Safety. Thousands of safety devices and demonstrations of accident prevention will be on view at the Exposition, which will cover three floors of the Palace and be open to the public for a week.

Dr. Charles F. Chandler, emeritus professor of chemistry of Columbia University, has been dangerously ill at his summer home in New Hartford, Conn. Word received August 18th stated that he was improving rapidly from a serious operation and that it was thought he would be able to sit up the following week.

A get-together meeting will be held by the Technical Association of the Pulp and Paper Industry at the Third National Exposition of Chemical Industries, Grand Central Palace, New York City, on September 26, the day before the opening of their Fall Meeting at Holyoke, Mass. The invitation from the management of the Exposition was accepted by the Association at their Spring Meeting in Neenah, Wis. The Exposition authorities have offered free headquarters and meeting rooms, with every facility for the comfort and convenience of the members.

The Technical Association of the Pulp and Paper Industry will hold its Ninth Meeting at Holyoke, Mass., September 27 to 29, 1917, with headquarters at Hotel Nonotuck. The convention will open on Thursday morning, September 27, at the Knights of Columbus Hall, with an address of welcome by the mayor of the city, followed by responses for the Association. President Caruth will then deliver an address reviewing the work of the Association, after which the reports of officers and committees will be presented and discussed. The afternoon session will open with a paper by Prof. H. O. Keay, of McGill University, on "An Investigation of Stresses in Digester Shells." Other papers for this session include, "A Review of Different Processes for Causticizing Sodium Carbonate Liquors and the Separation of the Sludge," by Martin L. Griffin, Oxford Paper Co., Rumford, Me., and "Some Observations on the Retention of China Clay by Paper Pulp," by Dr. Otto Kress and G. C. McNaughton, Forest Products Laboratory, Madison, Wis. In the evening a banquet will be served at the Hotel Nonotuck, with Arthur C. Hastings, president of the American Writing Paper Co., as toastmaster. The program for Friday, September 28, provides a round of visits to the numerous paper mills of Holyoke, South Hadley Falls and vicinity. Saturday, September 29, will be devoted to an automobile tour of the papermaking centers in the Berkshire Hills. Members who wish to concentrate their visits of inspection to particular mills should communicate with the chairman of the Mill Visiting Committee, Wm. L. Nixon, Chemical Paper Manufacturing Co., Holyoke. If in doubt on any point concerning railroad arrangements, communicate with the chairman of the Transportation Committee, George E. Williamson, Strathmore Paper Co., Mittineague, Mass.

INDUSTRIAL NOTES

The Barrett Company, Frankford, Philadelphia, have given a contract for the erection of a one-story reinforced concrete building, to cost about \$40,000, for the manufacture of coal-tar by-products.

It is reported from England that the discovery of a new method of nitrogen fixation from the air has been made by a British subject and that a plant for the manufacture of nitrogenous products from this nitrogen is in process of construction at Manchester, England, and should be working within six months. National considerations preclude details being given at present, but it is believed that with this process nitrogen can be "fixed" anywhere in England at a very low cost and with the highest efficiency ever achieved by any nitrogen fixation process. The International Nitrogen & Power Co., 8 Waterloo Place, London, hold the exclusive rights to work the process in Great Britain.

Sarco Company, Inc., of New York, have received orders for temperature regulators for each of the sixteen cantonment camps, as well as for the Selfridge Aviation Field, near Mount Clemens, Mich., and the League Island Navy Yard at Philadelphia.

According to *The Chemical Technology* the third balance sheet of the Nippon Dyestuff Manufacturing Company shows a total loss of about 30,000 yen. The Government subsidy, however, is about 120,000 yen.

A new celluloid-like product called "Satalite" has been invented by Mr. S. Sato, assistant professor in Sendai University, and The Satalite Company has been established with a capital of 2,000,000 yen (about \$1,000,000). Satalite is a galalith made of glucose of soya bean coagulated by formaline. It is said to be produced much cheaper than ordinary celluloid and to have more merits in its use than the latter. The factory is to be built at Mukojima and the actual manufacturing will begin this autumn.

The Grasselli Chemical Company, Cleveland, O., has entered the manufacture of high explosives by the incorporation under Ohio laws of the Grasselli Powder Company, a \$5,000,000 concern, which will take over the American High Explosives Co., the Burton Powder Co., and the Cameron Powder Manufacturing Co. Mr. Job Burton, of Pittsburgh, now president of the Burton Powder Co., will be the president of the new organization.

It is stated in the *New York Journal of Commerce and Commercial Bulletin* of July 30th, that a simple process for manufacturing nitric acid direct from coal gas, or other gases, by compression and subsequent explosion, has been applied in Germany with success. Experiments conducted before the war by Prof. Haeusser on waste gases from coke ovens demonstrated its practicability and the method has since been developed to meet war conditions. Further details are given in the above reference.

The du Pont Company have formally announced their entrance into the dye industry, and it is expected that the dye plant being built at Deepwater Point, N. J., adjoining the Company's chemical department, will be ready for business in a few months.

The du Pont Company announce the opening of their dyestuff sales department for New England, at Turk's Head Building, Providence, R. I., with George M. Snow, manager, and Charles H. Hudson, assistant manager.

The Nitrogen Fixation Corporation has been incorporated in New York by Messrs. J. F. A. Consett, J. R. Rubin and S. M. Weil, with a capital of \$1,000,000, to manufacture chemicals and allied specialties.

According to the *Nouvelles Presse* there have been great developments in the Austrian chemical industry during the war. Calcium nitrate and nitric acid are new industries, founded on the utilization of nitrogen from the air. Sulfuric acid plants have been extended and new factories set up for the manufacture of benzene, toluene, glycerin, acetone and chlorine.

Manufacturing will begin immediately in the new belt factory of the Chas. A. Schieren Company, of New York City, built as an addition to its tannery at Bristol, Tennessee. The buildings are entirely completed and the equipment of machinery is being installed for the manufacture of the machine belts, the greater portion of which will be shipped to southern plants. A working force sufficient to produce 24,000 lineal feet of belting daily will be employed at the start and gradually added to, as skilled help can be secured, until the full capacity of the plant, 50,000 feet daily, is reached.

Charles Engelhard, 30 Church St., New York City, is now producing a new Pyrometer tube, corresponding to the Marquardt Mass imported tubes.

The Solvay Process Company, Syracuse, N. Y., have issued a new edition of their Blue Book entitled "Solvay Alkali," owing to the popularity of the preceding edition as a ready reference book. The book deals with the various forms and uses of alkali and contains notes on alkalimetry and various chemical and commercial tables useful to the consumer.

With a view to the development of the British chemical industry after the war, in consequence of the capture of the German trade, the Council of the Liverpool University Committee has formed an advisory committee consisting of four members of the chemical staff of the University and six members representing Brunner-Mond, Gossage, Crofields, Salt Union, United Alkali, Lever Brothers, and Castner-Kellner.

The Research Corporation, organized under the laws of New York State and under the auspices of the Smithsonian Institution, announces the establishment of an annual fellowship open to general competition for the purpose of encouraging and assisting scientists in the prosecution of their investigations. The competition for the first scholarship is to be decided before December 1st by a jury consisting of the presidents of the National Academy of Sciences, the American Chemical Society and the Research Corporation, and the secretary of the Smithsonian Institution. The fellowship runs for one year, but may be extended by the Corporation for two renewals of one year each, in exceptional cases, upon the recommendation of the jury. To the successful competitor the Corporation offers an honorarium of \$2,500 and their assistance in securing the privilege of laboratories specially adapted for the particular work. Discoveries or inventions which the fellow may make are to be deemed his personal property. The Research Corporation was organized as custodians of the Cottrell patents on the electrical precipitation of suspended particles, the profits from which must be applied to the advancement of scientific research and investigation.

The Senate, on August 10th, passed the Pittman Bill authorizing the exploration for and the disposition of potash and other chemical resources in Seaford Lake, California, and other portions of the public domain. The bill provides that the Secretary of the Interior shall be authorized under regulations to be prescribed by him to grant to applicants a prospecting permit which shall give the exclusive right to prospect for chlorides, sulfates, carbonates, borates, silicates or nitrates of potassium, or borates, carbonates or nitrates of sodium, or borates of calcium or associated salts in "lands of the United States not known to contain valuable deposits of the kinds above described," for a period of not exceeding two years, provided that the area shall not exceed 2,500 acres. Should such prospecting be made the permit shall be entitled to a patent of no more. The bill also contains provisions for leasing the prospecting. Every lease shall reserve to the President the right to fix the price of minerals extracted and sold from the leased premises at the expiration of time, to secure their distribution and use where within United States territory. On August 11th, the House passed a companion bill. The Committee on Public Lands, attached the bill, saying in part, "The long and short of it is that the people of the United States own the policy of conserving for the people of the United States the known means of obtaining potash, soda, and other minerals, and going back to the old and established policy that established the country a few years ago in prospecting for potash and soda and reserving a patent for such deposits." The Senate, however, declined to reconsider its vote and the bill, at this writing, is before the House, where it is expected to pass, probably with some amendment.

GOVERNMENT PUBLICATIONS

By R. S. McBride, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEES

Leasing of Oil Lands. Public Lands Committee of the Senate. 172 pp. Available only through members of Congress. This is Parts 1 to 3, inclusive, of the report on Senate Bill 45, as developed in hearings of April 13 to June 20, in reference to promotion of mining of coal, phosphate, oil, gas, potassium, and sodium on public domain.

Salvarsan. Committee on Patents of the Senate. 52 pp. Available only through members of Congress. This pamphlet reports on hearings on Senate Bill 2178, "Suspending during present emergency all rights arising out of any patent granted by United States upon any compound or medicine of which salvarsan is a constituent part" and on Senate Bill 2363, "Authorizing Secretary of War or Secretary of Navy to manufacture for use of army, navy, or the people of United States any drug, medicine, or other remedy or device which is protected by patent or patents, trade-mark or trade-marks, and which cannot be procured at reasonable price within United States."

Nitrate of Soda. Appropriations Committee of the House of Representatives. 26 pp. A report of hearing before subcommittee on Senate Joint Resolution 31 to appropriate \$10,000,000 for purchase of nitrate of soda for use as fertilizer, including statements of David F. Houston and Ellison D. Smith.

Niagara River Water Power. Foreign Affairs Committee of the House of Representatives. Report of hearings on Senate Joint Resolution 13 on "Diversion of Water from Niagara River," including statements of Newton D. Baker and others, May 25 to June 6. Two parts, a total of 93 pp. Also, Report to accompany House Joint Resolution 109, 1 page, dated June 26; numbered House Report 87.

COUNCIL OF NATIONAL DEFENSE

Organization of the Council of National Defense. 26 pp. This pamphlet shows the personnel, committees, and interrelations of parts of the Council. Issued June 11.

Medicines, Antiseptics, Disinfectants, etc. 27 pp. Issued June, 1917. This is Part 2 of a list of staple medical and surgical supplies selected to meet war conditions by the Committee on Standardization appointed by the Council of National Defense.

FEDERAL TRADE COMMISSION

News-Print Paper Industry. Unnumbered pamphlet. 162 pp. Paper, 10 cents. Issued June 13. This contains a general description of the news-print paper industry, jobbers' commissions and margins of gross profit, cost and profits of manufacture, supply and demand factors, evidence of violations of anti-trust laws, and statistical data of interest. This report and letter of transmittal, with the final report of the commission is also available as Senate Document 49.

Book-Paper Industry. Senate Document 45. 11 pp. This is a preliminary report only.

Report on Beet Sugar Industry in United States. House of Representatives' Document 158. 164 pp. Paper, 20 cents. This report covers a 5-year period, ending with the season of 1913-1914.

NATIONAL ACADEMY OF SCIENCES

Annual Report for Calendar Year 1916. 94 pp. Paper, 10 cents. Also available as Senate Document 707 of Second Session of 64th Congress.

NATIONAL MUSEUM

Remarkable Occurrence of Calcite in Silicified Wood. EDGAR T. WHERRY. Separate No. 2200 from Proceedings of the U. S. National Museum, Vol. 53 (June 1, 1917). 4 pp. and 3 plates.

PUBLIC HEALTH SERVICE

Biological Products. ANONYMOUS. "Public Health Reports," 32, 903-6 (June 8). This is a report including a list of establishments licensed for the propagation and sale of viruses, serums, toxins, and analogous products.

Mechanical Fans. Their Use to Increase the Efficiency of Fumigating Gases. S. B. GRUBBS. "Public Health Reports," 32, 699-702 (May 11). "There are practical difficulties to the routine use of fans during fumigation, but if these are overcome the procedure will be of considerable value. Electric fans are often found in the living quarters of vessels or in buildings, and when possible these should be used when such places are fumigated."

WATERTOWN ARSENAL

Report of Tests of Metals and Other Materials. Unnumbered publication. 328 pp. and numerous plates. Cloth, \$1.00. This is a report for the fiscal year, 1915, on the tests made at the Watertown Arsenal of metals and other materials.

GEOLOGICAL SURVEY

Tungsten Minerals and Deposits. FRANK L. HESS. Bulletin 652, 73 pp. Paper, 25 cents. "An attempt is made to gather into this bulletin the known general facts about tungsten, the minerals in which it is found, the kinds of deposits from which these minerals have been obtained, and other information which will answer as many as possible of the questions asked the Survey, and to show by illustrations, colored and uncolored, the appearance of typical specimens of the various tungsten minerals. The purpose has been to make this paper of interest and use to the prospector and miner, and also to those who have no particular knowledge of minerals."

Sand-Lime Brick in 1916. JEFFERSON MIDDLETON. Mineral Resources of the United States, 1916, Part II, pp. 5-6. Published May 31. 2 pp. "The sand-lime brick industry made considerable progress in 1916. Both the quantity and the value of the material sold showed large increase compared with 1915, the value reaching its maximum and exceeding that of 1913, the previous year of maximum value, by \$235,748, or 19 per cent. This industry, in common with others, suffered considerably from scarcity of labor; otherwise the output in 1916 would probably have been even larger. The prospects for 1917 appear to indicate that the output and value for 1916 will be exceeded."

Geology and Ore Deposits of the Mackay Region, Idaho. JOSEPH B. UMPLEBY. Professional Paper 97, 115 pp. Paper, 35 cents.

Zinc. C. E. SIEBENTHAL. Bulletin 666-Y, 4 pp. The following table shows the increase in spelter production and in exports of zinc and brass and their manufactures by six-month periods

during the war. The first war demands were for spelter and sheet zinc, the exports of which averaged between 10,000 and 13,000 tons a month up to the middle of 1916. During the last half of 1916 and the first three months of 1917 the exports were nearly doubled, averaging over 21,000 tons monthly. The exports of brass grew rapidly, being four times as large in the last six months as they were in the first six months of 1915, and almost doubling the monthly rate, in the first three months of 1917. The exports of manufactures of zinc and brass and also of cartridges grew rapidly, being now about seven times as great as in the first six months of 1915.

The fact that this great consumption of munitions has had no more effect on the price of spelter than to raise it to 13 cents for a short time in November and December, 1916, seems to indicate that the zinc-smelting capacity has been brought up to the point where it is able to meet every demand. In fact, it has been suggested that there has been some overproduction of spelter and that stocks have probably accumulated. Be that as it may, it is not likely that there can, under present conditions, be any further material decline in the price of spelter, for that would probably so reduce the output of sphalerite concentrates from the sheet ground of the Joplin region as to react upon the price of spelter, causing it to rise again.

SPELTER PRODUCED IN UNITED STATES AND ZINC AND BRASS EXPORTED 1914-1917

—EXPORTS OF ZINC AND BRASS—						
Spelter produced (short tons)	Spelter and sheets domestic foreign & dutiable (short tons)	Zinc dross (short tons)	Brass brass (short tons)	Old brass (short tons)	Value of manufactures of zinc and brass including cartridges	Total value of exports
1914						
Jan.-June, 175,058	2,878	286	1,542	6,774	\$3,841,237	\$6,337,416
July-Dec., 177,991	72,490	2,249	2,015	3,582	6,712,225	17,162,383
1915						
Jan.-June, 216,532	70,326	2,932	18,126	4,331	25,070,587	44,088,252
July-Dec., 272,987	61,306	1,235	15,010	456	43,154,056	70,479,204
1916						
Jan.-Jun., 316,452	78,204	28	51,543	1,284	123,135,226	177,343,769
July-Dec., 351,004	128,163	20	70,723	2,194	174,210,117	253,456,204
1917						
Jan.-Mar.,	64,049	1,909	63,464	1,252	83,821,780	138,670,854

BUREAU OF THE CENSUS

Manufacture of Glass. 13 pp. This and the following three pamphlets are part of a series issued as a result of the 1914 quinquennial "Census of Manufactures." Statistics are presented in three sections: (1) Summary and analysis, which gives general data for the industry; (2) special statistics of materials, products, and methods of manufacture; and (3) State tables, giving summaries for 1904, 1909, and 1914 in comparison, as well as detailed figures for 1914.

Paper and Wood Pulp. Unnumbered pamphlet. 19 pp. (See preceding abstract.)

Flour-mill and Grist-mill Products. Unnumbered pamphlet. 20 pp. (See second preceding abstract.)

Sugar Industry. Unnumbered pamphlet. 13 pp. (See third preceding pamphlet.)

BUREAU OF FISHERIES

Mortality of Fishes on West Coast of Florida. HARDEN F. TAYLOR. Document 848. 24 pp. Paper, 5 cents. This report of the results of an investigation of excessive mortality of fishes in this locality in the late fall of 1916 includes a discussion of the possible causes, some of which relate to the chemical character of the waters at that time.

BUREAU OF LABOR STATISTICS

Industrial Poisons Used or Produced in Manufacture of Explosives. ALICE HAMILTON. Bulletin 219. 141 pp. Paper, 15 cents. This publication describes the physiological action of poisons, the processes of manufacture involved, and the methods for prevention or treatment of industrial poisoning cases in the explosives industry.

BUREAU OF MINES

Sandstone Quarrying in the United States. OLIVER BOWLES. Bulletin 124. 130 pp. Paper, 25 cents.

The Mining Industry in the Territory of Alaska During the Calendar Year, 1915. SUMNER S. SMITH. Bulletin 142. 58 pp. Paper, 10 cents.

Answers to Questions on the Flotation of Ores. OLIVER C. RALSTON. Technical Paper 149. 23 pp. Paper, 5 cents. "So rapidly is the art of flotation advancing that any complete treatise on the subject is likely to be out of date by the time it is printed. However, as the Bureau of Mines is continually receiving inquiries regarding a number of more or less practical questions that are seemingly not answered with sufficient clearness in the existing literature, attempt is made in this paper to answer such questions as are more pertinent and important. Answers to some of the questions are to be found in the literature of flotation, but the majority, possibly because they are decidedly practical, seem to have been overlooked or left unanswered. This paper does not attempt to discuss the theories put forth to account for the facts accumulated by the many experiments with flotation nor does it attempt to describe in detail flotation plants nor the procedure in different mills. Rather it seeks to answer questions that are apt to be asked by persons who wish to know the possibility of successfully applying flotation to a given ore or mixture of ores."

The treatment is by answering 24 specific questions of general interest.

Motor Gasoline. Properties, Laboratory Methods of Testing, and Practical Specifications. E. W. DEAN. Technical Paper 166. 20 pp. Paper, 5 cents. "The present paper is intended to aid the public in becoming generally acquainted with methods of testing gasoline, in the hope that a sufficiently wide application of the principles set forth will result in perfecting specifications as satisfactory as those used in transactions involving many other commodities."

BUREAU OF STANDARDS

Standardization of Bomb Calorimeters. Circular 11. 3rd Ed. Issued June 23.

Standard Samples: General Information. Circular 25. 6th Ed. Issued June 20. This revision has several minor changes and additions; it describes the system of issuing standard samples of materials, and gives rules for ordering.

DEPARTMENT OF AGRICULTURE

Experiments in the Determination of the Digestibility of Millets. C. F. LANGWORTHY and A. D. HOLMES. Bulletin 525. Contribution from the States Relations Service. 9 pp. Paper, 5 cents. Published April 7. This is a report of studies of the digestibility of millet in relation to its use as food and is of interest to investigators and students of human nutrition.

Validity of the Survey Method of Research. W. J. SPILLMAN. Bulletin 529. Contribution from the Office of Farm Management. 15 pp. Paper, 5 cents. Published April 8. A study of the accuracy of farm records obtained in farm management investigations.

The Results of Physical Tests of Road-Building Rock in 1916, Including all Compression Tests. FREDERICK HERBARD and FRANK H. JACKSON, JR. Bulletin 537. Contribution from the Office of the Public Roads and Rural Engineering. 23 pp. Paper, 5 cents. Published April 21. This is a supplement to Department Bulletin 479, and is of interest to road engineers and contractors.

Detection of Lime Used as a Neutralizer in Dairy Products. H. J. WICHMANN. Department Bulletin 524. Contribution from the Bureau of Chemistry. 23 pp. Paper, 5 cents. This bulletin will be useful to officials of State dairy and food departments.

Timber Storage Conditions in the Eastern and Southern States with Reference to Decay Problems. C. J. HUMPHREY. Bulletin 510. Contribution from the Bureau of Plant Industry. 43 pp. and numerous plates. Paper, 20 cents. Describes causes of decay in stored timber and suggests methods of prevention.

Crossities Purchased and Treated in 1915. ARTHUR M. MCCREIGHT. Bulletin 549. Contribution from the Forest Service. 8 pp. Paper, 5 cents. A compilation of statistics on the number of crossities purchased in the United States during 1915 by the steam and electric roads, and electric light, heat, and power companies.

A Comparison of Several Classes of American Wheats and a Consideration of Some Factors Influencing Quality. L. M. THOMAS. Bulletin 557. Contribution from the Bureau of Plant Industry and the Office of Markets and Rural Organization. 28 pp. Paper, 5 cents. Of interest to grain and food inspectors, and millers generally. Partial survey of the results of investigations involving milling tests with wheat and baking tests with flour.

Chemical Studies of the Efficiency of Legumes as Green Manures in Hawaii. ALICE R. THOMPSON. Bulletin 43. Hawaii Agricultural Experiment Station. 26 pp. Paper, 5 cents. Presents data giving the results of the first year's experiments to determine the relative efficiency of various species of legumes on different soil types.

Yearbook of the Department of Agriculture. 783 pp. and numerous plates. Cloth, \$1.00. This report for the calendar year, 1916, includes two articles of some chemical interest, as follows:

(1) **Some American Vegetable Food Oils, Their Sources and Methods of Production.** H. S. BAILEY.

(2) **Importance of Developing Our Natural Resources of Potash.** FREDERICK W. BROWN.

Chemical Testing of Milk and Cream. ROSCOE H. SHAW. Unnumbered publication from the Bureau of Animal Industry. 42 pp. Paper, 10 cents; issued May 10th.

A Study of Methods of Estimation of Metabolic Nitrogen. E. B. FORBES, C. E. MANGELS and L. E. MORGAN. "Journal of Agricultural Research," 9, 405-411 (June 18).

Toxicity of Various Benzene Derivatives to Insects. WILLIAM MOORE. "Journal of Agricultural Research," 9, 371-381 (June 11).

Season, and Water on the Bacterial Activities of the Soil. J. E. GREAVES, ROBERT STEWART and C. T. HIRST. "Journal of Agricultural Research," 9, 293-337 (May 28).

Effect of Decomposing Organic Matter on the Solubility of Certain Inorganic Constituents of the Soil. CHARLES A. HENSEN. "Journal of Agricultural Research," 9, 253-268 (May 21).

Relation of the Transformation and Distribution of Soil Nitrogen to the Nutrition of Citrus Plants. I. G. MCBETH. "Journal of Agricultural Research," 9, 183-251 (May 14).

Composition of Citrus Leaves at Various Stages of Mottling. CHARLES A. HENSEN. "Journal of Agricultural Research," 9, 157-165 (May 7).

Yearbook of the U. S. Department of Agriculture, 1916. 783 pp. 169 plates and figures. Cloth, \$1.00. Obtainable free only through members of Congress. This yearbook contains the annual report of the Secretary of Agriculture and 33 miscellaneous articles. These articles will later be available as separates.

The Sanitary Control of Tomato-Canning Factories. BURTON J. HOWARD and CHARLES H. STEPHENSON. Department Bulletin 569. Contribution from the Bureau of Chemistry. 29 pp. Paper, 5 cents. Issued June 25.

Carbon Disulfide as an Insecticide. W. E. HINDS. Farmers' Bulletin 799. 21 pp. This is a revision of Farmers' Bulletin 145.

Utilization of Ash. W. D. STERRETT. Department Bulletin 523. Contribution from the Forest Service. 52 pp. Paper, 15 cents. Of interest to manufacturers of wood products.

Variation in the Chemical Composition of Soils. W. O. ROBINSON, L. A. STEINKOENIG and WILLIAM H. FRY. Department Bulletin 551. Contribution from the Bureau of Soils. 16 pp. Paper, 5 cents. Issued June 26. The report includes complete analyses of 45 samples of soils from four soil provinces.

The Determination of Bacteria in Ice Cream. S. HENRY AYERS and W. T. JOHNSON, JR. Department Bulletin 563. Contribution from the Dairy Division, Bureau of Animal Industry. 16 pp. Paper, 5 cents. The results of experiments indicate that bacteria are distributed quite evenly in commercial ice cream.

DEPARTMENT OF COMMERCE

List of Publications. This list is the 15th Edition, revised to May 8, 1917, indicating all of the publications now available for distribution.

BUREAU OF FOREIGN AND DOMESTIC COMMERCE

Substitutes for Tin Cans: How to Offset any Possible Shortage. Unnumbered leaflet, 4 pp., issued in coöperation with the Bureau of Standards.

Markets for Paper, Paper Products, and Printing Machinery in Cuba and Panama. ROBERT S. BARRETT. Special Agents Series 132, 44 pp. Paper, 5 cents. This is the first of a series of reports on paper and printing supplies which is planned to cover countries of Latin America. The booklet gives a brief review of market conditions with respect to these commodities, detailed discussion of imports of paper, a description of printing machinery now on hand, and the prospects for increasing sales from United States.

Cane Sugar Industry. Anonymous. Miscellaneous Series No. 53. 462 pp. Paper, 50 cents. This report covers a detailed study of agricultural, manufacturing and marketing conditions of the sugar industry in Louisiana, Cuba, Porto Rico, and Hawaii.

COMMERCE REPORTS—JULY, 1917

The British Ministry of Munitions has formulated rigid regulations requiring licensing for the manufacture, use, and sale of sulfuric acid. (P. 4)

Efforts are being made to encourage the cultivation of sugar beets in England. (P. 6)

Special courses in coal-tar chemistry have been established at the Technical College at Huddersfield, England, where the large dye factory of British Dyes, Ltd., is located. (P. 40)

A potash mine, similar to the Stassfurt deposits, has been discovered in Abyssinia: it is claimed that there are 850,000 tons of 55 per cent potash. A railway and plant are being constructed. (P. 246)

The output and consumption of copper ore in Japan shows a marked increase. (P. 175)

The output of manganese ore from Brazil, in 1916, was over 500,000 tons, as compared with 180,000 tons in 1914. (P. 262)

Among the chemicals required in Italy, which may be furnished by the United States, are: Oleic acid, oxalic, salicylic and sulfuric acids, sodium carbonate, sodium and potassium silicates, ammonium salts, and copper sulfate. (P. 302)

Efforts are being made to increase the use of peat for fuel in Switzerland. (P. 324)

A \$20,000,000 plant for refining nickel ore is to be erected in the Sudbury district, Canada. (P. 326)

Coal gas is being used extensively in England as a substitute for gasoline for motor bus fuel. (P. 337)

Chinese wood-oil varnish is made from tung oil, by heating with a ferruginous clay, and native red lead. The varnish is used for waterproofing silks, pongees, etc. (P. 180)

An electric power rolling mill is to be installed in connection with the electric furnace steel plant at Stavanger, Norway. (P. 342)

SPECIAL SUPPLEMENTS ISSUED DURING THE MONTH

SPAIN—14b	ARGENTINA—38a
SWITZERLAND—17a	URUGUAY—47a
COSTA RICA—24a	CHINA—52b and 53c
DUTCH WEST INDIES—27a	FRENCH INDO-CHINA—54a
GUATEMALA—29a	AUSTRALIA—60a
PANAMA—35a	

The Spanish Government has taken over the platinum and potash deposits in Spain, but has not yet done any extensive work upon them. (Supplement 15a)

STATISTICS OF EXPORTS TO THE UNITED STATES

CANADA—263	LONDON—293	DUTCH WEST INDIES—Sup. 27a
Wood alcohol	Rubber	Aloes
Paper	Tin	Divi divi
Coal	Hides	Hides
Coke	Indigo	Mangrove bark
Calcium acetate	SPAIN—Sup. 13a	Salt
Sulfuric acid	Copper	Sugar
Calcium carbide	Hides	Fustic
Gum chicle	Iron ore	Logwood
Senega root	Pyrites	
Fertilizers		
Hides	COSTA RICA—Sup. 24a	PANAMA—Sup. 35a
Leather	Gold	Balata
Rubber	Hides	Gold
Aluminum	Manganese ore	Hides
Asbestos	Rubber	Ipecac
Copper	Sugar	Manganese ore
Copper ore		Rubber
Pero alloys	ARGENTINA—Sup. 38a	Tagua nuts
Nickel	Bones	Tallow
Pyrites	Quebracho extract	
Oil cake	Glycerine	
Oil	Guano	AUSTRALIA—Sup. 60a
Wood pulp	Hides	Copper
SWITZERLAND—Sup. 17a	Rubber	Coke
Drugs	UREGUAY—Sup. 47a	Copra
Gelatin	Bones	Gold
Glue	Blood	Hides
Hides	Glue Stock	Nickel matte
Artificial silk	Hides	Chrome ore
Aniline dyes	Rubber	Manganese ore
	Tin ore	Chromite
		Tin

BOOK REVIEWS

The Founder's Manual. A Presentation of Modern Foundry Operations for the Use of Foundrymen, Foremen, Students and Others. By DAVID W. PAYNE. 676 pp. 245 illustrations. D. Van Nostrand Co., 1917. Price, \$4.00.

The author's plan has been to summarize information contained in separate publications which have appeared in the proceedings of various associations, and in the scientific and trade journals.

Chapters 1 to 7, inclusive, pp. 1 to 240, consist of reference tables covering the fields of mathematics, mechanics, etc., taken largely from standard handbooks on civil engineering and mechanical engineering. The remainder of the book treats of the properties of cast iron as influenced by its composition, the composition of iron required for various uses, and the mixing of iron, based on chemical analysis. Methods of testing and analyzing cast iron are given. The effect of the structure of iron upon its physical properties is discussed. The manufacture of malleable cast iron and of steel castings is described. General foundry practice and foundry accounts are treated, and the book closes with a pig iron directory, showing the average composition of the pig irons made at the various furnaces in the United States.

The book as a whole is what it purports to be, *vis.*, a summary of useful information, rather than a treatise of which the author's own experience and ideas form any material part.

From a chemist's and metallurgist's standpoint one might disagree with the statement on page 241, which implies that cementite is found in iron only in the presence of manganese, chromium, etc., or on page 242, that the atomic weight of pig iron is 54.5. One might also wonder why, on pages 104 to 106, space is given to tables concerning brick-lined well construction.

The book is a compilation, the contents of which will be useful

JAMES O. HANDY

Standard Methods of Chemical Analysis. Edited by WILFRED W. SCOTT, Research Chemist, General Chemical Co. XXXI + 864 pp. D. Van Nostrand Co., New York, 1917. Price, \$6.00 net.

This book was written in collaboration with H. A. Baker, L. E. Burton, F. G. Brewer, B. S. Clark, W. G. Derby, W. E. Doeringer, D. K. French, H. A. Gardner, A. H. Gill, F. F. Hale, R. E. Hickman, W. B. Hicks, R. K. Meade, I. C. Olsen, R. S. Owens, W. L. Savell and I. A. Schaeffer. According to the preface, assistance was also rendered by W. S. Allen, F.

Bedtel, A. W. Betts, J. M. Cratty, C. W. Ferguson, F. A. Gooch, T. T. Gray, N. F. Harriman and Allen Rogers.

Part I, with 496 pages, treats of the qualitative detection and quantitative determination of all the common elements and some of the less common ones such as cerium, glucinum, iridium, palladium, osmium, ruthenium, tantalum, thorium, columbium and zirconium. Part II, with 277 pages, contains chapters on special subjects: acids, oils, fats, waxes, paints, cements, alloys, coal, illuminating gas, and assaying. Part III contains 45 pages of specific gravity tables, conversion factors and other useful data; the Centigrade and Fahrenheit scales are compared from -200° to $+1000^{\circ}$ C. at 5° intervals; the number of acres in a hectare is given as well as the number of grams in an apothecaries' ounce (to 6 significant figures) and the heats of formation and of combustion of substances like amylene, allylene and crotonylene are shown.

The aim of the book, as stated in the preface, is to give carefully selected methods of technical analysis in sufficient detail to enable one with only an elementary knowledge of chemistry to follow the directions. Measured by this standard, Part II is very well done. The methods given there are certainly technical methods and they have been written up by men thoroughly conversant with this sort of chemical work. Each writer has written his special chapter according to his own ideas and although the methods of treatment are often quite different and the literary styles vary markedly, it is clear that this part of the book is typical of the methods in common use in this country. Frequent reference is made here to the useful bulletins published at Washington. On account of the independent way in which this part of the book was written, there is considerable repetition which could have been avoided by careful cross-reference, had been used. There is, moreover, very little that is new in this, or in any other part of the book.

In Part I the elements are considered in alphabetical order. First of all the atomic weight, specific gravity, melting point, boiling point and characteristic spectra are given. Next comes a discussion of the characteristic reactions by means of which the qualitative tests are made. Following this are methods for preparing suitable solutions, methods of separating the element from interfering elements, and finally gravimetric and volumetric methods are described for the determination of the element. The author states that lengthy qualitative, theoretical, dissertation and experimental data are purposely excluded.

but he has attempted in all cases to make the chemistry of the reactions understood and there is a liberal use of chemical equations.

The material in Part I is borrowed very largely from other well-known textbooks and in many cases proper credit is not given. Thus credit is in one case given to an eminent chemist, but the directions used are copied literally from those worked out by another chemist some thirty years later.

The alphabetical arrangement does not always work out satisfactorily. Similar elements, such as barium, calcium and strontium are widely separated from one another. This also necessitates a great deal of repetition which would be avoided by any system of bringing related elements together.

The editor has very carefully avoided reference to the modern theory of solutions. Thus he explains the failure of magnesium hydroxide to precipitate upon the addition of ammonia in the presence of ammonium chloride in two different ways, in different sections of the book. At one place it is stated that the magnesium remains in solution because the ammonium chloride furnishes, by hydrolysis, sufficient hydrochloric acid to dissolve magnesium hydroxide and in another place the non-precipitation of the magnesium is said to be due to the formation of a soluble double salt. There is no hint regarding the effect of ammonium ions upon the ionization of ammonium hydroxide.

The methods chosen in Part I are, for the most part, very good ones. As a rule, the directions are given in good English, but here and there are evidences of inexcusable carelessness, *i. e.*, there are too many instances of a plural noun and a singular verb being used together; sodium hydroxide is sometimes called by this name but at other times it is merely "caustic" or "sodium hydrate." At one place the following sentence occurs: "The cooled mass is digested with water to remove soluble sodium compounds among which is silica." At another place "fluor-spar" is called "feldspar." On page 550, it is stated that bismuth subnitrate can be used instead of sodium bismuthate in the volumetric determination of manganese. Passing hydrogen sulfide into a solution is called "gassing" and a precipitate is sometimes "copped out" from a beaker. On page 25, this phrase occurs: "When all is in solution and the color has changed to a straw." At one place, 1.5 milligrams of silver chloride are said to dissolve in a liter of water but farther on in the book it is claimed that this substance is "almost absolutely insoluble."

The appearance of the book is excellent and there are comparatively few misprints. The book will be welcomed in every technical library and will doubtless have a good sale.

WILLIAM T. HALL

The American Fertilizer Hand Book. Ware Bros. Co., Publishers, Philadelphia, 1917. Price, \$1.00.

The purpose of this volume is to furnish a standard reference book and directory of the Commercial Fertilizer Industry and allied trades. It contains a complete list of the fertilizer manufacturers of the United States, showing location and capacity with other information relating to the nature of their business; a classified directory of the allied fertilizer trades, a directory of the cottonseed oil mills, and a directory of the packers and renderers arranged by states.

The book contains very complete statistics covering production, imports, consumption and prices of fertilizer ingredients for the past year, and the consumption of fertilizers by states for the years 1909 to 1916 inclusive. In addition there are a number of interesting articles pertaining to different phases of the industry, which are of special interest at the present time.

As a reference book this volume is very valuable for those engaged in the fertilizer or allied industries, and the publishers are to be congratulated for the production of this valuable compilation.

The book is printed on good paper, neatly bound and has a convenient thumb index.

F. B. CARPENTER

Manual for the Essence Industry. By ERICH WALTER. iii + 427 pp., 32 figures. John Wiley & Sons, New York, 1916. Price: Cloth, \$4.00.

This book is devoted to the explanation of the principles involved in transferring an agreeable taste or flavor to beverages and certain foods, with a description of the methods of manufacture employed in this art. It embraces, therefore, a wide variety of subjects, including the raw materials from which the flavoring constituents are obtained, the methods of isolating the flavoring essence, and a description of the apparatus and methods used for this purpose. It also gives specific directions for manufacturing a great number of beverages, both alcoholic and non-alcoholic, as well as the essences used in confectionery, cooking, and in cosmetics, and in addition the coloring matters used in foods and beverages are also discussed.

As a large part of the book is devoted to formulae, the descriptive part necessarily treats of the subjects discussed in quite a general manner so that the book is valuable rather on account of the breadth of its scope than the completeness with which any branch of the subject is treated. The work does not contain a bibliography or references to original sources of information so that it is adapted to the use of those who know little about the subject and not to the student of a particular branch.

P. C. McILHINEY

Laboratory Manual of Bituminous Materials. By PREVOST HUBBARD, Assoc. American Society Chemical Engineers; Chemical Engineer; Chief, Division of Road Material Tests and Research, Office of Public Roads and Rural Engineering, United States Department of Agriculture. xi + 153 pp. 7 tables and 39 illustrations. John Wiley & Sons, Inc., New York. Price, \$1.50 net.

Although the author states in the introduction that the "manual is primarily intended as a laboratory guide for the student of highway engineering," the treatise will be found of value as a text for students in industrial chemistry, chemists in laboratories of companies manufacturing bituminous materials, and engineers and chemists connected with state, country and municipal highway departments.

From the standpoint of the student of chemistry or highway engineering, the book covers concisely: classification and refining of all types of bituminous materials used in highway engineering; details of methods of making all of the tests usually employed for the determination of physical and chemical properties of oils, tars and asphalts; and a discussion of the limitations and interpretations of the results of tests.

The highway chemist and engineer will find the manual of especial value in drafting specifications for bituminous materials to be used in different methods of construction and maintenance, as the author has thoroughly presented and discussed the several groups of tests which should form the basis of such specifications. A careful study of Part III on "Characteristics of the More Important Bituminous Materials" should enable the highway engineer to interpret specifications intelligently and to correlate the results of the use of bituminous materials in order to advise those responsible for the drafting of specifications wherein the requirements should be modified in order to secure the bituminous materials most suitable for the different types of construction and maintenance.

The manual covers methods of testing, qualitative and quantitative analyses, and the apparatus used therewith, with such careful attention to detail and such clearness of presentation that students and instructors of highway engineering and industrial chemistry now have at hand an ideal textbook for their guidance.

ARTHUR H. BLANCHARD

NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- Analysis: Procedures in Qualitative Analysis.** C. J. ROBINSON. 8vo. 26 pp. Price, \$0.50. The Author, Louisville, Ky.
- Applied Mechanics.** A. P. POORMAN. 8vo. 246 pp. Price, \$2.00. McGraw-Hill Book Co., New York.
- Applied Science: Les Sciences physiques et naturelles avec leurs applications à l'agriculture, à l'industrie, etc.** J. DUTILLEUL AND E. RAMÉ. 8vo. 192 pp. Price, 1 fr. 50. Larousse, Paris.
- Cement: A Handbook for Cement Works' Chemists.** F. B. GATEHOUSE. 2nd Ed. 8vo. 204 pp. Price, 5s. Charles Griffin & Co., London.
- Chemical Calculations.** R. H. ASHLEY. 8vo. Price, 8s. Archibald Constable & Co., London.
- Chemistry: Manual of Chemistry.** W. SIMON AND D. BASE. 8vo. 648 pp. Price, 18s. Baillière, Tindall & Cox, London.
- Chemistry: Practical Chemistry for Medical Students.** A. C. CUMMING. 2nd Ed. 8vo. 165 pp. Price, 3s. 6d. James Thin, Edinburgh.
- Coal Mining: A Text Book of Coal-Mining.** H. W. HUGHES. 6th Ed. 8vo. 578 pp. Price, 24s. Charles Griffin & Co., London.
- Colliery Engineers' Pocket Book of Notes and Formulae.** T. A. O'DONAHUE. 32mo. 128 pp. Price, 1s. 6d. T. Wall & Sons, Wigan.
- Compressed Air: Theory and Computations.** E. G. HARRIS. 2nd Ed. 8vo. 192 pp. Price, \$2.00. McGraw-Hill Book Co., New York.
- Concrete: A Treatise on Concrete, Plain and Reinforced.** F. W. TAYLOR. 3rd Ed. 8vo. Price, 23s. Chapman & Hall, London.
- Dyestuffs: The Synthetic Dyestuffs.** J. C. CAIN AND J. F. THORP. 3rd Ed. 437 pp. Price, 16s. Charles Griffin & Co., London.
- Flour Milling.** P. A. KOZMIN. 8vo. 584 pp. Price, 21s. G. Routledge & Sons, London.
- Gold: Getting Gold.** J. C. F. JOHNSON. 8vo. 72 pp. Price, 2s. 8d. W. Thacker & Co., London.
- Mathematics: Elementary Mathematics for Engineers.** E. H. SPRAGUE. 12mo. 236 pp. Price, \$1.50. D. Van Nostrand Co., New York.
- Milk: The Modern Milk Problem in Sanitation, Economics and Agriculture.** J. S. MACNUTT. 8vo. 258 pp. Price, \$2.00. The Macmillan Co., New York.
- Milling: A Treatise on Milling and Milling Machines.** CINCINNATI MILLING MACHINE CO. 8vo. 409 pp. Price, \$2.00. G. E. Stechert & Co., New York.
- Mining: The Elements of Mining and Quarrying.** C. DEN. FOSTER. 3rd Ed. 8vo. 341 pp. Price, 7s. 6d. Charles Griffin & Co., London.
- Paint Researches and Their Practical Application.** H. A. GARDNER. 8vo. 384 pp. Price, \$5.00. The Author, Washington, D. C.
- Physics, with Applications.** H. S. GILBERT AND H. N. CHUTE. 8vo. 469 pp. Price, \$1.25. Allen & Bacon, Boston.
- Power Plants and Refrigeration: Mechanical Equipment of Buildings.** Vol. 2. L. A. HARRISON AND A. C. WILLYARD. 8vo. 766 pp. Price, \$5.00. John Wiley & Sons, New York.
- Strength of Materials.** J. E. ROSS. 8vo. 380 pp. Price, \$3.00. McGraw Hill Book Co., New York.
- Valves: Locomotive Valves and Valve Gears, with a Special Treatise on Valve Setting.** I. H. VOODER AND G. B. WHEAREN. 8vo. 272 pp. Price, \$4.00. D. Van Nostrand Co., New York.
- Wire Rope Lubrication.** TEXAS COMPANY. 8vo. 48 pp. The Texas Co., New York.
- Engineers' Part in Prosecuting the War.** E. W. RICE, JR. *General Electric Review*, Vol. 20 (1917), No. 8, pp. 603-605.
- Fertilizer: A Dictionary of Fertilizer Materials.** T. C. PINKERTON. *The American Fertilizer*, Vol. 47 (1917), No. 3, pp. 29-34.
- Flotation: Principles of Flotation.** I. T. A. RICKARD. *Mining and Scientific Press*, Vol. 114 (1917), No. 1, pp. 9-15.
- Fuel: The Use of Low-Grade Mineral Fuels and the Status of Powdered Coal.** F. P. COPPIN. *General Electric Review*, Vol. 20 (1917), No. 8, pp. 606-631.
- Gas: Industrial Processes and Appliances Using Gas.** XIX. E. F. DAVIS. *The Gas Age*, Vol. 40 (1917), No. 3, pp. 117-119.
- Gases: Mixing Gases.** A. B. MACBETH. *Natural Gas and Gasoline*, Vol. 11 (1917), No. 7, pp. 181-192.
- Grading: Influence of Grading on the Value of Fine Aggregate Used in Portland Cement Concrete Road Construction.** F. H. JACKSON, JR. *Journal of Agricultural Research*, Vol. 10 (1917), No. 5, pp. 263-274.
- Granite in Kansas Wells.** PARK WRIGHT. *Bulletin of the American Institute of Mining Engineers*, No. 128 (1917), pp. 1113-1120.
- Industrial Processes for Utilizing Wood.** J. S. BATES. *Paper*, Vol. 20 (1917), No. 18, pp. 11-16.
- Industrial Research in the United States.** A. P. FLEMING. *Chemical News*, Vol. 116 (1917), No. 3006, pp. 4-5.
- Intercooler: What the Intercooler Can Do.** FRANK RICHARDS. *Power*, Vol. 46 (1917), No. 4, pp. 117-119.
- Iridium: Sur les chlorures et les chlorosels de l'iridium.** M. DELÉPINE. *Annales de chimie*, Vol. 7 (1917), pp. 277-339.
- Iron: Tayeh Iron Ore Deposits in China.** CHUNG YU WANG. *The Iron Trade Review*, Vol. 61 (1917), No. 4, pp. 193-194.
- Labor-Saving Machinery.** C. H. HORTON. *Industrial Management*, Vol. 53 (1917), No. 5, pp. 727-733.
- Leather Belting Research.** L. W. ARNY. *Industrial Management*, Vol. 53 (1917), No. 5, pp. 639-641.
- Metallurgy of Ferrochromium.** R. J. ANDERSON. *The Iron Trade Review*, Vol. 61 (1917), No. 2, pp. 75-78.
- Nickel: A Rapid Method for Estimating Nickel and Cobalt in Ores and Alloys.** W. R. SCHOELLER. *The Analyst*, Vol. 42 (1917), No. 495, pp. 189-199.
- Oils and Fats: The Estimation of Unsaponifiable Matter in Oils, Fats and Waxes.** J. M. WILKIE. *The Analyst*, Vol. 42 (1917), No. 495, pp. 200-202.
- Panama Canal Foundry at Balboa.** P. A. STANLEY. *American Machinist*, Vol. 47 (1917), No. 5, pp. 191-194.
- Paper: A Chart for Determining Output of Paper.** W. F. SCHAFHORST. *Paper*, Vol. 20 (1917), No. 21, pp. 18-17.
- Petroleum: Remedies for the Petroleum and Gasoline Situation.** F. G. CLAPP. *Engineering and Mining Journal*, Vol. 104 (1917), No. 8, pp. 196-201.
- Petroleum Geology of Colorado.** R. D. GEORGE. *The Mining American*, Vol. 75 (1917), No. 1848, pp. 11-13.
- Photomicrographic Study of Paper.** E. A. HUNTER. *Paper*, Vol. 20 (1917), No. 19, pp. 14-16.
- Producer Gas: Use of Producer Gas without Regenerators.** J. H. BARTLETT, JR. *Iron Iron Age*, Vol. 100 (1917), No. 8, pp. 110-111.
- Purple Color of Lamp Globes.** M. LUCKHISH. *General Electric Review*, Vol. 20 (1917), No. 8, pp. 671-672.
- Pyrite: R. R. Hill.** *General Chemical Abstracts*, Vol. 3 (1917), No. 10, pp. 181-187.
- Pyrites: Determination of the Explosibility of Pyrites.** A. R. GARDNER. *The American Engineer*, Vol. 25 (1917), No. 3, pp. 181-18.
- Reclaiming the Scrap Pile.** R. F. CHAPMAN. *Engineering Magazine*, Vol. 53 (1917), No. 3, pp. 34-36.
- Silica Brick: Progress in Making Silica Brick.** F. R. NORMAN AND M. I. BELL. *The Iron Age*, Vol. 100 (1917), No. 8, pp. 114-115.
- Soils: Movement and Distribution of Moisture in Soils.** F. R. HARRIS AND H. W. FORBES. *Soil Science Society of America*, Vol. 10 (1917), No. 3, pp. 113-114.
- Sulfate Processes: Newer Details of the Sulfate Process.** J. S. MARR. *Power*, Vol. 46 (1917), No. 7, pp. 11-13.
- Sulfite Pitch Deposits in Paper.** J. S. MARR. *Power*, Vol. 46 (1917), No. 3, pp. 11-13.
- Sulfur: Sources of Sulfur in Oils.** J. E. PERRY. *Engineering Magazine*, Vol. 53 (1917), No. 3, pp. 34-36.
- Sulfuric Acid Industry.** A. M. PERRY. *Engineering Magazine*, Vol. 47 (1917), No. 3, pp. 113-115.
- Volumetric Determination of Sulfur in Pyrites.** J. A. COOK. *Engineering Magazine*, Vol. 53 (1917), No. 3, pp. 113-115.
- Wastes: Reclaiming Wool Wastes and Rags.** T. E. HARRIS. *Engineering Magazine*, Vol. 53 (1917), No. 3, pp. 113-115.

RECENT JOURNAL ARTICLES

- Acetic Anhydride: Examination of Acetic Anhydride.** L. G. RADCLIFFE AND S. MEDENDORP. *Journal of the Society of Chemical Industry*, Vol. 36 (1917), No. 12, pp. 678-680.
- Benzoylbenzoic Acid: Dérivés des acides benzoylbenzoïques.** I. FÉRAUD. *Annales de chimie*, Vol. 7 (1917), pp. 310-311.
- Blast Furnace Gas under Bidders.** H. C. KRONMEYER. *The Iron Trade Review*, Vol. 61 (1917), No. 4, pp. 191-192.
- Bluestone: Uses of Bluestone in the Dyehouse.** W. H. BUTLER. *Textile World Journal*, Vol. 53 (1917), No. 4, pp. 57-58.
- Capillary Phenomena and Supercooling.** S. LANGENBERG AND E. A. RYKIN. *Journal of Physical Chemistry*, Vol. 21 (1917), No. 6, pp. 114-115.
- Cementation by Gas under Pressure.** E. C. LANGENBERG. *American Inst. Engng.*, Vol. 3 (1917), No. 3, pp. 211-212.
- Chemical Control.** T. G. GORHAM. *Journal of the American Leather Chemists' Association*, Vol. 12 (1917), No. 7, pp. 332-334.
- Chromite.** I. S. DILLER. *Mining and Scientific Press*, Vol. 115 (1917), No. 3, pp. 93-94.
- Coal: Handling Coal and Ashes in Textile Plants.** H. I. EDGAL. *Textile World Journal*, Vol. 53 (1917), No. 5, pp. 43-45.
- Compressed Air.** L. HARRISON. *Industrial Management*, Vol. 53 (1917), No. 4, pp. 563-577.
- Cyanuric Acid: Isolation of Cyanuric Acid from Soil.** L. I. WISE AND T. H. WATKINS. *Journal of Agricultural Research*, Vol. 10 (1917), No. 2, pp. 85-91.

MARKET REPORT—AUGUST, 1917

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON AUG. 20

INORGANIC CHEMICALS

Acetate of Lime.....	100 Lbs.	5.25	@	5.50
Alum Ammonia lamp.....	100 Lbs.	4.50	@	4.75
Aluminum Sulfate, high grade.....	Ton	70.00	@	75.00
Ammonium Carbonate, domestic.....	Lb.	10 1/4	@	11
Ammonium Chloride, white.....	Lb.	—	@	—
Aqua Ammonia, 26° drums.....	Lb.	13	@	14
Arsenic, white.....	Lb.	16 1/2	@	17
Barium Chloride.....	Ton	80.00	@	90.00
Barium Nitrate.....	Lb.	11 1/4	@	12
Barytes, prime white, foreign.....	Ton	28.00	@	30.00
Bleaching Powder, 35 per cent.....	100 Lbs.	1.50	@	2.00
Blue Vitriol.....	Lb.	9 1/2	@	10
Borax, crystals, in bags.....	Lb.	7 1/4	@	8 1/2
Boric Acid, powdered crystals.....	Lb.	18	@	13 1/4
Bromine, crude, domestic.....	Long Ton	55.00	@	60.00
Bromine, technical, bulk.....	Lb.	55	@	60
Calcium Chloride, lump, 70 to 75% fused.....	Ton	30.00	@	32.00
Caustic Soda, 76 per cent.....	100 Lbs.	8.75	@	9.00
Chalk, light precipitated.....	Lb.	4 1/4	@	4 1/4
China Clay, imported.....	Ton	18.00	@	30.00
Feldspar.....	Ton	8.00	@	15.00
Fuller's Earth, foreign, powdered.....	Ton	—	@	35.00
Glauber's Salt, in bbls.....	100 Lbs.	75	@	85
Green Vitriol, bulk.....	100 Lbs.	1.00	@	1.05
Hydrochloric Acid, commercial, 18°.....	Lb.	1 1/4	@	1 3/4
Hydrochloric Acid, C. P. conc., 22°.....	Lb.	1 1/4	@	2
Iodine, resublimed.....	Lb.	3.50	@	3.55
Lead Acetate, white crystals.....	Lb.	16	@	16 1/2
Lead Nitrate.....	Lb.	15 1/2	@	16
Litharge, American.....	Lb.	11	@	11 1/4
Lithium Carbonate.....	Lb.	—	@	1.25
Magnesium Carbonate, U. S. P.....	Lb.	20	@	22
Magnesite, "calcined".....	Ton	60.00	@	65.00
Nitric Acid, 36°.....	Lb.	7	@	7 1/2
Nitric Acid, 42°.....	Lb.	8	@	8 1/4
Phosphoric Acid, sp. gr. 1.710.....	Lb.	33	@	37
Phosphorus, yellow.....	Lb.	2.15	@	2.25
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, cakes.....	Lb.	38 1/2	@	39
Potassium Bromide, granular.....	Lb.	1.00	@	1.10
Potassium Carbonate, calcined, 80 @ 85%.....	Lb.	70	@	75
Potassium Chlorate, crystals, spot.....	Lb.	50	@	55
Potassium Cyanide, bulk, 98-99 per cent.....	Lb.	2.30	@	2.40
Potassium Hydroxide, 88 @ 92%.....	Lb.	83	@	85
Potassium Iodide, bulk.....	Lb.	—	@	2.90
Potassium Nitrate.....	Lb.	29	@	31
Potassium Permanganate, bulk.....	Lb.	4.00	@	4.25
Quicksilver, flask.....	75 Lbs.	115.00	@	118.00
Red Lead, American, dry.....	Lb.	13	@	13 1/2
Salt Cake, glass makers'.....	Ton	22.00	@	24.00
Silver Nitrate.....	Oz.	52 1/4	@	55 1/4
Soapstone, in bags.....	Ton	10.00	@	12.50
Soda Ash, 58%, in bags.....	100 Lbs.	3.90	@	4.10
Sodium Acetate.....	Lb.	10 1/4	@	11
Sodium Bicarbonate, domestic.....	100 Lbs.	2.45	@	2.60
Sodium Bichromate.....	Lb.	16 1/2	@	17
Sodium Chlorate.....	Lb.	23 1/2	@	24 1/2
Sodium Fluoride, commercial.....	Lb.	18	@	19
Sodium Hyposulfite.....	100 Lbs.	1.75	@	1.85
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	4.27 1/4	@	4.30
Sodium Silicate, liquid, 40° Bé.....	100 Lbs.	2.10	@	2.20
Sodium Sulfide, 60% crystals, in bbls.....	Lb.	3 1/4	@	3 1/2
Sodium Bisulfite, powdered.....	Lb.	6 1/4	@	7
Strontium Nitrate.....	Lb.	28	@	30
Sulfur, flowers, sublimed.....	100 Lbs.	3.05	@	3.45
Sulfur, roll.....	100 Lbs.	2.85	@	3.25
Sulfuric Acid, chamber, 66° Bé.....	Ton	30.00	@	32.00
Sulfuric Acid, oleum (fuming).....	Ton	40.00	@	50.00
Talc, American white.....	Ton	10.00	@	12.00
Terra Alba American, No. 1.....	100 Lbs.	85	@	90
Tin Bichloride, 50°.....	100 Lbs.	19.25	@	19.50
Tin Oxide.....	Lb.	64 1/4	@	65
White Lead, American, dry.....	Lb.	11 1/2	@	12
Zinc Carbonate.....	Lb.	23	@	25
Zinc Chloride, commercial.....	Lb.	16 1/2	@	17
Zinc Oxide, American process XX.....	Lb.	16 1/4	@	16 1/2

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	51	@	52
Acetic Acid, 56 per cent, in bbls.....	Lb.	10	@	10 1/2
Acetic Acid, glacial, 99 1/4%, in carboys.....	Lb.	36	@	37
Acetone, drums.....	Lb.	32 1/2	@	33
Alcohol, denatured, 180 proof.....	Gal.	1.00	@	1.01

Alcohol, grain, 188 proof.....	Gal.	4.02	@	4.04
Alcohol, wood, 95 per cent, refined.....	Gal.	1.00	@	1.02
Amyl Acetate.....	Gal.	4.00	@	4.25
Aniline Oil.....	Lb.	27 1/2	@	28
Benzoic Acid, ex-toluol.....	Lb.	3.00	@	3.25
Benzol, 90 per cent.....	Lb.	51	@	54
Camphor, refined in bulk, bbls.....	Lb.	84 1/2	@	85
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	42	@	43
Carbous Bisulfide.....	Lb.	7	@	7 1/2
Carbon Tetrachloride, drums, 100 gals.....	Lb.	16 1/2	@	17
Chloroform.....	Lb.	60	@	61
Citric Acid, domestic, crystals.....	Lb.	72	@	75
Creosote, beechwood.....	Lb.	1.90	@	2.00
Cresol, U. S. P.....	Gal.	1.25	@	1.30
Dextrine, corn (carloads, bags).....	100 Lbs.	6.35	@	6.40
Dextrine, imported potato.....	Lb.	15	@	16
Ether, U. S. P., 1900.....	Lb.	31	@	39
Formaldehyde, 40 per cent.....	Lb.	16	@	16 1/2
Glycerine, dynamite, drums included.....	Lb.	65	@	63 1/2
Oxalic Acid in casks.....	Lb.	46	@	47
Pyrogallic Acid, resublimed, bulk.....	Lb.	3.80	@	3.85
Salicylic Acid.....	Lb.	1.40	@	1.50
Starch, cassava.....	Lb.	—	@	—
Starch, corn (carloads, bags) pearl.....	100 Lbs.	5.05	@	5.10
Starch, potato.....	Lb.	12 1/2	@	13
Starch, rice.....	Lb.	10	@	12
Starch : sago flour.....	Lb.	6	@	6 1/2
Starch, wheat.....	Lb.	5 1/4	@	6 1/2
Tannic Acid, commercial.....	Lb.	80	@	95
Tartaric Acid, crystals.....	Lb.	80	@	82

OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	65	@	65
Black Mineral Oil, 29 gravity.....	Gal.	13 1/4	@	13 1/4
Castor Oil, No. 3.....	Lb.	26	@	27
Ceresin, yellow.....	Lb.	14	@	18
Corn Oil, crude.....	Lb.	13 1/2	@	14
Cottonseed Oil, crude, f. o. b. m. d.....	Gal.	1.02	@	1.03
Cottonseed Oil, p. s. f.....	Lb.	15	@	15 1/2
Menhaden Oil, crude (southern).....	Gal.	—	@	—
Neat's-foot Oil, 20°.....	Gal.	—	@	1.75
Paraffin, crude, 118 to 120 m. p.....	Gal.	7 1/2	@	7 1/4
Paraffin Oil, high viscosity.....	Gal.	29 1/4	@	30
Rosin, "F" Grade, 280 lbs.....	Bbl.	5.85	@	—
Rosin Oil, first run.....	Gal.	35	@	—
Shellac, T. N.....	Lb.	58	@	—
Spermaceti, cake.....	Lb.	25	@	—
Sperm Oil, bleached winter, 38°.....	Gal.	—	@	nominal
Spindle Oil, No. 200.....	Gal.	18	@	19
Stearic Acid, double-pressed.....	Lb.	23	@	24
Tallow, acidless.....	Gal.	1.38	@	1.40
Tar Oil distilled.....	Gal.	33	@	34
Turpentine, spirits of.....	Gal.	41	@	41 1/4

METALS

Aluminum, No. 1, ingots.....	Lb.	48	@	50
Antimony, ordinary.....	Lb.	16	@	16 1/4
Bismuth, N. Y.....	Lb.	3.00	@	3.10
Copper, electrolytic.....	Lb.	27	@	27 1/2
Copper, lake.....	Lb.	27 1/2	@	28
Lead, N. Y.....	Lb.	10 1/4	@	11
Nickel, electrolytic.....	Lb.	55	@	56
Platinum, refined, soft.....	Oz.	105.00	@	—
Silver.....	Oz.	86 1/2	@	—
Tin, Straits.....	Lb.	62 1/4	@	62 1/4
Tungsten (Wo):.....	Per Unit	23.00	@	23.50
Zinc, N. Y.....	Lb.	8 1/4	@	8 1/4

FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	6.85	@	7.00
Blood, dried, f. o. b. Chicago.....	Unit	—	@	6.42 1/2
Bone, 4 and 50, ground raw.....	Ton	32.00	@	35.00
Calcium Cyanamid.....	Unit of Ammonia	4.00	@	—
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	—	@	nominal
Phosphate acid, 16 per cent.....	Ton	15.00	@	16.00
Phosphate rock, f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	3.15	@	3.25
Tennessee, 78-80 per cent.....	Ton	5.50	@	6.00
Potassium "muriate," basis 80 per cent.....	Ton	340.00	@	350.00
Pyrites, furnace size, imported.....	Unit	—	@	nominal
Tankage, high-grade, f. o. b. Chicago.....	Unit	6.30	@	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

AT EASTON, PA.

Volume IX

OCTOBER 1, 1917

No. 10

Editor: CHARLES H. HERTY

Assistant Editor: LEOLA E. MAERS

Advertising Manager: G. W. NOTT

ADVISORY BOARD

H. E. BARNARD, H. K. BENSON, F. K. CAMERON, B. C. HESSE, A. D. LITTLE, A. V. H. MORY, M. C. WHITAKER

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly; single copy, 60 cents.
Price per single copy to American Chemical Society members, 50 cents. Foreign postage, seventy-five cents. Canada, Cuba and Mexico excepted.
Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879.

All communications should be sent to The Journal of Industrial and Engineering Chemistry,

Telephone: Vanderbilt 1930

35 East 41st Street, New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

ANNUAL MEETING AMERICAN CHEMICAL SOCIETY:

- Address of Welcome. Richard Cockburn Maclaurin. 922
Address. William H. Nichols. 924

ORIGINAL PAPERS:

- Coal Distillation under Pressure. J. H. Capps and G. A. Hulett. 927
A New Method for the Recovery of Salts of Potassium and Aluminum from Mineral Silicates. J. C. W. Frazer, W. W. Holland and E. Miller. 935
On the Relation between the Physical Properties and Chemical Composition of Glass. VII—Etch Figures. Edwin Ward Tillotson, Jr. 937
The Determination of Iron in Glass Sand. John B. Ferguson. 941
The Formation of Tri-Calcic Aluminate. Edward D. Campbell. 943
Low Temperature Distillation of Lignite Coal. H. K. Benson and L. L. Davis. 946
The Determination of Sulfur Dioxide. O. R. Sweeney, Harry E. Outcault and James R. Withrow. 949
The Separation of Aluminum from Iron by Means of Ether. Samuel Falkin. 951
A Method for the Colorimetric Estimation of Small Amounts of Aniline. Elias Elvove. 953
A Modification of the Price Method for the Separation of the Permitted Coal-Tar Colors to Include Tartrazine. E. H. Ingertoll. 955
Detection of Added Water in Milk by Means of a Simplified Molecular Concentration Constant. Leslie W. Ferris. 957
A Method for the Determination of the Volatile Oil Content of Citrus Fruits. C. P. Wilson and C. O. Young. 959
The Determination of Available Oxygen in Pyrolusite. O. L. Barneby. 961
A Contribution to the Theory of Emulsification Based on Pharmaceutical Practice—II. William G. Crockett and Ralph E. Oesper. 967

LABORATORY AND PLANT:

- The Use of Textile Fibers in Microscopic Qualitative Chemical Analysis. E. M. Chamot and H. I. Cole. 969
A New Illuminator for Microscopes. Alexander Silverman. 971
A New Model of the Burrell and Oberfell Apparatus for the Analysis of Illuminating Gas. J. R. Suydam, Jr. 972
A Useful Distilling Head. Orlo Stearns. 972
An Electrically Heated and Controlled Air Bath. Walter P. Schuck. 973

ADDRESSES:

- Stellite as a Substitute for Platinum. Elwood Haynes. 974
The Influence of Added Substances on the End-Point in the Iodometric Titration of Hydrogen Sulfide. Alfred R. Jayson and Ralph E. Oesper. 975

THE HANDLING AND TRANSPORTATION OF LIQUIDS ON AN INDUSTRIAL SCALE:

- The Storage and Transportation of Liquids. Floris R. Baxter. 978
Transportation and Storage of Liquids in Small Packages. L. R. Atkins. 979
The Handling and Transportation of Liquids. M. H. Eisenhart. 980

CURRENT INDUSTRIAL NEWS

982

SCIENTIFIC SOCIETIES:

- Calendar of Meetings. Fifty-Fifth Meeting American Chemical Society, Boston, September 10-14, 1917. The Industrial Chemist in War Time. 983

NOTES AND CORRESPONDENCE

985

WASHINGTON LETTER

986

PERSONAL NOTES

987

INDUSTRIAL NOTES

988

GOVERNMENT PUBLICATIONS

989

BOOK REVIEWS

990

NEW PUBLICATIONS

991

MARKET REPORT

1000

ANNUAL MEETING AMERICAN CHEMICAL SOCIETY

The spacious buildings of the Massachusetts Institute of Technology in their new and beautiful setting on the banks of the Charles River in Cambridge, Mass., constituted a symbolical environment, in this new period of chemistry in America, for the Fifty-Fifth Meeting of the American Chemical Society, which was held from September 10 to 13, 1917. In spite of the unusual demands made upon chemists at this time, the registration exceeded seven hundred, and it was the unanimous sentiment that a fresh and vitalizing stimulus had been gained from this convention for all branches of chemical activity. Three features stood out preëminent as characteristic of the meeting: *first*, the intense loyalty and patriotism of chemists; *second*, their eagerness to learn in what ways they might possibly be of assistance to the government; *third*, the woeful shortage of chemists in every line to meet the present intensified demand.

On Monday afternoon, September 10, the Council of the Society met in the rooms of the Engineers' Club, sixty-eight Councilors being present. The Committee on Constitutional Amendments regarding modifications in the method of election of the President and the creation of a Board of Control reported informally. As a result of the discussion which followed, the Committee was enlarged to five members and continued for the purpose of reporting to a later meeting of the Council. It was voted that a Code of Ethics for the Society is not desirable. To the proposal that the Society should unite with other national bodies in the formation of a national organization of technical societies, the Council expressed its appreciation of the invitation and of its desire to cooperate in every way possible with the other scientific societies on any matter pertaining to national welfare; nevertheless, it was felt that the present well organized activities of the Society would be hampered by a formal union such as was proposed.

Dr. E. G. Love was re-elected Treasurer for a three-year term. Dr. W. A. Noyes having tendered his resignation of the office of Editor of the *Journal of the American Chemical Society*, Dr. A. B. Lamb, of Harvard University, was unanimously elected to this office. Mr. E. J. Crane and Dr. Chas. H. Herty were also unanimously re-elected Editor of *Chemical Abstracts* and Editor of the *Journal of Industrial and Engineering Chemistry*, respectively.

To serve upon the committee advisory to the President of the Society on national affairs, Drs. B. C. Hesse and M. C. Whitaker were elected from the Councilors-at-Large.

The Council unanimously recommended to the Society the election to honorary membership of Professor Victor Grignard of the University of Nancy, France, now a Major in the French Army and serving on a commission to this country.

The invitation of the Cleveland, Ohio, Section to hold the next Fall Meeting in that city, was accepted.

The time, place and desirability of holding a Spring Meeting was referred to the Directors.

A hearty vote of thanks was passed in appreciation of the courtesies extended by the Massachusetts Institute of Technology and members of the various Local Committees whose efficient labors added so materially to the success of the meeting and the comfort and pleasure of the members.

Immediately after adjournment the Council was entertained at dinner at the Engineers' Club by the Northeastern Section.

After dinner the meeting of the Directors was held.

At the General Meeting, on Tuesday morning, which filled to overflowing the large lecture room of the Chemistry Department, Prof. H. P. Talbot, Chairman of the Local General Committee, in gracious words welcomed the Society and introduced Dr. R. C. Maclaurin, President of Massachusetts Institute of Technology.

ADDRESS OF WELCOME

By RICHARD COCKBURN MACLAURIN

President Massachusetts Institute of Technology

It must always be an honor to welcome the American Chemical Society: it is especially so to me under present circumstances of place and time. I am sure that all my colleagues at Technology share my gratification that you are meeting within the walls of these buildings that have been so recently dedicated to the great cause of science. It seems especially appropriate that you should meet in Cambridge, longer than any other city in the country a centre of intellectual effort and influence. Your meeting here will recall to your minds the long line of great teachers and thinkers who have made this city of Cambridge famous, and you will think with sympathy of the immense influence that has radiated therefrom throughout the length and breadth of the land. It may link you, too, in imagination to the older Cambridge and through the associations of that historic university to the intellectual accomplishments of Europe as a whole. Happily for men of science they are subject less to intellectual isolation and consequently to intellectual provincialism than are most other men. In the field that you cultivate you simply must know much of what is going on in other parts of the world. In this sense you men of science are necessarily internationalists.

Happily, however, no man is merely a scientist. As healthy human beings, men of science are keenly alive to all the grave issues of life, and so to-day, all are taking sides in the greatest of all moral issues—that raised by the war. Of course I have no thought of discussing these issues, but it would be absurd when we are meeting at one of the greatest crises of our national history, to pass by the greatest of all the questions of the day.

It would indeed be peculiarly absurd because there are so many questions raised by the war that seem full of significance to all who think seriously of the great work that your society is doing and will do. I venture to hope, therefore, that when you get down to business you will give serious consideration at this meeting to the problems of the war that are related to the work of the chemist. The man in the street may not pay much attention to the proceedings of your society, but none the less it is probably true that no body of men similarly associated is capable of contributing so much to the solution of the great problems that the war presents as are the chemists. I need hardly refer to the possibilities, nay the actual achievements, in the opera-

tions of the war. Much is being done by the members of your society, the best of it quietly and without being heralded in the press, so that it will probably not be till the war is over that the public learns of the actual accomplishments of American chemists in the field that I have indicated. When the story is told it will add luster to the name of American science.

After all, however, it is in the beneficent paths of peace that the labors of the chemist do their greatest and most lasting good. We cannot see the dawn of peace yet, but we can see that when it comes it will bring pressing problems to the man of science and particularly to the chemist. Indeed some of the problems are pressing urgently now. Think only of one of them—What can be done to offset the prodigious cost of war? Congress has already appropriated billions for war purposes and of course that is only the beginning. How is such a load of debt to be carried? Clearly only by spending less and earning more. Every patriotic citizen to-day, whatever his calling, should be preaching and practising the doctrine of economy—the absolute necessity for avoiding all needless expenditure, which is only another word for waste.

This must be done everywhere—in our households, in our business, in our government—and few can render so much service in saving waste as the chemist. You must rub this into the minds of all who are in a position to make changes, and rub it in by particular instances and not merely by general statements. I could name a single invention made in the last few years, and scarcely heralded at all by the newspapers, that means the saving of over a hundred millions annually to the people of this land. Doubtless you could name similar instances and you see of course that it does not take many such improvements to pay for even so costly a war as this.

There is, however, more to be done than to avoid waste: there is the development of countless new ways of earning more. I need not refer in this presence to the practically infinite possibilities of the great science that you represent, possibilities resting not on the baseless fabric of a dream, but on the solid rock of scientific knowledge. To make these possibilities actual we must have two things: *first*, a large supply of competent and well trained men; and, *second*, appreciation on the part of men of business of the possibilities of science. Happily we are getting both, although of course there is still room for improvement. In such matters an ounce of experience is worth many tons of speculation, and so I may be permitted to refer to the recent experience of this Institute in the field that I have just indicated.

We have been much encouraged, not only by the rapidly increasing numbers who are taking chemistry for a profession, but what, of course, is of far more import, by their quality. And we have been particularly encouraged by our experience in conducting chemical education in cooperation with manufacturing concerns in various States of the Union. We have been dealing of course with a selected group, but we have no reason to suppose that there are not many other concerns with an equal appreciation of the value of sound scientific training to business enterprise and an equal readiness to cooperate with scientific workers.

May I add that I see great good in such cooperation, not only to business but to science. It will bring about, I think, among men of science, more appreciation of the scope and intellectual interest of practical problems. There has been too much monasticism in science, too much aloofness from the affairs of daily life, too much looking down on the world as from another sphere. Even in the field of chemistry itself, the relations between so-called "pure" chemistry and so-called "applied" chemistry have been oftentimes far from ideal. And the cooperation of which I have spoken will also bring about, I hope, a greater appreciation among business men of the value to business of the scientific method and spirit.

When this appreciation becomes general, the victory will be

complete. We have, I think, good grounds for looking forward to a time when science will be cultivated by the minds best adapted for its progress and under circumstances that make for its steady improvement. The day will dawn when there will be none of the niggardliness and littleness in the support of scientific research that marked the earlier generations, and that still are too much with us. We may look forward with confidence to an era of great accomplishment, not merely in the application of science to the so-called "practical" problems, but within the strict realm of science itself. It should go without saying that these two things should move forward together, each helping the other and with full appreciation of the importance of both. And I feel sure that one of the great instruments for bringing about this splendid development will be the American Chemical Society, whose members I have the pleasure of welcoming to-day.

In behalf of the Society, President Stieglitz thanked Dr. Maclaurin for his hearty welcome and assured him that the American Chemical Society had thoroughly organized its forces and stood ready to aid the Government in every way possible. He also pointed out tremendous strides which the chemical industries have taken during this war period, and spoke with strong confidence of the future of chemistry in this country.

The Society adopted unanimously the recommendation of the Council that Prof. Victor Grignard be elected an honorary member of the Society.

Dr. Arthur L. Day, Director of the Geophysical Laboratory, Washington, D. C., aroused the enthusiasm of the meeting by his portrayal of the activities of his laboratory in meeting the shortage of optical glass so necessary to the proper equipment of our Army and Navy with periscopes, range finders, field glasses, etc. His account of the rapidity and thoroughness with which the work has been prosecuted, and his statement that next month the output will be 45,000 lbs., furnished another stirring illustration of the ability with which chemists have met the sudden calls upon their resourcefulness.

Professor Grignard having arrived during the address by Dr. Day, President Stieglitz stated, after the close of the address, that he desired to inform Professor Grignard officially of his election to honorary membership in the Society. Professor Grignard was invited to the platform, and President Stieglitz addressed him as follows:

"Professor Grignard, it is my valued pleasure as President of the American Chemical Society, to inform you that in consideration of your brilliant and fundamental contributions to chemistry, and especially to the theory and experimental methods of organic chemistry, and in consideration also of your invaluable services to the cause of freedom and democracy through your scientific activity in this war, the American Chemical Society has elected you at its meeting to-day to honorary membership in the Society. We welcome the fact that we may count you as one of our associates and trust that you will find yourself quite at home with us as your devoted friends and countrymen."

Professor Grignard, speaking in his native tongue, expressed his deep appreciation of the honor which had been conferred upon him, with thanks. However, he considered us [untranslated] not quite his personally, but an *équipe* to France which had given him chemistry such illustrious men as Lavoisier, Dumas, Berthelot,

and many others, and also as a tribute to our ally with whom we are now standing shoulder to shoulder in the common cause of the world's struggle for liberty.

Continuing the program, Dr. E. C. Kendall of the Mayo Clinic, Rochester, Minnesota, gave a paper on "The Isolation and Identification of the Iodine-Containing Compound which Occurs in the Thyroid."

Special interest attached to the Tuesday afternoon General Session because of the direct bearing of the program on the many questions connected with the war situation. The first speaker was Dr. William H. Nichols, Chairman of the Committee on Chemicals of the Council of National Defense.

ADDRESS

By WILLIAM H. NICHOLS

Chairman Committee on Chemicals, Council of National Defense

It cannot be impressed too frequently or too strongly on the minds of the American people that the war on which we have entered is one which will require the faithful services and intelligent coöperation of every loyal citizen of the Republic, male and female, until the very end. No half-way measures will suffice. We are pitted against a power which has been preparing for many years and which did not strike until its preparations were complete. With that thoroughness for which the German people are deservedly noted, assisted and guided at every step by a highly intelligent Government, which, for many years, knew what it was aiming to accomplish, and intended to be ready for any eventuality, there was probably nothing which could be foreseen by human intelligence which was not provided for when the Belgian frontier was crossed. While this was true in all fields it was particularly true in the field of chemistry, which was proved to be in many ways the most important science made use of in the titanic struggle. Many of those present will remember the striking lecture of Dr. Berntsen, delivered during the 8th International Congress of Applied Chemistry to an audience which packed the hall in its eagerness to learn the last, and to many the first, word on the fixation of atmospheric nitrogen. Probably no one among them realized the enormous influence which the process described was so soon to have on the fate of the world. We had been accustomed to consider that nitrogen fixation was practically dependent upon the electric arc and involved the consumption of enormous electrical energy. Dr. Berntsen's exposition of what is known as the "Haber Process" was so clear and so skillful that even those who gave it only a passing thought could see the great potentialities of employing hydrogen instead of oxygen in the fixation process. Since the date of the delivery of that lecture in 1912, the production in Germany of nitric acid and ammonia in its several forms has become colossal and it may be safe to say that without the process alluded to the war, from the German side, would long ago have languished from scarcity of explosives, and the fields have become barren from lack of nitrogen. It is conceivably not too much to infer that the war was not launched until the way was clear for the production of nitrogen compounds after the vast accumulated stores of Chilean nitrate had become exhausted. This is one instance of many which might be cited to show the extreme preparedness of the German nation. From my own knowledge I can say that by comparison, the English and French were unprepared, both in men and equipment, and this was thoroughly understood by their enemies. As for Russian preparation, it was carefully looked after in Berlin.

While the beginning of the war found England and France not only unprepared but almost stunned by the suddenness of the shock, they lost no time in getting under way. At first many mistakes were made, and many steps taken which had to

be retraced, but fortunately no vital errors were committed. As a result of the gigantic program laid down, covering every phase of preparedness, these countries found themselves able to supply the vast armies which they organized, with every article, to the last detail, needed to make them effective. This offers one of the most extraordinary examples of intelligent coöperation which the world has ever seen. It is little short of a miracle.

It was well known in Germany that England and France were but comparatively small producers of fuming sulfuric acid or oleum. Not having a great dye industry, they felt little need for it outside of their explosive requirements and these were not large except in commercial explosives, used in mining and the like. But modern warfare cannot be conducted without oleum; and in a war like the present the quantities used of this article are enormous.

I have been told that the chemical works in England built since the beginning of the war, particularly for the production of war chemicals, such as oleum and nitric acid, covers an area of 27 square miles. Compared with anything existing anywhere previous to this time, such a chemical plant is unheard of. My informant, who spent some time inspecting it, referred more than once to the fact that a large proportion of the labor was done by young women who were reported to be extremely efficient. He saw them firing boilers and doing work of like heavy character and apparently thriving on it. These great chemical works are the backbone of the enormous output of munitions that has made the English artillery, as well as every other branch of the service, so efficient. I presume many of you are aware that the chemical engineer who superintended the construction of these great plants in England is an American.

Hardly less astonishing, and from many points of view more so, was the work done in France. When the history of the war shall have been written, one of its most brilliant and inspiring pages will be that recounting the exploits of the French chemists and the marvelous increase in the output of French munitions.

I have touched on these matters in order to indicate the great task confronting this country in organizing its forces. We have not yet a plant for the fixation of nitrogen, but I think I can truthfully say that this is not the fault of the chemists. We have, fortunately, a large output of oleum. I regret to say politics continues to be spelled with a capital P while patriotism is too frequently spelled without it. Up to the time when this country was forced to take part we may just as well admit that we as a people were living in a fool's paradise with little thought, except in the minds of a few, that we would be drawn into the whirlpool sooner or later. One of the great battle-cries of the last presidential campaign, which had much to do with the result, was "He kept us out of war." It seemed as if the height of the ambition of vast numbers of our people were to keep out of war no matter what it cost in moral fiber or self-respect. To many who hold the same views as I do, it was astonishing that in view of what was taking place on the other side of the ocean we did not in ordinary prudence prepare long ago for a shower in case the wind should change and come our way, which it was almost certain to do. The fact that we had not commenced preparing three years ago is, to my mind, the reason why we are in the war at all; but at this late date there is little to gain by discussing what might have been or what should have been. We have now definitely entered and we are committed to do our part until the end and this part we pledge ourselves to make worthy of our great Nation and its traditions. We are fighting for great principles under a leader who is able to state them so that all may understand who will.

Promptly after the declaration of war our authorities at Washington proceeded to take steps with commendable rapidity. They have been criticized a great deal because these steps have not been more rapid, but those who are acquainted with the

difficulties of the situation realize that this criticism is not merited. We are a peace-loving people and had been at peace many years. There are a good many things which the ordinary citizen does not know and cannot be told—not that he cannot be trusted, but the intelligence might carry too far. Ours is a Democratic Government and no one man or group of men has had such powers as will be found to be necessary before we can hope to effect an organization able to cope with the demands that will be made upon it. Our organization at present is, in my opinion, temporary. Of course, the President is and must be its head. Next to him is the Council of National Defense, composed of six members of the Cabinet. After this Council comes the Advisory Commission of the Council of National Defense and the War Industries Board, whose duties are not yet clearly defined. The Advisory Commission is divided up into several committees, among them one on raw materials. The Committee on Chemicals is one of the sub-divisions of this, and its functions are advisory. Why one of the most abstruse of all the sciences having to do with some of the most delicate and highly refined finished products should come under the head of Raw Materials is hard to see, but such is the case. We chemists are accustomed to being misunderstood.

I was honored with the chairmanship of this committee and have organized it along lines which previous experience led me to believe would be efficient. The work has been divided into the following heads: Acids, Fertilizers, Alkalies, Electro-Chemicals, Coal-Tar By-Products (including Ammonia), Pyrites, Miscellaneous Chemicals, Phosphate Rock.

I was able to secure the services of men well known to the industry as chairmen of these sub-divisions and they in turn were fortunate in obtaining many of the best men in the industry for their special committee members. In all, the Chemical Committee, with its sub-committees, includes some thirty-seven men. These chairmen meet twice a month in Washington and in the interval are at work endeavoring to solve the problems of production which are assigned to them. I think you understand all the work of the Committee on Chemicals has to do with the actual materials, not with research. This latter subject is in charge of the National Research Council, the chairman of whose Chemical Committee is a member *ex-officio* of the Committee on Chemicals, thus keeping both branches in close and constant touch. The Bureau of Mines is represented by its able director.

The committee is located in inadequate offices in the Interior Building, fortunately adjoining the office of the honored secretary of this Society, whose services are thus easily and quickly obtained at any time. Our duties are many, some merely routine, such as obtaining information for various departments, procuring satisfactory prices for articles needed, keeping in touch with the Railway Commission to see that goods move as freely as possible, and many others of a like character, which will occur to you. In addition to these there are many duties of a more serious character, requiring much active and intelligent work. Generally speaking, the manufacturers have responded admirably and there are many instances of sacrifices being made for which recognition is not expected and probably will not be received. It would be idle to state that there are no exceptions, but every effort is being made to produce satisfactory results without resort to higher authority. We feel confident that as the war progresses the ability of the committee will be found to be equal to the problems as they arise. It, however, it should be found that they are not, we understand perfectly that we will be expected to make room for those who are better qualified. The main point is that our Army and Navy must be supplied with everything that the chemist can give, while at the same time our industries shall be interfered with as little as necessary. It may happen as time passes, that in spite of all precautions the industries may suffer to some extent, but you can depend upon it that this will not be the case

if it can be avoided by human foresight. There must come a time when this war shall end and we should be constantly preparing ourselves not only to provide its requirements while it lasts, but to meet conditions as we find them at its termination. Many theories have been advanced as to what will happen when peace once more blesses our staggering world, but I believe we should so plan our affairs that whether expansion or contraction results, we shall be able to meet either condition with a bold front.

One of our most serious difficulties arises from the unwillingness of the military authorities to recognize the wisdom of exempting chemists as a class from the draft. Almost from the beginning of our work we took up this question from various angles, realizing, as we do, the vital importance of keeping chemists at work in their profession not only at the present time but more particularly for the future. Our civil, mechanical, electrical, and other engineers can be made good use of at the front and not only contribute greatly to the success of our forces, but, by the valuable experience obtained in their profession, can improve themselves for future service at home. This is not true of chemists, with an exception here and there. Once in the Army and at the front, if he be only recently out of college, he is lost to chemistry forever. They are not slackers and are just as anxious as any other red-blooded young men to get into the fray, and therefore I have believed it wise not only to have them exempted from the draft, but declined in case they should enlist. Already serious trouble has come to many of our chemical plants and plants employing chemists, as a result of the draft, and unless wise provision be soon made we can foresee a condition which it will cost months to rectify. Why should we not take advantage of the experience of our English friends who have passed through this same situation and learned that there is a large class of men who can do more valuable work behind the lines than they can in the trenches?

The one great need of any colossal organization is the complete coordination of all its parts. No one can claim that the organization in Washington has yet reached this stage or even approximated it. Many things are done several times over and many others needed are not done at all. I presume this condition is unavoidable at this stage of our progress, but it must not be allowed to continue indefinitely. We have the utmost confidence that the President and his advisers can be relied upon to produce the required organization coordinated and articulated so perfectly that it will work with giant force and with little friction. This will come after politics have given place to patriotism, and this will happen, I believe, when the people of the country thoroughly appreciate the fact that we are at war. In any event, I am sure the country can rely upon the 10,000 chemists of this Society to do everything that lies in their power to see that the chemistry branch, possibly the most important of all, is not found lacking in either ability or patriotism.

Dr. Nichols was followed by Professor Marston T. Bogert, Chairman of the Chemistry Committee of the National Research Council, who gave an account of the organization of the research workers of the country and a general outline of the many problems arising within the purview of that committee. We hope to publish this address in full in our November issue.

In continuation of the lectures, Dr. Ruyter Adams, of the University of Illinois, explained the unique development of the synthetic dye industry in America, and a small commercial sample of some of the products.

On the invitation of President Auguste Lombard, Engel, of the French Commission, addressed the Society as follows:

I desire, first of all, to express the most cordial welcome to you from those who are most needed and to place them in the

trenches, as we did ourselves, and have lost them where they are most needed, in the laboratories and the industries. We made this great mistake at the beginning of the war. We took all chemists available and sent them into the regiments, mostly the infantry. Perhaps we lost 60 per cent of our mobilized chemists below the age of 40; for instance, the School of Chemical Engineering, Paris, has a casualty list of 35 per cent. At the Normal School, in the scientific department, there was a loss of about 52 per cent in the first ten months of the war. I cannot tell you emphatically enough that we must in all of our allied nations do our best to keep scientific men where they are most needed, not only for war problems, but for the future upbuilding of these nations. In general, the slowness to recognize scientific men by the military authorities was because they did not realize for what they were needed. For a long time they worked with the old methods of warfare and believed that all conditions were provided for, but when the method of attack changed, as Dr. Bogert has mentioned, when the gas attacks came, the military authorities saw that the time had come to adapt new materials to the new methods. That involved an enormous amount of work, not only in chemistry, but in physics and all branches of engineering.

"After three years of experience our scientific departments are well and satisfactorily organized. The organization is simple. The 'Front Laboratories,' mainly toxicological, detect poison in the water supply, for example, and provide chemicals to neutralize the effect if possible. These laboratories exist in large numbers, one with every brigade, or perhaps with every division, and are connected with a central army corps laboratory. In the front laboratory, in the field, there is often not even a tent, simply a box containing the needed supplies. The chemists work in the mud, on the ordinary ground, taking samples of the water, making chemical tests for nitrites, nitrates and chlorine. Thus they discover whether the water is pure or of slight doubt. If the latter is the case, the sample is sent to the army laboratory, where a bacteriological test is made. These army laboratories are usually located in the towns behind the lines, using in many cases school laboratories. Chemical advisers are connected with the general staff.

"At the rear there is an organization located in the schools where new compounds are studied, also unburst shells, samples of gases, parts of masks, in fact, any material which can be obtained. Other laboratories take care of factory supervision. Chemical manufacturers are producing gases and explosives.

"The manufacture of explosives is almost entirely under government monopoly. Previous to the war, hunting and war powders were made under government control. Only a few dynamites and safety powders were made under government control by supply contractors. The government is able thus to control entirely the explosive work.

"Speaking of general problems of research, I am interested to see what wonderful scientific organization there is here. You have more laboratories and facilities, more credit involved, your field of activity is tremendous. I am struck to see that in so short a period so many problems have been solved. It is an honor to be able to say that you have solved questions in a better way in three months than we took three years to do. You have been obliged to do over again much that we had already done. From now on we hope to work in such close connection with Dr. Bogert and others as to bring all data together and render work easier and avoid duplication. We hope to succeed in working very closely with you."

In conclusion, Dr. A. A. Noyes, of the Government Nitrate Supply Committee, spoke of the findings of that committee (published in detail in the September issue of *THIS JOURNAL*).

Immediately after the adjournment of the Conference, more than 400 members enjoyed the boat trip to

Pemberton where a delightful shore dinner was served, immediately followed by a smoker in one of the adjoining hotel buildings. Great enthusiasm was aroused by the singing of the Marseillaise, led by Dr. L. H. Baekeland. Toward the close of the smoker, Professor Talbot, acting as an informal toastmaster, introduced President Stieglitz, who responded for the visiting chemists in appreciation of the many courtesies extended. Professor Grignard was then introduced and spoke with much feeling, but in French. For the benefit of many of his hearers Lieutenant Engel, upon request, gave in English the substance of Professor Grignard's remarks, in which he concurred most heartily.

"Professor Grignard considered the organization and administration of the American Chemical Society the best in the world. Hitherto Germany had led in this regard, but he felt that the Germans had never possessed the spirit of democratic friendship which characterized the members of this Society. France is now preparing to imitate the American Chemical Society in its organization. The Chemical Society of France consisted formerly only of distinguished men in pure science. As the chemical industries developed, effort was made to form an industrial section, but this idea was rejected. A few months ago preliminary steps were taken under the stress of war for the organization of a French Society of Chemical Industry. However, in the light of what he has learned here as to the mutually helpful union of men of the universities and of the industries, he felt confident that in the future the two French organizations will be merged and that a truly national organization similar to the American Chemical Society will result. He hopes to see organized an American branch of this greater French Society so that joint work may be best promoted."

Dr. Baekeland followed, speaking in his happiest vein, to the very great delight of his hearers. The final speaker was Dr. A. D. Little, who spoke in lighter vein of some typical local chemical exploits, such as the extraction of gold from sea water, etc. Turning, however, to the more serious side, he pointed out that the payment of the great national debt due to this war should result most largely through the activities of the American chemists. Waste must be avoided: waste in city government, fire losses, manufacturing, railroading; waste of power, forest and labor.

Wednesday morning and afternoon were devoted to conferences and divisional meetings. A synopsis of the conference in the Division of Industrial Chemists and Chemical Engineers on "The Industrial Chemist in War Time" is printed in this issue.

On Wednesday evening, in Huntingdon Hall, Boston, before a large audience, President Stieglitz delivered his Presidential Address on the subject: "The Outlook for Chemistry in the United States." This address will be published in full in the *Journal of the American Chemical Society*.

Thursday was devoted to a continuation of the divisional meetings, including the Metallurgical Symposium in the Division of Industrial Chemists and Chemical Engineers. The Division of Water, Sewage and Sanitation made a trip to Ayer to inspect the United States Camp located there. Under the guidance of Mr. R. S. Weston they were given unusual facilities to see the cantonment, including the barracks and the excellent water and sewage disposal systems.

ORIGINAL PAPERS

COAL DISTILLATION UNDER PRESSURE

By J. H. CAPPS AND G. A. HULETT

Received May 14, 1917

The many uses of coal may be roughly classified under two general heads. It is burned directly as a fuel, or it is destructively distilled (or "carbonized"). Coal is most frequently carbonized with either gas or coke in view as the primary product of manufacture.

Coke ovens and gas retorts subject the coal to widely different conditions as regards rate of heating, duration of heating, etc., because the conditions which produce the maximum yield of the best coke are different from those that produce the highest possible yield of gas. Certain other conditions, however, such as pressure and maximum temperature attained are practically the same in either case.

In making gas or coke, the retort or oven which contains the coal is subjected to a temperature of about 950 to 1000° C. while most of the volatile matter is driven off before the coal itself reaches 600°. During the distillation the different layers of coal from the retort walls to the center vary not only in temperature but also in rate at which they are distilled.

In general, the vapors, after leaving the coal, enter regions where they are subjected to decidedly higher temperatures than that of their origin, so that secondary and uncontrolled "cracking" takes place, forming, again, decomposition products, together with carbon residues which separate in the form of flakes or droplets and float along with the vapors until mechanically caught with the condensing oils and water to form the tar. It is evident, therefore, that the technical distillation of coal is a most complicated process from the standpoint of both the chemical and physical changes which take place. The present work is a preliminary attempt to get information about the products which may be obtained from a given type of coal and how these products vary with the temperature, pressure and time or rate of distillation. Our apparatus was designed with a view to avoiding the secondary "cracking" of the vapors after they leave the coal and also with a view to heating the whole mass of coal as uniformly, as to time and temperature, as possible.

If the first layer of coal is heated rapidly, the second layer at a different rate, and so on, it is obvious that the first products of decomposition and distillation of one layer will be mixed with the later products of outer layers in a hopeless manner. This situation may be improved somewhat by heating slowly to a given temperature which is maintained until the reactions for that temperature are completed, then heating to a higher temperature and holding it until the reactions for this new temperature are over, and so on. However, with a slow rate of heating we undoubtedly get different reactions and vapor mixtures than when the coal is heated rapidly. We aimed to heat uniformly and still at a fair rate.

Practically all the work done on the carbonization of coal has been at atmospheric pressure, save some work under diminished pressure,¹ so that our knowl-

edge as to the pressure factor is restricted to a small range of from a few millimeters to one atmosphere. We first attempted to find out something about the variations with pressure up to twenty atmospheres.

After much experimentation and many failures we evolved the apparatus described below.

APPARATUS

The retort used in this work was a steel cylinder of 1.9 liters capacity (Fig. I, *A*) into which was sealed (cemented) the neck *B* of a $\frac{1}{8}$ in. walled $\frac{3}{4}$ in. steel tube. Into this were brazed a brass side tube of $\frac{1}{4}$ in. inside diam. and 2 in. long, at *E*, and a small copper tube, at *F*, which led to the pressure gauge *G* and could be disconnected at the union *T*.

The "first trap" *C* (see detail) was made from a seamless, spun-bottomed steel tube of $\frac{1}{8}$ in. inside diam. and $\frac{1}{16}$ in. walls. The brass inlet and outlet tubes ($\frac{1}{4}$ in. diam.) were brazed in with silver. The tube *X* was let down through the cap to prevent the spurting of condensed liquids across the trap and into the outlet. The seat of the cap was bedded with lead, which sealed the tube *X* into the cap and very effectively and conveniently sealed the trap itself when the top was screwed into place. This joint withstood temperatures up to 220° and pressures as high as 20 atmospheres very satisfactorily.

The "second trap" *D* was of glass blown in our laboratory. In the side tube to the left, condensation of the light oils took place, whence they flowed into the main (receiver) part of the trap. The uncondensed gases passed out through the stopcock *H* to be measured and sampled for analysis. The Liebig gas washing bulbs *J* were made in the laboratory to contain a standard acid solution which would collect the ammonia from the gas as it bubbled through. The question of ammonia, however, was dropped because sufficient information could be obtained from the analyses of the coal and resulting coke. Also the analyses of our cokes showed that a great part of the nitrogen was still retained after low temperature carbonization.

The top of the neck *B* was sealed by an ordinary cast-iron cap through the top of which a hole had been drilled for the introduction of the "internal condensation tube" *K*. This was practically a reflux condenser and its object was to condense and return the heavier volatile products to the coal mass where they would have further chance of cracking. If we had attempted to cool the neck of the retort, these constituents would have flowed down the hot sides of the retort where cracking would have occurred with a deposition of carbon residue, while, by the arrangement employed, there was returned directly onto the coal where cracking took place on and at the temperature of the coal.

With good heating at a rapid rate during the period in which the condensable products were given off, the cooling surface exposed to them by the internal condensation tube was undoubtedly too small and its temperature also not probably higher than the heating

¹ Bureau of Mines, Technical Paper 140.

point of the liquid inside, so that the condensations were not as complete as are possible at the indicated temperatures.

In view of this inefficiency and of the results of some subsequent work in this laboratory which have not yet been published, we disregard, in this paper, our data on the effect of this reflux condensation.

The heater used, *L*, was an electric resistance furnace of which the heating element was a single spiral of nichrome "flattened wire." This coil was cemented in place with a mixture of kieselguhr and cement and

nichrome resistance ribbon to maintain the desired temperature within the heater. We made only one separation of the liquid distillate and found it best to have our first condensation at such temperature that no water would remain with the heavy oils in the first trap. For this purpose, this heater kept the temperature of the first trap about 20° above the boiling point of water at the pressure used.

The cold water jacket *N* facilitated the liquefaction of the vapors as they passed to the second trap and also prevented the conduction of heat along

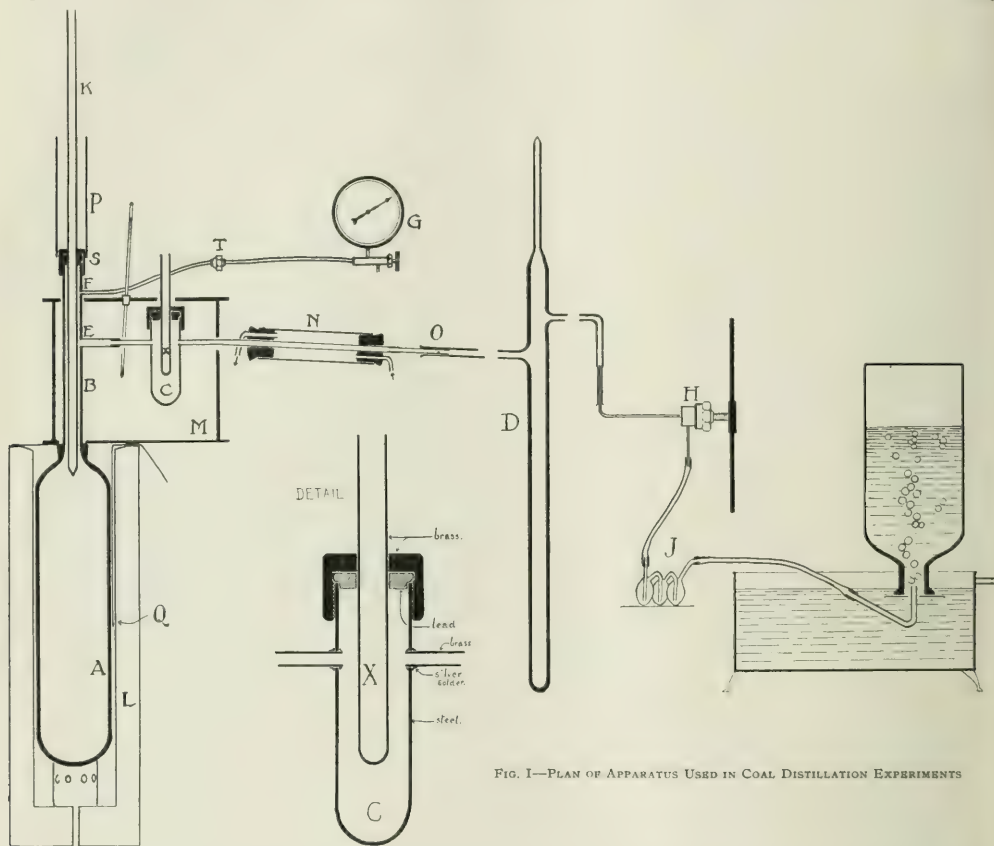


FIG. 1.—PLAN OF APPARATUS USED IN COAL DISTILLATION EXPERIMENTS

around it was wound sheet asbestos to a thickness of $\frac{1}{2}$ in. An air space of $\frac{1}{4}$ in. was left and then two layers of "corrugated" asbestos were wound around this. Several wrappings of thick asbestos felt completed the insulation. In the bottom of the furnace the resistance ribbon was wound into a flat spiral. Through the center of the floor a $\frac{1}{4}$ in. hole permitted a stream of illuminating gas to be led in, in order to keep a reducing atmosphere around the hot steel retort during a run.

The outside heater *M* was constructed of heavy asbestos cement board with a double glass window in front. Strung upon the floor were four coils of small

the brass tube from the heater *M* to the cement joint at *O*. The glass tube jacket *P*, containing boiling water, served the double purpose of keeping the lead bedding in the cap below its melting point and of acting as a condenser for the vapors of thymol or aniline in the internal condensation tube. Temperature was read outside the retort by the Pt-PtRd couple *Q*, insulated in a glass tube and placed next to the steel retort, but separated from the heating coil by sheet asbestos.

PROCEDURE

The charge of coal was introduced into the retort through the neck, and the cap *S* screwed firmly into

place. Then the short arm of the first trap was fastened to the side tube at *E*, by soldering with lead.

The retort was then set in place in the furnace, the outside couple adjusted and the heating box *M* put in its place. The second trap was now connected to the first trap by sealing with Khotinsky cement at *O*.

The next step was to displace the air in the apparatus with illuminating gas by alternately evacuating at the cock *H*, and admitting the gas at the union *T*. The connection at *T* was then made with the pressure gauge, the stopcock was closed and the outfit was ready for a "run."

The electric current was from the A. C. lighting circuit and between 600 and 1000 watts were used, according to the temperature of the furnace and to the rate at which the temperature was to be raised. Current was regulated by a water-cooled sliding resistance in series.

The temperature was raised at the rate of about 4 or 5° per minute from room temperature to about 450° C. (reading of couple, *Q*) and from 450 to 600° it was advanced at the rate of practically 1° per minute. Under these conditions later experiments with this apparatus showed that the temperature in the center of the coal followed the temperature outside the retort fairly uniformly at about 50° lower, except at the stage where the exothermic reactions are most pronounced.

Pressure in the retort was built up simply by confining the gases liberated from the coal. When the desired pressure was reached, the cock was opened enough to let out gas as fast as it formed.

At 10-minute intervals, readings were recorded of temperature, current through furnace, pressure, volume of water and of light oil in second trap. Rate of flow of gas (cc. per min.), and the total gas volume were also known. Samples of the gas were taken for analysis at the following temperatures: 450°, 500°, 550°, and 600° C. If the rate of evolution of gas be plotted against temperature of the coal, the temperatures indicated above lie on the curve, respectively, at the points where it first begins to rise, where it shows the highest rate of evolution, where it begins to decline and further down the slope at the end of the run.

When the thermocouple indicated 600° the current was shut off and the pressure let down to atmospheric, all gases being measured as usual. Then the top of the second trap was broken off with a file scratch and the water and oil withdrawn by means of a siphon pipette; these were weighed separately and the oil sealed in glass tubes to await analysis. The first trap was next disconnected, opened and emptied and the heavy oil weighed and sealed in a tube.

When the retort had cooled it was opened at *S* by removal of the cap. The coke within was in a single brittle cake which had to be broken into small enough bits for removal. This was done by pounding the cake with an iron rod and shaking out the broken coke which was then weighed, sampled for analysis and bottled.

Four typical coals¹ were investigated with this apparatus: a West Virginia steam coal (New River), Pittsburgh bituminous, Illinois soft coal, and a Wyoming sub-bituminous coal. With the New River and Pittsburgh coals twelve runs each were made—four at each of three different condensation temperatures. For instance, with aniline (b. p. 184°) in the internal condenser, runs were made at 1, 5, 10 and 20 atmospheres pressure, all conditions except pressure being kept as nearly as possible the same for the series. Then another such series was made with thymol (b. p. 230°) boiling in the condenser and finally a series in which there was nothing in the condenser. In the case of the Illinois coal only two series were made (eight runs in all), one series with aniline condensation and another with no condensation. Only six runs were made on the Wyoming coal, one series with no condensation and two runs (1, and 20 atmospheres) with aniline boiling in the condenser.

OILS

We were most interested in the oils. The most obvious data on these are the variations in their amounts due to changes of pressure.

The yields of light and heavy oils (as percentage by weight of the original coal), when plotted against pressure, bring out certain marked tendencies, as shown in the following table which sums up the curves in Fig. II.

TABLE I—EFFECTS OF PRESSURE INCREASE FROM 1 TO 20 ATMOSPHERES

COAL	HEAVY OIL	LIGHT OIL
New River	Decrease from 4.8% to 0.4%	Increase from 1.3% to 2.4%
Pittsburgh	Decrease from 8.8% to 1.6%	Increase from 3.75% to 4.8%
Illinois	Decrease from 8.2% to 1.5%	Increase at no condensation Decrease at 184°
Wyoming	Decrease from 5.2% to 1.1%	

The term "heavy oil" is applied above to that fraction which condensed during the run in the first trap. The temperature of this trap was slightly above that at which water boils under the pressure of the experiment.

"Light oil" refers to that fraction which did not condense at the above temperature, but did condense with the water at room temperature and was retained in the second trap.

The decrease in heavy oils is a better indication of the extent to which cracking has taken place than is the increase in light oils, because the latter represent only a part of the products of cracking of the heavy oils, the other products being gases and carbon residue.

Also the increase in light oil yield is due to other factors besides cracking of heavy hydrocarbons. For instance, the partial pressure of each of the constituent gases in the mixture passing over the condensed oils in Trap 2, is increased as the total gas pressure increases. Or these gases which do not condense from such a mixture at ordinary pressures, the less volatile will condense when their partial pressures are sufficiently increased. Also we must consider the solubility of these and other gases present in the condensed oils and water as following Henry's Law and the weight of these gases dissolved at high pressures.

¹ These coals were collected and examined by permission of the U. S. Bureau of Mines and were preserved in airtight containers until used.

TABLE II—EFFECT OF PRESSURE ON COMPOSITION OF THE OILS

Pressure in atmos- pheres	PER CENT LIGHT OIL BOILING BELOW 170° C.				PER CENT LIGHT OIL SOLUBLE IN NaOH				WYOMING COAL		ILLINOIS COAL					
											Per cent Boiling Per cent Soluble					
											below 150° in NaOH					
	NEW RIVER COAL				PITTSBURGH COAL				NEW RIVER		PITTSBURGH COAL					
	a	b	c	d	e	f	g	h	i	j	k	l	m	n	o	p
	No	230°	184°	No	230°	184°	Aromatic from d	230°	184°	No	230°	184°	Per cent boiling Soluble in NaOH	Per cent below 150°	No	184°
	con.	con.	con.	con.	con.	con.		con.	con.	con.	con.	con.	below 150°	con.	con.	con.
1	9.7	22.4	17.8	15.4	12.6	Lost	6.6	Lost	Lost	25.0	39.2	37.5	8.75	28.0	9.7	13.3
5	38.2	38.2	38.6	29.5	19.8	25.1	7.5	31.6	34.1	28.2	36.0	33.6	5.7	24.0	18.7	19.7
10	42.1	48.3	44.2	25.2	30.0	22.7	9.7	27.4	22.5	36.2	32.4	25.1	12.35	9.0	21.0	25.0
20	Lost	34.8	49.2	35.2	29.4	39.1	14.7	20.8	25.8	23.8	27.4	24.3	Lost	Lost	22.1	17.0
															43.2	46.2

is consequently correspondingly greater than at low pressures.

OIL COMPOSITION

The analysis of these oils presented a great many difficulties. A scheme was worked out by which the oils were first subjected to fractional distillation, the colors, densities and weights of all oils and fractions being recorded. Cuts were made at (1) 170° C., (2) 230°, (3) 270° and (4) above 270°. Fractions (1) and (2) were then analyzed as follows: Bases, pyridine, etc., were extracted with 20 per cent H_2SO_4 ; acids and phenols, with 10 per cent NaOH; unsaturated substances with concentrated H_2SO_4 and the aromatic hydrocarbons by washing with dimethyl sulfate or liquid SO_2 .

Fractions (3) and (4) were allowed to stand several days to allow any anthracene present to crystallize. This was then separated by filtering with suction in a Gooch crucible, washed with pyridine and weighed. The filtrates from this separation were then analyzed as Fractions (1) and (2). Everything not extracted by these various processes was called "paraffin hydrocarbons."

A tabulation of some of the figures so obtained in Table II shows something of the effect of pressure on the composition of the oils. These data are plotted in Fig. III.

Columns a, b, c, d, e, f and n show the increase in percentage of more volatile components in the light oils with increasing pressure. Column g shows the increase in cracking the heavier paraffin and unsaturated hydrocarbons with increasing pressure. Columns h, j, k, l, m and o show how pressure decreases the amounts of phenols and "tar acids" in the oils—although it is not clear to what this tendency can be due.

In regard to the oil analysis data, those on the fractional distillation and on the "per cent soluble in NaOH" are probably the most trustworthy because the largest obtainable samples were worked with and these were the first values determined in each oil.

All oil samples lose so much from simple manipulation in tubes, pipettes, and pycnometers by adhesion to the walls and by solution in the wash liquids that, with the (small) samples available, such a series of operations made considerable error in the results but these results are of value from the standpoint of relative changes due to pressure. In considering the data so far obtained it seemed best to fall back on the following simple scheme with the oils of the Illinois coal: We took the densities and weights of the light oils, washed out the phenols and tar acids with 13 per cent NaOH and weighed the residues. The residual oil was then fractionally distilled, cuts being made at 75, 100, 125, 150, 175, 200, 250 and 300° C. Weights and densities of each of the fractions were recorded. The sum of the fractions boiling below 150° was called motor fuel.

Curves p, r, s and t in Fig. III sum up the data on the fractional distillation and the phenols and tar acids of the Illinois coal oils.

COKE

The amount of coke residue left in the retort after this partial carbonization is notably increased by pressure, as the curves in Fig. IV show. Ordinates are percentages of the original coal.

It is to be noticed, especially in the curves for New River and Pittsburgh coals, that practically all of this increase is brought about by the first 10 atmospheres and most of it by the first 5 atmospheres.

COKE COMPOSITION

The analyses of these cokes gave percentages of "fixed carbon," nitrogen, oxygen, sulfur, volatile matter and hydrogen and also the calorific value in B. t. u.

These percentages (on moisture and ash-free basis) were plotted against pressure. These curves in Fig. V are summed up in Table III in a tabulation of the tendencies apparent from them.

In the second column opposite "fixed carbon" is found "+ 1 per cent" which means that increase of pressure from 1 atmosphere up to 20 atmospheres is shown to affect an increase in the percentage of fixed

TABLE III—COKE INFLUENCES OF PRESSURE
AVERAGE CHANGES FOR ALL CONDENSATION TEMPERATURES

A—PERCENTAGE OF COKE					B—PERCENTAGE OF CONSTITUENTS				
	N. R.	Pgh.	Ill.	Wyo.		N. R.	Pgh.	Ill.	Wyo.
Fixed C.....	+1.0	+1.0	+1.2	—0.5	Fixed C.....	+1.10	+1.1	+1.4	—0.6
N.....	—0.05	—0.05	—0.10	..	N.....	—2.0	—2.0	—4.5	..
O.....	—0.25	—0.5	+0.5	..	O.....	—12.0	—12.0	—10.0	+8.0
S.....	—0.10	—0.10	S.....	—10.0	—10.0
Volatile.....	—1.0	—1.0	—1.25	+0.5	Volatile.....	—10.0	—9.0	—10.0	+3.0
B. t. u.....	+50	+60	+1100	..	B. t. u.....
H.....	—0.10	..	+0.10	+0.10	H.....	—3.0	..	+3.0	+3.0
CHANGES IN NO CONDENSATION SERIES ALONE									
Fixed C.....	+1.5	+1.0	+3.5	..	Fixed C.....	+1.6	+1.1	+4.0	..
N.....	—0.05	—0.10	N.....	—2.0	—4.0	—4.5	..
O.....	—0.30	—1.0	—1.5	+0.7	O.....	—15.0	—25.0	—30.0	+12.0
S.....	—0.10	—0.10	S.....	—19.0	—10.0
Volatile.....	—1.2	—1.3	—3.5	..	Volatile.....	—17.0	—11.0	—28.0	..
B. t. u.....	+60	+60	+2300	+80	B. t. u.....
H.....	—0.10	+0.10	H.....	—3.0	+3.0

carbon in the coke to the extent of about 1 per cent of the coke, etc. Blank spaces indicate that the corresponding curves show no marked increase or decrease.

It must be borne in mind that the absolute values of some of these constituents are quite small so that a large percentage of change in the constituent would show as a very small change in percentage of the coke. In Table III arrangement B shows the interpretation of these same curves in percentages of the respective

constituents. Thus, in arrangement A, pressure causes a decrease of sulfur amounting to 0.1 per cent of the coke of New River coal. Since, however, the total amount of sulfur present is only about 0.8 per cent of the coke, the effect of pressure is to drive away about 12 per cent of the total sulfur. Thus in Table III the figures under B are more significant than those under A.

The general though slight increase in percentage of "fixed carbon" in the coke indicates that at higher

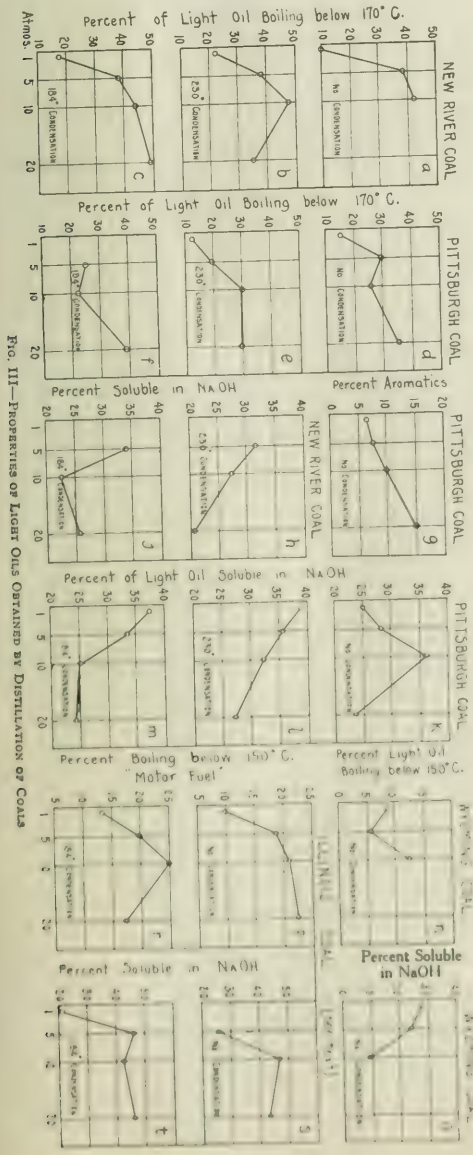


FIG. III.—PROPERTIES OF LIGHT OILS OBTAINED BY DISTILLATION OF COALS

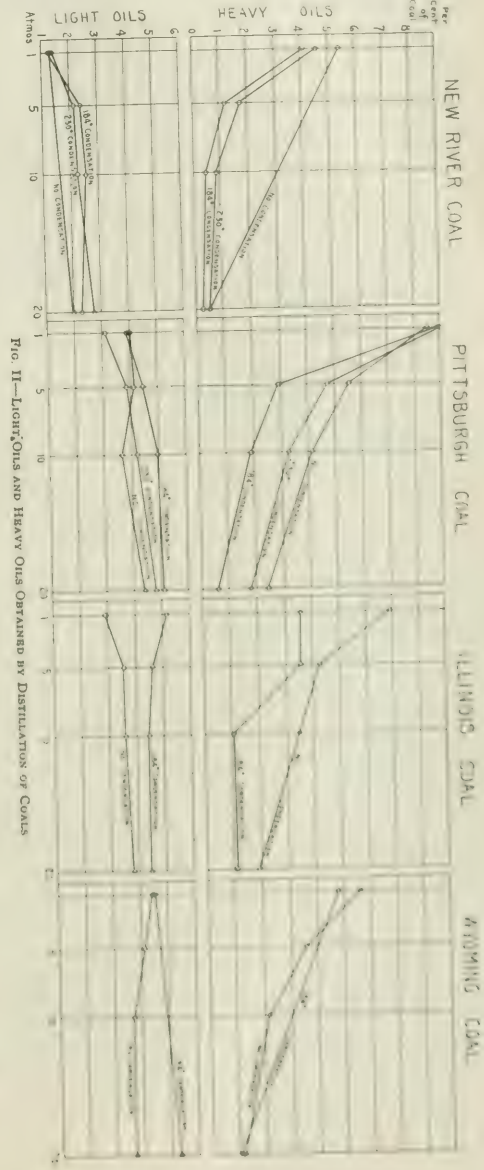


FIG. II.—LIGHT OILS AND HEAVY OILS OBTAINED BY DISTILLATION OF COALS

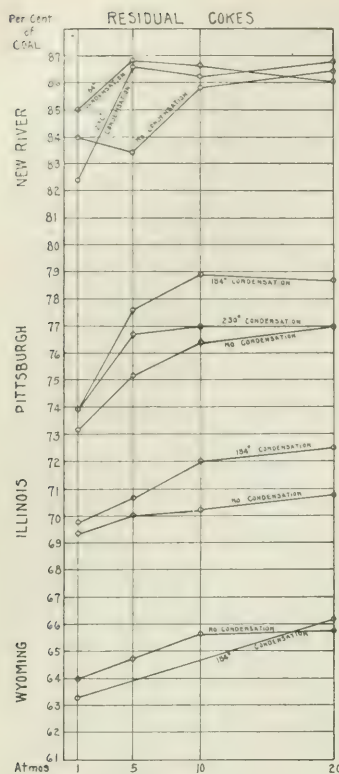


FIG. IV—RESIDUAL COKES OBTAINED

pressures more of the volatile products of distillation have undergone cracking, in contact with the coke residue than at lower pressures. It is to be noticed that the effect of pressure on Wyoming coal is to decrease the fixed carbon.

It has been shown that the cracking processes are time reactions. So, the effect of higher pressure is to hold back the volatile products in contact with the coke for a longer time, thus enabling the cracking to take place to a greater extent than at lower pressures. Also it increases the partial pressure of the heavier vapors, *i. e.*, their mass law concentrations, thus increasing the rate of cracking. This effect of pressure is also shown by the increase (2 to 4.5 per cent) in the percentage of the coal which is left as coke residue inasmuch as carbon is one of the products of the cracking reactions.

It has been shown¹ that by passing hydrogen through heated coke, much of the nitrogen therein can be removed as ammonia. The general decrease in nitrogen in the cokes may be accounted for as due to the increased partial pressure of hydrogen in contact with the coke.

A study of these curves brings out some interesting tendencies.

¹ *J. Gas Lighting*, 126, 329-331.

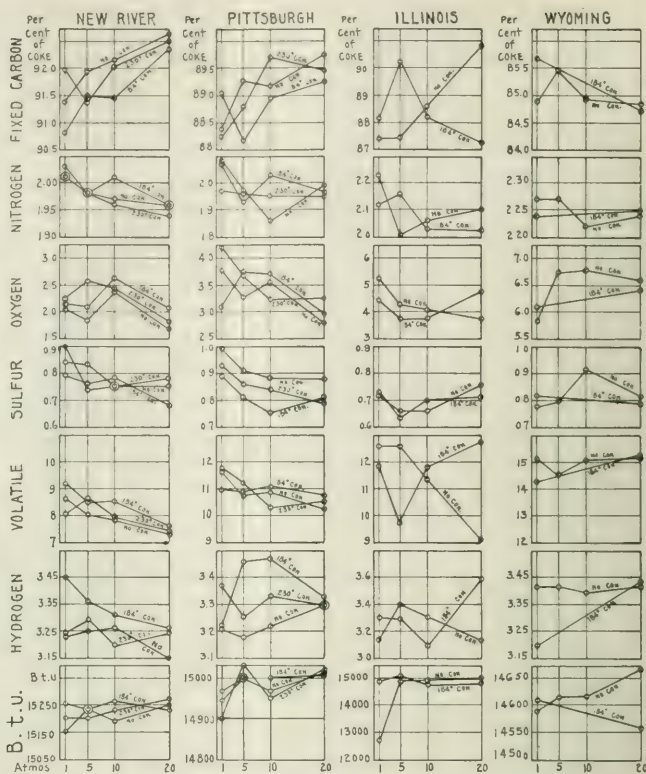


FIG. V—ANALYSES OF RESIDUAL COKES

Pressure increases the fixed carbon in all cokes except those of Wyoming coal in which fixed carbon is decreased. It decreases oxygen and volatile matter in all except Wyoming cokes but in these oxygen and volatile are increased. Hydrogen is decreased in New River and increased in Illinois and Wyoming cokes.

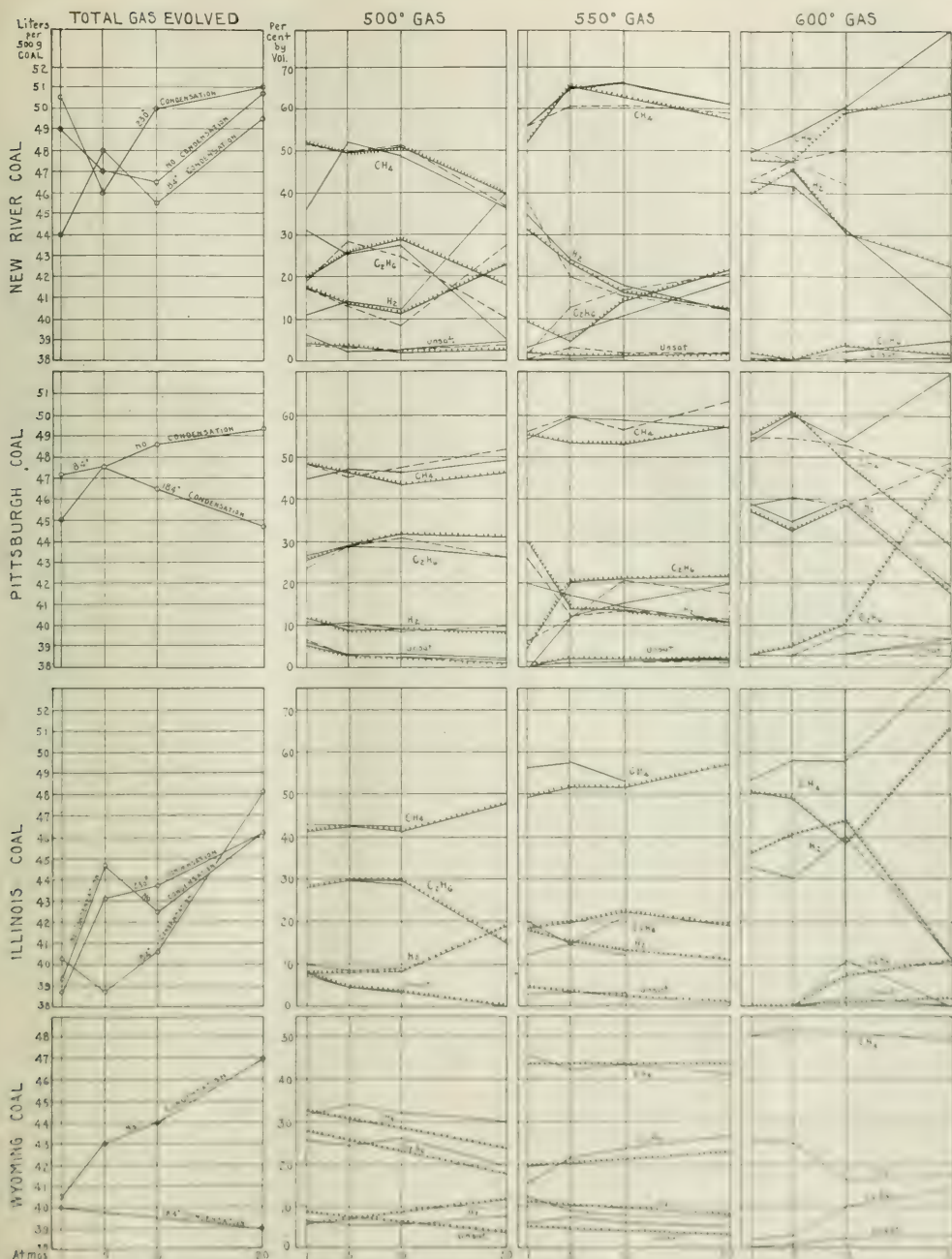
GAS

Pressure causes marked increase in the amount of gas liberated, particularly in the case of the Pittsburgh coal. With New River coal the effect is less pronounced. With both Wyoming and Illinois coals it increases the gas markedly when there is no internal condensation, while with 184° condensation there is a slight decrease in gas yield from 1 to 20 atmospheres. The curves in Fig. VI illustrate these tendencies.

GAS COMPOSITION

Gas samples, as mentioned before, were taken for analysis at about 450°, 500°, 550° and 600° from each run, except with high pressure runs, in which cases the desired pressure was not attained until the first of the above sampling temperatures had been passed.

With each of the coals studied, the building up of a pressure of 20 atmospheres was not accomplished until the temperature of the retort registered between

FIG. VI
GAS EVOLVEDFIG. VII
ANALYSIS OF GASES EVOLVED AT DIFFERENT PRESSURES

450° and 500°, and with such runs the first gas sample was taken at 500°.

Gas analyses gave per cent by volume of CO₂, C₂H₄, O₂, CO, CH₄, C₂H₆, H₂ and N₂. Something was learned of the effect of pressure on the gases evolved from the coal by plotting the values of each of these constituents against pressure—the coal, condensation temperature and temperature of sampling being the same. With four coals, two or three series of runs for each coal, four (or three) samples taken for each run and eight constituents determined in each sample, the number of curves necessary to cover the whole gas field is so great that they cannot all possibly be given herewith. The curves for hydrogen, unsaturated hydrocarbons, ethane and methane, which were deemed the most significant, must suffice. They are shown in Fig. VII.

Here the percentages of H₂, C₂H₄, etc., C₂H₆ and CH₄ are ordinates and the pressures, abscissae. Each graph represents gas samples taken at a single temperature from the various runs.

In the 500° gases, pressure increases the hydrogen, with some irregularities, in all cases except that of the Pittsburgh coal, where it causes no marked change. Unsaturated compounds, in all coals except New River, are somewhat decreased by pressure. Ethane shows (in general) a decrease, and methane no pronounced general effect.

In the gases taken at 550°, hydrogen decreases markedly with pressures. The effect seems to be more pronounced as the age of the coal increases. Unsaturated hydrocarbons show, if anything, a slight decrease. Ethane shows a general increase, nearly corresponding to the decrease in hydrogen. Methane shows (as at 500°) no general effect.

At 600°, hydrogen decreases more sharply. Unsaturated bodies are not perceptibly affected, except by a slight increase with Illinois and Wyoming coals. Ethane is generally, though irregularly, increased. Except with Wyoming, and possibly Pittsburgh coals, the striking rise in methane corresponds roughly with the decrease of hydrogen as the result of pressure.

Of the above curves those on the change in per cent of hydrogen with pressure are particularly significant.

With high-pressure runs the partial pressure of hydrogen is necessarily much higher than with low pressures. The high hydrogen concentration undoubtedly affects the composition of the oils of the coke. The decrease in nitrogen content of the coke with pressure is undoubtedly due to this factor.¹

We find the hydrogen percentage decreasing as pressure increases in spite of the fact that the increased cracking which takes place at higher pressures liberates more hydrogen than at low pressures. The hydrogen, therefore, must be used up in liberating nitrogen as ammonia from the coke as well as in saturating olefine and acetylene compounds present. This conclusion is borne out in the observed decrease of nitrogen in the cokes (Fig. V).

The increase of ethane at 550° and of ethane and methane at 600° may be regarded as a rough measure

¹ Loc. cit.

of the extent to which hydrogenation of unsaturated hydrocarbons and saturated ones has been affected by the high partial pressure of hydrogen.

It is somewhat doubtful whether a sample of gas taken from a high-pressure run can be compared with fairness to one taken at the same temperature from a low-pressure run. Thus, in the case of a 1-atmosphere run, since the gases are allowed to escape as rapidly as they are evolved from the coal, there is not much mixing of the gases from one stage of the distillation with those from another stage. In the case of a 20-atmosphere run, on the other hand, the whole of the gases produced in the earlier stages of distillation are confined within the retort to build up the pressure to the desired point, and these mix with the gases from later stages. In comparing two 500° samples, one from a 1-atmosphere and one from a 20-atmosphere run, it must be borne in mind that the sample withdrawn from the system in the first case represents pretty accurately the gases which are being evolved at that temperature, while in the second case the corresponding sample comprises gases formed at every stage of the distillation from its beginning to the point of sampling.

The degree to which the latter sample is contaminated with gases from earlier stages depends, of course, upon the amount of gas which has been formed up to the time of sampling. In a pressure run, the proportion of "earlier" gases is greatest in the first sample (500°) and grows less with succeeding samples. This is because gas is allowed to escape as fast as it is formed when once the requisite pressure is established.

On account of frequent breakage of the apparatus and occasional loss of oils, etc., a number of runs had to be repeated. In such cases some duplicate gas samples were obtained whose analyses furnish evidence as to the reproducibility of conditions in the retort.

Two sets of such "check" gases are given in Table IV, one of them in triplicate.

TABLE IV—NEW RIVER COAL: 184° CONDENSATION: 550° SAMPLES
PRESSURE: 10 ATMOSPHERES 20 ATMOSPHERES

	Run 61	Run 91	Run 62	Run 92	Run 65
CO ₂	1.1	1.5	2.0	2.4	2.4
C ₂ H ₄ , etc.....	1.2	1.8	1.6	1.9	1.6
O ₂	0.3	0.2	0.4	1.5	0.5
CO.....	2.0	1.5	1.4	1.95	1.0
C ₂ H ₆	62.7	59.1	57.7	58.2	57.2
CH ₄	14.2	21.1	21.7	24.8	22.4
H ₂	16.1	14.8	12.5	6.1	12.3
N ₂	2.4	0.0	2.7	3.15	2.6

When a run was finished and the retort registered 600°, the current was shut off and the gas let out until pressure within the apparatus was atmospheric.

TABLE V

	ILLINOIS COAL				WYOMING COAL			
	Run 101	Run 102	Run 103	Run 104	Run 84	Run 85	Run 86	Run 88
	10	20	5	1	2	6	1	1
CO ₂	4.1	1.9	4.7	4.2	2.7	9.5	6.6	11.9
C ₂ H ₄ , etc.....	0.4	0.8	2.0	2.5	2.7	2.7	3.7	5.8
O ₂	0.1	1.0	0.2	0.0	0.3	0.5	0.2	0.1
CO.....	6.6	6.2	4.0	4.8	5.2	6.2	7.7	4.9
C ₂ H ₆	73.5	38.8	65.8	59.2	39.2	51.4	45.2	48.2
CH ₄	0.0	7.2	10.7	10.7	19.1	10.1	12.6	16.4
H ₂	15.0	43.9	11.3	18.2	29.8	16.4	22.0	10.5
N ₂	0.3	0.2	1.3	0.1	0.1	3.2	2.0	2.2

During this "let down" from a high to a low pressure, the light oil in the second trap was observed to boil violently. In several runs, a number of gas samples were taken during this boiling of the light oil, in order

to ascertain what constituents were being vaporized so rapidly. Analyses of some of these samples are given in Table V.

From the observed increase in the gas of unsaturated compounds, carbon monoxide, ethane and hydrogen, it was concluded that these were the constituents which were boiling out of the oil when the pressure over it was released.

SUMMARY

This work has shown the influences of pressure on the carbonization of coal in some striking tendencies.

I—Pressures up to 20 atmospheres decrease the amounts of high-boiling compounds and increase the amounts of low-boiling compounds in the condensable vapors evolved from coal below 600° C. Also pressure causes an increase of low-boiling aromatic bodies in these oils.

These results are directly attributable to cracking or thermal decomposition which is brought about by subjecting the vapors of heavy compounds to temperatures considerably higher than their boiling points, as the increased partial pressures of these constituents retards their vaporization.

Pressure also decreases, in most cases, the amounts of phenols and acid bodies in the oils. The reasons for this are not clear.

II—Pressure increases the amount of coke left as residue and also the per cent of fixed carbon in the coke. These are effects of cracking oils in contact with the coal. The calorific value of the coke is increased and the nitrogen, oxygen, sulfur and volatile matter are decreased.

This decrease of nitrogen, sulfur and oxygen in the cokes is probably due to increased partial pressure of hydrogen in contact with the hot coke.

III—Pressure causes an increase in the volume of gas evolved from coal below 600° C.

Up to 20 atmospheres it increases the per cent of hydrogen in these gases at 500° and decreases it at 550° and 600°. The increase at 500° is probably due to cracking of heavy hydrocarbons. The decrease at 550° and 600° is attributed to the action of hydrogen at high concentration on nitrogen (and sulfur and oxygen) in the coke and upon unsaturated products of cracking. Increase of ethane and methane in the gas seems to bear out this last view.

The authors wish to acknowledge their indebtedness to Dr. W. D. Bonner of the University of Utah for valuable assistance in the analysis of oils and to the Pittsburgh Station of the U. S. Bureau of Mines for the analysis of gas and coke samples.

PRINCETON UNIVERSITY
PRINCETON, NEW JERSEY

A NEW METHOD FOR THE RECOVERY OF SALTS OF POTASSIUM AND ALUMINUM FROM MINERAL SILICATES¹

By J. C. W. FRASER, W. W. HOLLAND and E. MILLER

A great many efforts have been made to obtain salts of potassium from such silicates as sericite and orthoclase. These minerals are not attacked by

acids. The feldspars occur widely distributed and are the most abundant of all minerals. Orthoclase feldspar of a sufficient degree of purity occurs in such quantities as to make it a possible source of supply of potassium salts.

Owing to the fact that in normal times potassium salts can be obtained very cheaply from Germany, and, also to the further fact that such silicates as feldspar and sericite can be decomposed only with difficulty, any process for the successful treatment of such silicates must obtain by-products of value in addition to the potassium.

A great many patents have been obtained on processes for the treatment of feldspar. Most of them make use of very high temperatures and rely in many cases on the separation of the potash by volatilization. The greatest objection to such processes is that in addition to being expensive it is difficult to separate the potash from the other constituents after the silicate has been decomposed.

I wish to call your attention to the results of some experiments which were made last year in our laboratory for the purpose of making available the potassium and aluminum contained in such silicates as feldspar and sericite.

It was soon realized that for any such process to be successful all the constituents of the silicate must be recovered in valuable form and at a minimum expenditure of energy and cost. The truth of these statements is borne out by the great number of unsuccessful attempts which have been made recently to obtain potash from feldspar.

On this account it was decided to avoid, if possible, the method so frequently resorted to by others, of bringing about complete decomposition of the mineral, for by operating in this way there is avoided a resort to high temperature, which adds to the cost of operation and leads to final products, many of which are useless or can be separated only with difficulty.

The method finally adopted secures the transformation of feldspar by successive states into products analogous to certain well defined minerals occurring in nature. It is well known that most of the "available" potash which occurs in the soil comes from the weathering of feldspar. This so-called weathering process takes place slowly in nature and the final product of this reaction is a hydrated silicate of aluminum known as kaolinite ($H_4Al_2Si_2O_9$).

In addition to kaolinite there are certain minerals such as leucite which are intermediate in composition between feldspar and kaolinite though they probably do not appear in the course of the weathering process. The important difference between the feldspars and leucite is, that whereas feldspar is not attacked by mineral acids, leucite is easily decomposed under these circumstances, giving salts of potassium and aluminum and liberating silica.

Our experiments soon showed that an alteration of feldspar to a substance analogous in composition to

¹ Presented at the Buffalo Meeting of the American Institute of Chemical Engineers, June 30 to July 1, 1917.

leucite could be secured by treatment of feldspar with a strong alkali under conditions given more in detail later on. This reaction possesses for our purpose two distinct advantages: (1) it is one very easily brought about when the proper conditions are obtained; (2) the product of the reaction possesses the convenient property of fractional decomposition when treated with dilute mineral acids.

METHOD

A quantity of finely ground feldspar (about 50 mesh) is brought in contact with about 0.8 its weight of potassium or an equivalent amount of sodium hydroxide dissolved in a small quantity of water in order to obtain an intimate mixture of the two. The mixture is then heated in an open iron vessel until the water has evaporated and thereafter for a period of about one hour at a temperature of 275 to 300° C. During this latter stage of heating a reaction takes place between the alkali and the feldspar which consists essentially in the withdrawal by the alkali of one of the three silicic acid residues of the feldspar, forming a new silicate and an equivalent quantity of alkali silicate. This new silicate when completely dry has approximately the composition of leucite:



It is insoluble in water and may be separated from the soluble portion which consists of the excess alkali used for the decomposition and the alkali silicate simultaneously produced.

The alkali employed in bringing about this reaction which is now in solution, part as hydroxide and part combined with the silica removed from the feldspar, can be entirely recovered by causticizing the solution with lime and filtering off the calcium silicate which is precipitated. This solution, when evaporated, is used for the treatment of other fresh portions of feldspar, the only loss being the unavoidable mechanical losses which in our laboratory experiments performed on one kilogram lots amounted to about one per cent.

The "artificial leucite" which contains all the potash and alumina and $\frac{2}{3}$ of the silica of the original feldspar can be made to yield its constituents one at a time by proper treatment with acids, thus avoiding expensive methods of separation by evaporation, crystallization, etc., the corresponding salts of potassium and aluminum being produced in succession. The basis for this treatment is the fact that the potassium contained in this new silicate is very much more loosely held than is the aluminum.

This can be illustrated in a number of ways. By suspending some of the silicate in water between two platinum electrodes, one can, on passing the current, bring practically all the potassium from the substance suspended in the water as potassium hydroxide or the potassium contained in the silicate can be titrated with a mineral acid and methyl orange as an indicator and with sufficient time towards the end of the titration obtain a fairly satisfactory end-point. The method of separating the potassium from this so-called

artificial leucite is based on this fact and the method of utilizing this property of the mineral for removing the potash is quite simple. The fact that the potassium in the silicate can be titrated with a fairly good end-point shows that the hydrogen-ion concentration of the solution necessary to bring this about is very small. Any mineral acid will serve the purpose and it is therefore possible to obtain the potassium directly as chloride, sulfate or nitrate without the removal of the aluminum. Ordinarily we have used hydrochloric acid for this purpose as most of the potash has been imported into the country as chloride. For this extraction the silicate is mixed with water, and dilute hydrochloric acid in amount equivalent to the potassium content of the silicate is added slowly with constant stirring. The only thing to be avoided at this point is a local excess of acid which would tend to bring into solution a portion of the aluminum. The potassium chloride solution is removed from the insoluble silicate of aluminum by filtration. The silicate of aluminum which remains is somewhat analogous to kaolinite, the final product of the weathering of feldspar. The separation of the aluminum from silica in this silicate is comparatively easy because of the readiness with which mineral acids effect its decomposition. If this silicate is treated with an amount of sulfuric acid equivalent to the aluminum it contains, aluminum sulfate is produced and gelatinous silica separates. As it is necessary to render this silica insoluble by evaporation, the sulfuric acid employed for the decomposition will not be very dilute. After dehydrating the silica the aluminum sulfate is dissolved in water and separated from the silica by filtration.

The same product is obtained by the treatment of other silicates such as sericite and clay.

RECOVERY OF PRODUCTS

The recovery of the products by this method is about as follows: the yield of potassium chloride is practically theoretical; the yield of aluminum sulfate is about 86 per cent of the theoretical. On a feldspar running 10 per cent K_2O one would obtain about $\frac{1}{4}$ of a ton of potassium chloride of 80 per cent purity, which is the grade usually imported for commercial purposes, and about one ton of crystallized aluminum sulfate. By a consideration of these figures it will be seen at once that in normal times the aluminum sulfate is more valuable than the potassium chloride produced and under these conditions the process is an aluminum sulfate process with potash as a by-product. There are certain advantages in this since the importation of cheap German potash after the war would affect the process less than it would if potassium chloride were the principal product. For these reasons the value of the process in normal times will depend largely on the cost of producing iron-free aluminum sulfate by this method as compared with the method now used in making it from bauxite.

ON THE RELATION BETWEEN THE PHYSICAL PROPERTIES AND CHEMICAL COMPOSITION OF GLASS VII—ETCH FIGURES

By EDWIN WARD TILLOTSON, JR.

Received June 21, 1917

When glass is exposed to the vapor of hydrofluoric acid, or dipped in a solution of hydrofluoric acid, with or without the addition of soluble fluorides, the surface is etched unevenly, there being produced "etch figures" of varying forms, and more or less crystalline in appearance.

An explanation of the formation of these figures was first offered by Leydolt,¹ who supposed them to be due to "preexisting crystals" in the glass, for the figures obtained by etching with hydrofluoric acid and also with steam possessed a remarkable similarity to crystal forms. This work was repeated in 1857 by Daubree,² who found no evidence for pre-existing crystals, and explained the figures as being produced by a protective coating of insoluble substances, such as K_2SiF_6 , which might be deposited locally on the surface of the glass. In 1866, an exhaustive study of this phenomenon was carried out by Weatherill,³ who observed that, in general, these etch figures were in relief and therefore supported the protective-layer theory; but, in one instance, a star-shaped acicular figure was found to be etched out, and this was regarded as disproving the view set forth by Daubree. Reinitzer⁴ noticed that the crystal form of the etch figures corresponded to that of the insoluble substances which might be formed, such as potassium or calcium fluosilicates, and therefore supposed them to be due to the formation of these substances on the surface of the glass. He also observed, as further evidence of this protective action, that concentrated HF, and HF and H_2SO_4 did not form etch figures, since these reagents were sufficiently active to dissolve both glass and the insoluble substances. Jackson and Rich⁵ attempted to correlate the etch figures with lack of homogeneity of the glass. They demonstrated by differential flotation of glass powders that ordinary glass is not homogeneous; but were unable, by the method employed, to detect any lack of homogeneity in optical glass. Nevertheless etch figures were obtained with optical glass as well as with the more common kinds. Lately Frink⁶ has announced that it is possible to differentiate between good and faulty glass by reason of differences in the etched surfaces produced by hydrofluoric acid, and to determine whether the fault is due to chemical inhomogeneity or to mechanical strains. Frink also inclines to the view that these figures are caused by preexisting crystals.

There are, therefore, two well defined opinions regarding the cause of the etch figures: the one supposes "preexisting" crystals within the glass, while the

other is based on the protecting action of insoluble fluorides and fluosilicates formed during the etching process.

It seemed distinctly worth while that this question should be settled, not only because of its importance in the practical etching of glass, but also for whatever bearing it might have on the theory of the molecular structure of glass. A series of experiments was accordingly carried out in the endeavor to throw more light on this subject.

MATERIALS

The materials used in this investigation were C. P. hydrofluoric acid, containing about 45 per cent HF, and C. P. ammonium fluoride. The etching solutions were prepared in platinum dishes, and the ingredients were weighed with an accuracy of about 1 per cent.

The following glasses were available and were used:

Window glass	Potash-lead glass for cutting	Fused silica
Plate glass	Borosilicate laboratory glass	Microscope slides

The microscope slides were from an unopened box and were therefore presumably uniform in composition. These slides also approached more nearly to optical glass in homogeneity than the other glasses which were used.

EXPERIMENTAL

The first series of experiments was made with the microscope slides, using etching solutions varying in composition from pure hydrofluoric acid, to a solution¹ of hydrofluoric acid saturated with ammonium fluoride. The etching solution was applied by immersing the slides in the solution.

Figs. 1 to 6 show photomicrographs of this series enlarged 60 diameters. It should be mentioned that a very troublesome optical illusion is associated with these etch figures both under the microscope and in the photographs. At one instant they appear as "pits" in the glass, and at another instant they appear to be protuberances or pyramidal figures projecting outward from the surface of the plate. The figures under the writer's observation have been without exception "in relief," as noted by Weatherill; that is, they are protuberances and not pits.

In examining Figs. 1 to 6, it is apparent that pure hydrofluoric acid dissolves the glass, in general, evenly, and with the production of only occasional etch figures. When, however, the amount of ammonium fluoride is increased, the etch figures become more and more definite in shape. For low concentrations of ammonium fluoride, as shown in Fig. 1, the etch figures are largely of an acicular or crystalline form, with higher concentrations, the figure becomes more nearly equilateral and "polygonal" in appearance. It is of interest to note that the shape of the etch figures is noticeably altered on increasing the amount of ammonium fluoride beyond the molecular ratio, $SiF_4 : HF$.

When these specimens are made up in a paste with an inert filler, the structure of the etch is changed in the direction of producing a fine grain, that is, the

¹ *Chem. Abstr.* **12**, 561 (*Comp. rend.* **34** (1853), 591) (*Eng. Ass.* **66**, 104, 136, 164).

² *Comp. rend.* **45** (1857), 70.

³ *Am. J. Sci.* **31**, 41 (1856), 12.

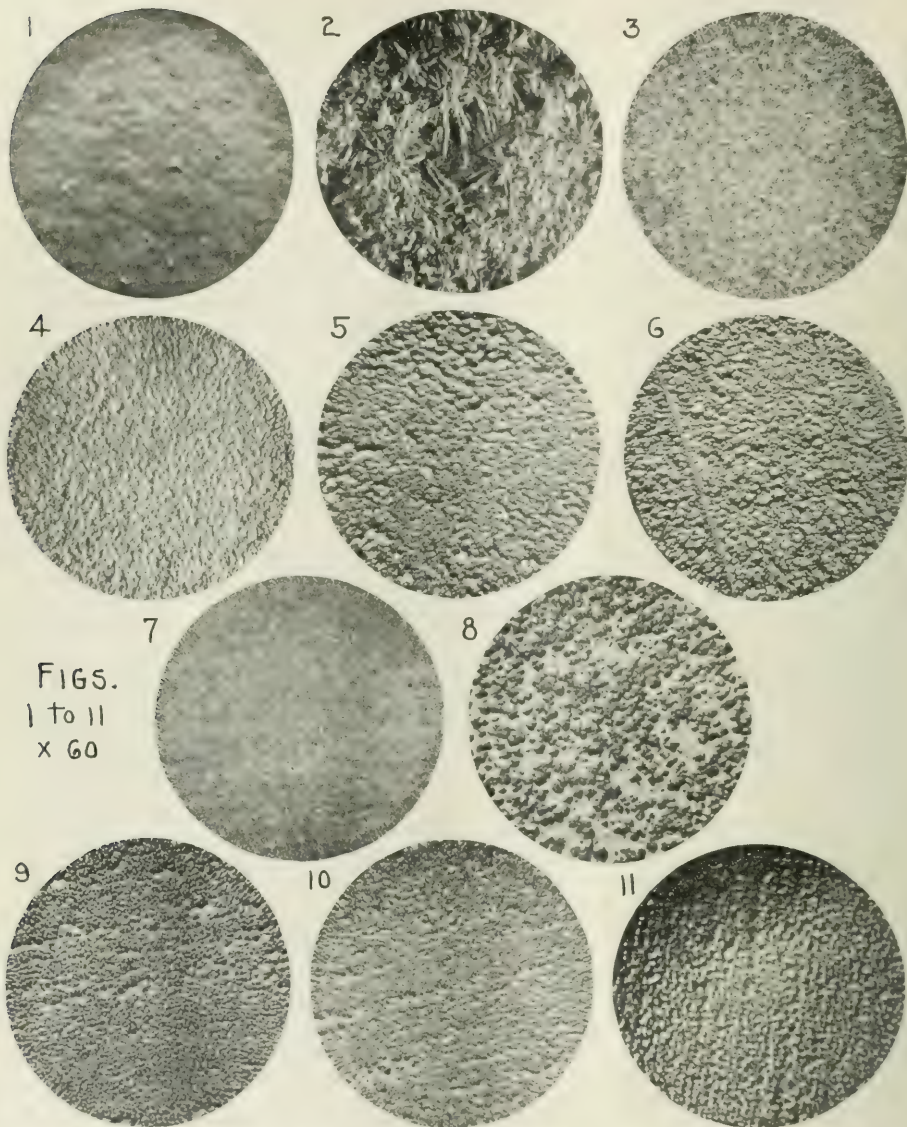
⁴ *Procter's Pat. & T.* **262** (1866), 325.

⁵ *J. Chem. Ind.* **20** (1901), 419.

⁶ *Trans. Am. Chem. Soc.* **39**, 11 (1916), 100; **44** (1922), 60; **45** (1923), 10.

⁷ *Trans. Am. Inst. Chem. Appl. Chem.* **5** (1914), 3.

⁸ *Trans. Am. Chem. Soc.* **45**, 104 (1923), 104. The etch figures are described as "acicular crystals" by the writer. It is interesting to note that the structure of the etch is noticeably altered on increasing the amount of ammonium fluoride beyond the molecular ratio, $SiF_4 : HF$.



FIGS.
1 to 11
x 60

MICROSCOPIC SLIDES ETCHED WITH SOLUTIONS VARYING IN COMPOSITION FROM PURE HYDROFLUORIC ACID TO A SOLUTION OF HYDROFLUORIC ACID SATURATED WITH AMMONIUM FLUORIDE

ETCHING SOLUTIONS	FIG. 1	FIG. 2	FIG. 3	FIG. 4	FIG. 5	FIG. 6	FIGS. 7 TO 11
Hydrofluoric Acid	All	5 parts	5 parts	5 parts	5 parts	5 parts	Same as Fig. 4
Ammonium Fluoride	None	1 part	3 parts	5 parts	10 parts	20 parts	Same as Fig. 4

FIG. 7—ETCHING SOLUTION MADE WITH A PASTE WITH FLOUR

FIG. 8—ETCHING SOLUTION DILUTED WITH WATER

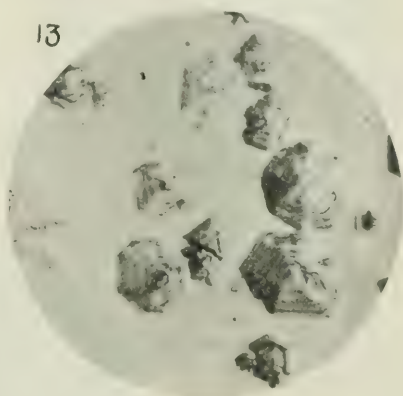
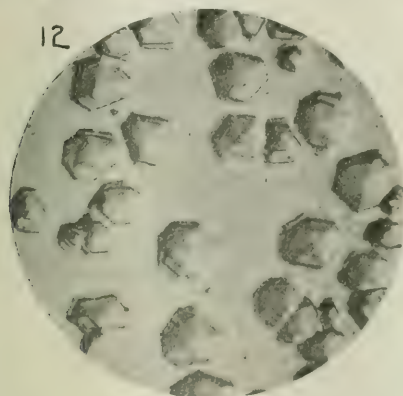
FIGS. 9 TO 11—ETCHED SURFACE IMMERSSED IN DILUTE HYDROFLUORIC ACID FOR

{ Fig. 9 15 sec.
Fig. 10 30 sec.
Fig. 11 60 sec.

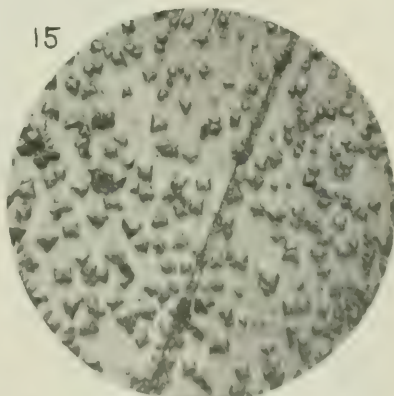
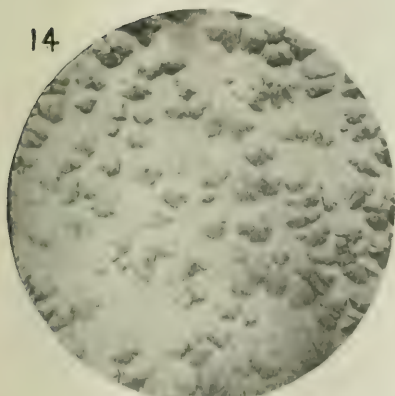
etch figures are smaller and more numerous. This is illustrated in Fig. 7. In general, too, the more concentrated the etching solution the smaller will be the etch figures. Fig. 8 shows the result obtained by diluting a concentrated solution (Fig. 4) with an equal weight of water. The result is to the eye a coarse and sandy surface, which, under the microscope, shows widely scattered etch figures possessing striking geometrical shapes.

It has been pointed out (Fig. 1) that a plane glass surface dissolves substantially evenly and uniformly

character of the glass surface, is made evident to the naked eye only as a slight decrease in the opacity of the glass. It should also be mentioned that similar depressions are occasionally observed when certain unetched glasses are immersed in pure hydrofluoric acid. This phenomenon is characteristic of mechanically polished glass surfaces, and of the resistant borosilicate glasses; and, because in such cases these depressions appear in lines or rows, it seems probable that they result from minute scratches in the glass surface. They are therefore not true etch figures since they



FIGS.
12
and
13
x 200



FIGS.
14
and
15
x 100

FIGS. 12 AND 13—WINDOW GLASS

FIG. 14—PLATE GLASS

FIG. 15—BOROSILICATE GLASS

in pure hydrofluoric acid. When an etched surface, as shown in Fig. 3, is immersed in a solution of hydrofluoric acid, a similar action takes place. Figs. 6 to 11 illustrate such action for one-quarter, one-half and one minute immersion in a solution of equal parts of concentrated hydrofluoric acid and water. That this result is a necessary consequence of uniform solution by the acid may be demonstrated geometrically. The first effect as shown in Fig. 6, is an enlarging and rounding out of the "valleys," finally resulting, as shown in Fig. 11, in a series of smooth "saucer-like" depressions. This operation, which changes in so profound a way the

result from a crystalline surface to a non-crystalline surface.

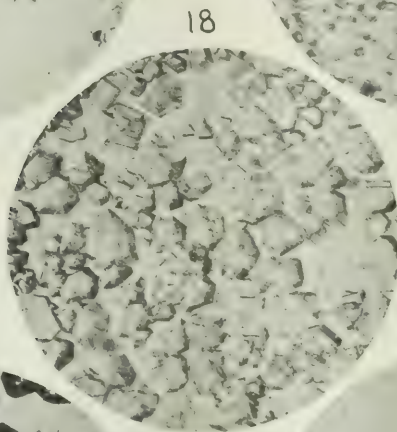
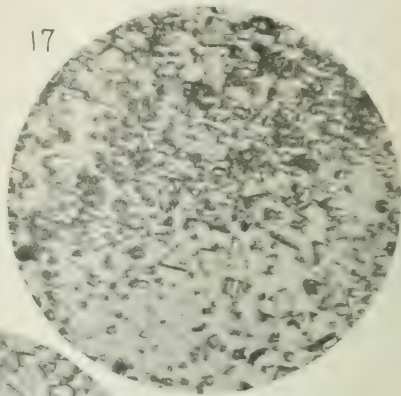
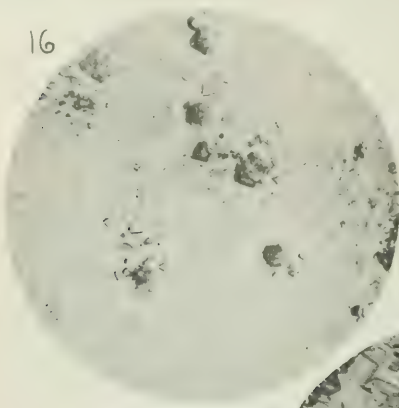
It was observed in general that all solutions which produced a mat-etch, as in Figs. 4, 5 and 6, when diluted, produced etch figures resembling true crystals, as shown in Fig. 8. Such a diluted solution was therefore employed with the original position of glass mentioned above. The etching solution was made up as follows: A solution of 10 parts hydrofluoric acid (47 per cent) to 90 parts water in glass.

Figs. 12 to 15 are microphotographs, enlarged 100 and 200 diameters, of etched glass plate glass,

potash-lead glass, laboratory glass and fused silica glass, etched in the solution given above. It is evident that the etch figures of all of these glasses are surprisingly similar in appearance. This makes it difficult to explain these results on the theory of "preexisting" crystals, especially when account is taken of the wide differences in the compositions of the glasses.

Certain differences are noticeable, however, which, in the light of later knowledge, support the generalization given above. The most noticeable differences appear with the borosilicate laboratory glasses (Figs. 16 and 17) and with the potash-lead glass (Fig. 15).

The final explanation for the formation of these figures was secured as a result of watching, with the



FIGS. 16 to 18
x 100

FIG. 19 x 40
FIG. 20 x 200

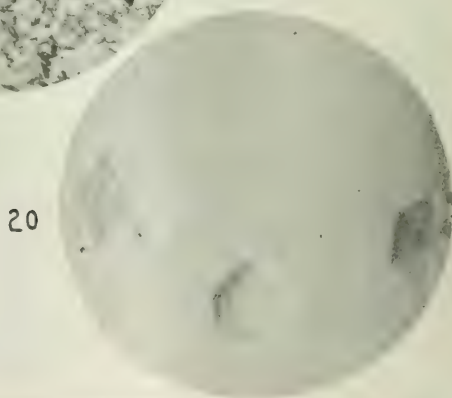
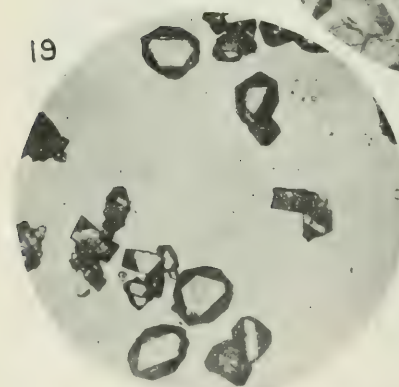


FIG. 16 LABORATORY GLASS (foreign)

FIG. 19 AMMONIUM FLUOSILICATE CRYSTALS

FIG. 17 LABORATORY GLASS (domestic)

FIG. 20 WINDOW GLASS (6 and 8 sided figures)

FIG. 18 FUSED SILICA GLASS

The facts brought out by these experiments appear to be, broadly, as follows: *The form of the etch figures is independent of the chemical composition of the glass, and is determined by the composition of the etching solution.*

This generalization speaks for the protective-coating theory, and against the preexisting crystal hypothesis.

microscope, the etching process. The solution was applied to the glass plate in the form of a hanging drop and was viewed through the plate from above in order to avoid as far as possible any corrosion of the microscope lenses. Within a few seconds after the solution came into contact with the glass, a great many small transparent crystals appeared floating in the solution.

These were in general of the same shape as the etch figures and increased rapidly in size as the etching proceeded. A certain percentage of these crystals was stationary and occasionally a moving crystal was seen to stop suddenly, as though it had become attached to the glass surface. Both the floating and stationary crystals grew rapidly in size as the etching proceeded. When the plate was then cleaned, etch figures, of the size and shape of these stationary crystals, were observed in their places. From this it appears that the etch figure is produced by the protective action of crystals which are formed as the etching proceeds.

The composition of the deposited crystals was then investigated. From the fact that etch figures were formed on fused silica (Fig. 18), it was suspected that the crystals consisted of ammonium fluosilicate. Ammonium fluosilicate was therefore prepared by partially neutralizing fluosilicic acid with ammonium hydroxide. A finely crystalline precipitate was obtained, which, on examination under the microscope, appeared identical with the crystals formed during the etching process. These are illustrated in Fig. 19. Analysis showed them to be ammonium fluosilicate:

Calculated for $(\text{NH}_4)_2\text{SiF}_6$	Found
Per cent NH_3 19.69	18.76 and 19.04

This substance crystallizes in the regular system, and, in general, the individual crystals are cubes modified by octahedral and dodecahedral faces.

As has been pointed out, the etch figures result from two simultaneous actions: the solution of the glass, and the growth of the crystal which is in mechanical contact with the glass surface. The etch figures are therefore neither pseudomorphs nor casts; and, consequently, can not be expected to be exact duplicates of the crystals. They are essentially silhouettes of crystals which are constantly growing. The figures often show striations normal to the direction of growth of the crystal (Fig. 13), which suggests that possibly the crystal growth or perhaps the solvent action is subject to rhythmic disturbances.

It has been observed that the etch figures are commonly hexagonal in appearance and it might be expected that other shapes should predominate if they were the result of the protecting action of cubic crystals. It is evident that, if the octahedron were in contact with the glass surface, and if the cubical and dodecahedral faces were to develop simultaneously, a hexagonal figure should result. This is apparently what occurs in the majority of cases, and no explanation, except that of habit, can be offered to account for it. It is to be expected that etch figures of triangular, square and octagonal outline should also be formed, and these figures are nearly always observed in limited numbers (Figs. 12, 13, 14, 18 and 20).

If this theory is correct, it is to be expected that the presence of other metals which form insoluble fluosilicates, will produce characteristic etch figures in accordance with their crystalline habit. This is illustrated in the case of the potash lead glass (Fig. 15); the etch figures are distinctly characteristic of potash, and, so far as the writer has observed, they are

always produced by an etching solution which contains potassium, irrespective of the composition of the glass. The laboratory glasses (Figs. 16 and 17) also illustrate some characteristic figures. These glasses were free from potash, but contained considerable percentages of boric acid, alumina and zinc oxide, and are extremely resistant to the action of the etching solution. As will be seen from the photomicrographs, the habit of these figures is "tabular" with square and triangular forms predominating, but six- and eight-sided figures are not uncommon. This theory also indicates that, if the etching solution contains no substance which produces insoluble fluosilicates or fluorides, the glass should be dissolved evenly, as with hydrofluoric acid alone, and without characteristic etch figures. This was found to be the case when the solution consisted of the acid fluorides of sodium, lithium, aniline, pyridine, zinc and urea. It is therefore apparent that the glass, *per se*, is dissolved evenly and as a whole by the etching solution, whatever the composition of the solution may be; and that the matness and etch figures result from a secondary protective action of whatever insoluble materials are formed in contact with the glass surface. The character of the etch figures will be determined by the most insoluble substance deposited; and this perhaps explains the results obtained with acid ammonium fluoride and the potash glass, and also with the borosilicate laboratory glass.

SUMMARY

From the foregoing it is concluded that:

I—All glasses dissolve evenly in acid fluoride solutions.

II—Matt etches and etch figures are obtained only when insoluble substances are formed in contact with the glass surface, and when the solution of the glass in such local areas is thereby prevented.

III—When the etching solution is acid ammonium fluoride, crystals of ammonium fluosilicate form the protecting material.

IV—The etch figures result from a solution of the glass and the growth of crystals, deposited from the solution, in contact with the glass surface. Both reactions take place simultaneously.

THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH
PITTSBURGH, PA.

THE DETERMINATION OF IRON IN GLASS SAND

BY JOHN B. FERGUSON

RECEIVED FEB. 26, 1917

One of the absolute necessities in the manufacture of optical glass is a supply of good glass sand, and one of the indispensable attributes of such a sand is a minimum iron content. In searching for such a sand one is compelled to rely on chemical analysis, and now that the problem of optical glass has become a question of national importance it is essential that no errors be made in the seemingly simple determination of the iron in a sand.

In the past, sand analyses generally have been run low on iron content, and some of the physical laboratory has taken up the problem of optical glass, this has been the source of some rather valuable

delays. In fact it has been necessary for us carefully to re-analyze practically all the sands under consideration, and it was while carrying out some of these analyses that the writer thought he had discovered the source of the trouble.

The usual method may be thus described: the sand sample of about 5 g. is digested with hydrofluoric and sulfuric acids repeatedly until all the silica disappears and no gritty particles remain. The heat is then increased until all the hydrofluoric acid is driven off and copious fumes of sulfuric anhydride arise. The vessel is cooled, its contents taken up with water and filtered. The iron is determined in the filtrate.

When a qualitative test¹ alone is desired, the sand is dissolved in hydrofluoric acid, and potassium ferrocyanide is added to the solution, a blue color indicating iron.

Both of these methods of attack assume that a sand is completely decomposed with hydrofluoric acid, and it is to this assumption that the writer wishes to draw attention. From a theoretical standpoint its validity is doubtful since a glass sand often contains such minerals as magnetite, ilmenite, tourmaline, staurolite, etc., minerals that do not break up readily under this treatment, and in practice the writer has found that in so-called good sands, sands in which the iron is practically all present in the heavy minerals, the greater part of the iron was lost under such treatment. Two cases may be cited as illustrations:

I—A sample of sand from Crystal City, Missouri, was analyzed in the usual manner and found to contain less than 0.01 per cent Fe_2O_3 , a result in agreement with the analyses of the sand usually reported. The microscopic examination, for which I am indebted to Dr. H. E. Merwin, of this laboratory, raised some doubt as to the correctness of previous results and another analysis was made: the residue left after filtration was fused with iron-free potassium pyrosulfate and the cake so obtained dissolved in dilute sulfuric acid and added to the original filtrate. This time the iron content was found to be approximately 0.03 per cent, and a third analysis confirmed this latter figure.

II—A sand from Altmont Springs, Florida, was given the same treatment as that given in Case I and then in addition boiled with 1 : 1 hydrochloric acid. The solution so obtained was found to contain practically no iron. Upon careful examination the presence of staurolite grains still undecomposed was discovered and when these were broken up by fusion with sodium carbonate for half an hour the iron content was found to be 0.021 per cent of the sand.

Further evidence on this point may be deduced from the analyses presented in a report on glass-making material by Ernest F. Burchard.² The American Window Glass Company and the Pittsburgh Plate Glass Company each submitted to him four sand analyses. The American Window Glass Company's analyses show for the Fe_2O_3 content—a trace, 0.006,

0.011 and 0.021 per cent, respectively, and of these sands they say: "No. 1 is suitable for the highest grades of glassware and flint glass. Nos. 2 and 3 are suitable for tableware, plate-glass, chimneys, prescription ware, etc., and No. 4 is used for window glass." The Pittsburgh Plate Glass Company's analyses indicate 0.003, 0.002, 0.0024, 0.0036 per cent, respectively, for the same sands and their comment is: "For sands with analyses comparable with the above, no decolorization is attempted in manufacturing plate glass. Sand containing more iron than is shown in the tables may be used in making green glass bottles and cheap glassware or with the addition of decolorizing agents in making window glass." Such comments and analyses do not agree. The coloring indicated by the comment corresponds to much more iron than is shown in any one of the eight analyses, and since the glass-makers watch their products with much more care than their raw materials the analyses must be at fault.

In this connection it is interesting to note that Henry B. Kummel and R. B. Gage,³ upon removing the heavy minerals from some New Jersey sands, obtained analyses of the purified material comparable with those quoted above and their experience with these sands led them to the belief that most of the iron was present in such minerals: "The amount of iron and titanium found by analysis is readily explained by these minerals in the sands and one cannot question the conclusion that the iron content which is especially detrimental is due solely to these minerals, particularly ilmenite."

Before starting such an analysis it would be best for the analyst to obtain a microscopic examination of the sand and base his method of attack on this information. Failing this, the following procedure is recommended as one in which the analyst may have reasonable confidence.

PROCEDURE

Weigh out 5 g. of the sand in a large platinum crucible or small basin; moisten with 5 cc. 1 : 1 sulfuric acid and then add 40 cc. hydrofluoric acid. Evaporate until white fumes of sulfur trioxide begin to be given off; cool, and if upon examination silica can be seen, add more hydrofluoric acid and repeat the evaporation. Two such evaporations generally suffice, but if necessary a third should be made. The use of some form of radiator similar in principle to the well known survey radiator is recommended and may be easily improvised. After the final evaporation the temperature is increased until copious fumes of sulfur trioxide are given off and all the hydrofluoric acid removed. The crucible is cooled, its contents diluted with distilled water and filtered. The black residue remaining on the filter will consist principally of carbonaceous matter derived from the hydrofluoric acid which is usually kept in ceresin bottles, and this carbonaceous matter will prevent the analyst from ascertaining the completeness of the decomposition. The filter containing this residue, without washing,

¹ Geological Survey, *Bull.* 285 (1906), 454.

² "The Requirements of Sand and Limestone for Glass Making," Geological Survey, *Bull.* 285 (1906), 454.

³ Report of the State Geologist, New Jersey, 1906.

is removed from the funnel, placed in a small platinum crucible, dried and ignited. The funnel is carefully rinsed with distilled water, the rinsings being allowed to run into the filtrate. After ignition the residue is fused with a little iron-free potassium pyrosulfate and the cake so obtained is dissolved in dilute sulfuric acid. If no residue is left the decomposition is complete and the two solutions may be combined, and the iron then determined in the resulting solution. If dark particles may still be seen, and this will be the case if staurolite is present, they are filtered off, ignited and fused with iron-free sodium carbonate in a platinum crucible. Upon treating this fusion with dilute sulfuric acid careful examination should show no black particles and after filtering to remove any insoluble sulfates the three filtrates are combined and the iron determined in this resulting solution.

The writer prefers to reduce the iron with stannous chloride and then to titrate with potassium bichromate, determining the end-point electrometrically as suggested by Joel H. Hildebrand,¹ and for this reason dissolves the fusions in 1:1 hydrochloric acid instead of sulfuric acid. The exact conditions required by this method have been studied by Hostetter and Roberts of this laboratory, and the writer wishes to thank them for the information and assistance they have given him.

Other well known methods would probably give equally good results.

In making analyses such as these the purity of one's platinum and reagents becomes a question of prime importance. While careful blank determinations will eliminate errors due to the latter they cannot be relied upon in the case of the former and no iron-bearing platinum may be used.

It cannot be too strongly emphasized that no "Analyzed Chemical" can be relied upon without test for work such as this.

CONCLUSIONS

Before the correct iron content of a sand can be determined the sand must be completely decomposed. Simple treatment with hydrofluoric acid and sulfuric acid is not sufficient. Fusion of the residue with potassium pyrosulfate must be resorted to and even subsequent fusion with sodium carbonate in rare cases.

GEOGRAPHICAL LABORATORY
CARNEGIE INSTITUTION OF WASHINGTON
WASHINGTON, D. C.

THE FORMATION OF TRI-CALCIC ALUMINATE

By EDWARD D. CAMERON

Received April 21, 1917

As early as 1883, Le Chatelier came to the conclusion that the two essential constituents of Portland cement were tri-calcic silicate and tri-calcic aluminate. All efforts to produce a sound cement of the empirical formula



failed, free lime always being found in materials of this composition. Later, Newberry suggested that the essential constituents were tri-calcic silicate and di-calcic aluminate and proposed the formula



Even this latter formula gives a mixture almost always containing some free lime, so that in practice it is customary to keep the lime ratio a little below that called for by the Newberry formula in order to produce a uniformly sound cement.

The existence of tri-calcic silicate as first suggested by Le Chatelier received a strong confirmation from the work of A. H. White,¹ and in 1915 essentially pure crystals 0.03 mm. in diameter were described by Shepherd, Rankin and Wright.² Later, by very slowly cooling a solution of di-calcic silicate and calcium oxide in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ as solvent, the author³ obtained crystals of essentially pure tri-calcic silicate 7 mm. in length.

Two facts in connection with tri-calcic silicate should be noted: (1) large crystals of tri-calcic silicate can be best obtained by slowly cooling a solution of di-calcic silicate and calcium oxide in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$; (2) as pointed out by Le Chatelier, when tri-calcic silicate is treated with water, one molecule of calcium oxide readily forms calcic hydroxide, leaving a hydrated di-calcic silicate which gradually undergoes further hydrolysis. These two facts relative to the formation and behavior of tri-calcic silicate would suggest the idea that calcium oxide may, under suitable conditions, unite with di-calcic silicate to form crystals in which the calcium oxide would bear a relation to the di-calcic silicate exactly analogous to that borne by the water of crystallization to the hydrated salt with which it is united.

Essentially pure tri-calcic aluminate was prepared and its properties described in 1909 by Shepherd, Rankin and Wright.⁴ Some of the properties of tri-calcic aluminate were described in 1915 by Rankin and Wright⁵ as follows:

"This compound occurs in equant colorless grains 0.1 mm. and less in diameter, often hexagonal or rectangular in outline, with indications of imperfect cleavage after the octahedron or rhombicdodecahedron, crystal system, isometric; refractive index, $N_{\text{NaD}} = 1.71$; hardness, 6; fracture conchoidal; luster, vitreous. Occasionally faint gray interference colors were observed and were evidently due to strain."

The experimental data from which Shepherd, Rankin and Wright drew their conclusions are shown in the accompanying diagram taken from the two publications mentioned. This diagram assumes that tri-calcic aluminate, composed of 37.78 per cent Al_2O_3 and 62.22 per cent CaO , is a stable phase in all mixtures containing less than 37.78 per cent Al_2O_3 and at all temperatures up to its melting point, $1,535^\circ \pm 5^\circ \text{C}$, at which point it "dissociates into CaO and liquid." It is stated that because of the composition at the melting point into CaO and liquid, pure tri-calcic aluminate is

¹ This Journal, 1 (1883), 6.

² This Journal, 39 (1917), 29 (1917), 30.

³ This Journal, 6 (1914), 30.

⁴ This Journal, 28 (1916), 30.

⁵ This Journal, 39 (1917), 1.

¹ J. Am. Chem. Soc., 26 (1904), 371.

"best obtained by crystallization from glass of its own composition at a temperature below 1535° . It forms with the compound $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ (a eutectic mixture of the composition $\text{CaO } 50, \text{Al}_2\text{O}_3 \text{ } 50$), which melts at $1395^{\circ} = 5^{\circ}$. It does not form a eutectic with CaO ; but the composition $\text{CaO } 59, \text{Al}_2\text{O}_3 \text{ } 41$ is the quadruple (invariant) point at which these two compounds are stable in contact with liquid and vapor, the equilibrium temperature being 1535° ."

The preparation of the pure tri-calcic aluminate is described in 1909, as follows:

"In order to prepare the pure compound $3\text{CaO} \cdot \text{Al}_2\text{O}_3$, it is necessary to bake the charge a long time at about 1400° . This allows diffusion to occur with the elimination of the excess of CaO and $3\text{CaO} \cdot 5\text{Al}_2\text{O}_3$. Experimentally, we found that the 37.78 per cent charge held 21 days at 1400° was free of the excess phases. Similarly, the compositions 35 per cent, 34 per cent and 32 per cent of Al_2O_3 , when merely fused and crystallized, without the long exposure, show $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ with CaO and $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, but were transformed into CaO and $3\text{CaO} \cdot \text{Al}_2\text{O}_3$ by heating at 1400° for the same length of time. In order to accelerate the reaction we took the previously fused charges and ground them to a fine powder before starting the heat treatment. Such cases as this are not uncommon in silicate melts and the investigator must bear them constantly in mind or he will be led far astray."

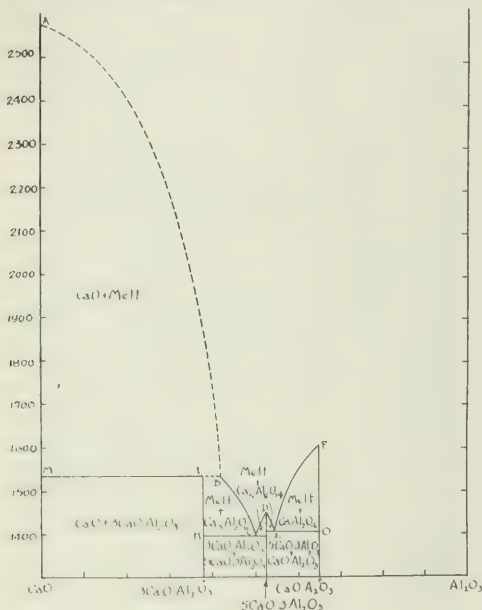


FIG. 1

The object of the research herein described, the laboratory work of which was carried out by G. W. Blanco, M.S., and B. A. Standerline, M.S., was to determine whether tri-calcic aluminate must be considered as a stable phase in the strict sense of the word in which it is employed in the phase rule, or whether regarding it either as a saturated solid solution of CaO in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, or else $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ with four molecules of CaO of crystallization, may not be in closer accord with the experimental facts than

if the tri-calcic aluminate is regarded as a definite phase stable at all temperatures up to 1535° .

The work is based on the conception that $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ is a solvent in which CaO is soluble, the concentration being a function of the temperature, and that the limit of solubility of CaO at temperatures below 1535° is when there are about four molecules of CaO to one of $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, that is, when an empirical formula corresponding to that of the tri-calcic aluminate has been reached.

Under this conception the melting point of the $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ would be lowered by the solution of CaO from 1455 to 1395° , at which point C in the diagram (Fig. 1) would represent the eutectic solution of CaO in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$. With increase in concentration of CaO the melting point would rise along the line CBA .

If a mixture of the empirical formula $4\text{CaO} + \text{Al}_2\text{O}_3$ were heated well above 1535°C. and then cooled slowly enough to allow an approach to chemical equilibrium, the resulting material must, if tri-calcic aluminate is a stable phase, consist of crystals or grains of CaO with $3\text{CaO} \cdot \text{Al}_2\text{O}_3$. This is indicated in the diagram since such a mixture would come in the field MLN , being well to the left of LN .

EXPERIMENTAL

The materials used were strictly C. P. calcium carbonate and the purest available alumina containing by analysis 99.60 per cent Al_2O_3 . These materials were thoroughly dried and mixtures were made by accurately weighing out in the proportion of four CaCO_3 to one of Al_2O_3 . Enough of the mixture was weighed out for each experiment to give approximately 60 g. of fused material. The mixture was first placed in portions in a covered cylindrical platinum crucible 48 mm. in diameter and 57 mm. deep and ignited over night at a temperature between 1100 and 1150°C. in order to drive off carbon dioxide and reduce the bulk of the mixture. The covered crucible was then heated in the same furnace and in substantially the same manner as that employed in the preparation of synthetic celite and large crystals of tri-calcic silicate already referred to.

A mixture of the empirical formula $4\text{CaO} + \text{Al}_2\text{O}_3$ would contain 68.06 per cent CaO with 31.94 per cent Al_2O_3 . In the first experiment a mixture of the above composition was placed in the covered platinum crucible and heated over night by means of a Méker burner. The temperature was measured as in our previous work by means of a standardized platinum rhodium thermocouple, the bead of which was within 2 or 3 mm. of the crucible containing the material under treatment. In the morning, blast was put on and the temperature, which was about 1150° at the start, was increased until the thermocouple indicated a little above 1600°C. , at which temperature it was held within less than 5° for one and one-half hours. After holding at 1600° the temperature was lowered at the rate of 25° per hour during seven hours, or until it had dropped to 1425° when the gas was turned off and the furnace allowed to cool over night. During the entire seven hours of cooling, with the exception of one instance when the temperature was 4° lower

than that aimed at, the thermocouple indicated at the end of each hour that the desired temperature had been reached within 2° . In order to remove the material, which had apparently been thoroughly liquefied, from the crucible, it was necessary to break it into a number of pieces by means of a small chisel. A micro section of this "G-1" mixture magnified 100 diameters is shown in Fig. II. This section clearly shows an apparently cellular structure, the cells being occupied by crystals or grains of calcium oxide, while the cell walls constitute the magma from which the crystals or grains of calcium oxide have separated.

Another mixture, "G-3," of the same composition as the preceding, was prepared by essentially the same method. The same rate of cooling from 1600° was used, the only difference being that the heat was turned off after 6 hrs., that is, when the temperature had lowered to 1450° instead of 1425° .

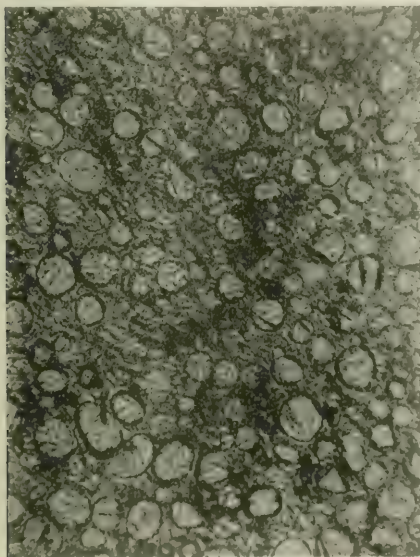


FIG. II. "G-1" $\times 100$ DIAMETERS

In order to remove any component of the "G-1" material which might be liquid below 1435° C. the same method of procedure was followed as the one used to remove the fluid constituent of synthetic celite from the crystal of tri- α -aluminate. A piece of the "G-1" mixture was placed on two discs and surrounded by a box cylinder of pure MgO , the cylinder being covered with a third disc of the same material. The thermocouple used to record the temperature was placed in the annular space around the stack and was two mm. of the cylinder surrounding the piece under treatment. In making the absorption the furnace was allowed to heat over night in order to bring the temperature to a little above 1400° C. Heat was put on in the morning and the temperature raised until the thermocouple in the annular space indicated 1435° .

at which temperature it was first held for four hours. It was then increased during one hour to 1425° , at which temperature it was held constant for another 4 hrs., or, in all, 9 hrs. An examination of the material after cooling over night showed little or no absorption by the magnesia discs.

A second heating of the same piece was then carried out in substantially the same manner as in the preceding experiment, except that the temperature after heating over night was raised quickly until the thermocouple in the annular space indicated 1463° C. It was then held between 1460 and 1465° for 4 hrs., raised during the next hour about 10° , then held 4 hrs. longer between 1475 and 1480° after which the furnace was again allowed to cool over night. A distinct, but not considerable, absorption was found.

In making an absorption of the fluid constituent of "G-3" a slight modification of the method was used. In addition to the thermocouple in the annular space a second standardized thermocouple was introduced, the bead of this latter being placed inside the magnesia cylinder and resting directly on the magnesia disc supporting the piece under treatment. In this way the exact temperature of the piece itself and the absorbing disc could be measured. In this absorption after preheating over night as usual, blast was put on and the temperature raised until the thermocouple in the annular space indicated 1450° , at which time the inner couple in contact with the absorption disc and piece under treatment was 1438° C. During the next $8\frac{1}{2}$ hrs. the temperature of the inner couple was between 1438 and 1446° except for a short time when it reached 1450° C. During most of the time the temperature of the thermocouple in the annular space indicated a temperature from 17 to 25° higher than that recorded by the inner couple. An examination of the material after cooling showed that a piece weighing 5.0580 g. lost by absorption 0.8779 g. or 17.3 per cent.

Portions of the magnesia disc showing absorbed material were dissolved and the weight of Al_2O_3 and of CaO determined, and the per cent of these constituents in the absorbed material calculated. These analyses showed that the material absorbed in the second experiment from the "G-1" contained Al_2O_3 47.76 and CaO 52.24, while that from the "G-3" gave Al_2O_3 41.24 and CaO 58.76 per cent.

Since the temperature readings of the two thermocouples in the third absorption showed that the thermocouple in the annular space indicated from 27 to 30° higher temperature than that actually existing at the point where the piece under treatment is heated, it would be evident that in the first absorption experiment during the 4 hrs. the thermocouple recorded 1435° as the annular space, was in fact under treatment must have been below the melting point of the entire "G-1" (1450°), while during the last four hours when the couple in the annular space recorded 1450° the material that must have been over 1400° as that temperature value is not favorable to the crystallization of melting aluminate. The fact that any absorption was found on the second peak

ment of this same piece of material would indicate the difficulty of converting the $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ into tri-calcic aluminate, even in the presence of a large excess of CaO .

Tri-calcic aluminate seems to be best formed when the $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ is held for a very long time in contact with CaO at a temperature just above the melting point of the eutectic solution of CaO (1395°), but below the melting point of the pure $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ (1455°). Under these conditions, if tri-calcic aluminate is either a metastable saturated solid solution of CaO in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ or is $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ with four molecules of CaO of crystallization, it would gradually form and separate or crystallize from the still fluid solution until in time saturation of the whole of the $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ had taken place. The entire mass would thus be converted into tri-calcic aluminate, unless there were present an amount of CaO in excess of what would be required to form tri-calcic aluminate with all of the Al_2O_3 .

If the problem is considered as a simple study of the solubility of CaO in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, we would then regard a mixture having the empirical formula $4\text{CaO} + \text{Al}_2\text{O}_3$ at 1600° as a saturated fluid solution of CaO in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ with some undissolved crystals or grains of CaO in suspension. On cooling such a solution at the rate of 25° per hour, since the solubility of the CaO in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ is a function of the temperature, the grains or crystals of CaO in suspension would gradually grow at the expense of the dissolved CaO , so that at any time during the cooling period down to the solidifying point of the eutectic solution the mass would consist of crystals or grains of CaO in a matrix made up of a solution of CaO in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ saturated at the temperature at which the material is held.

Since the separation of tri-calcic aluminate seems to require that the solution of CaO in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ be slightly supersaturated and held at a constant temperature for a very long time, and since the "G-1" and "G-3" mixtures were in a supersaturated state below the melting point of tri-calcic aluminate for three hours only, comparatively little tri-calcic aluminate would separate. Three hours compared with twenty-one days is a short time, but even in three hours some tri-calcic aluminate might be expected to be found if a careful petrographic examination of the material were made.

The composition of the liquid drawn off from "G-3" at temperatures between 1438 and 1446° agrees, as closely as experimental work could be expected, with that of a solution having the same melting point as shown in the diagram in Plate I.

CONCLUSIONS

I—A binary system of CaO and Al_2O_3 containing more than 47.8 per cent CaO should be regarded as a study in solubility of CaO in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$.

II—Tri-calcic aluminate should be regarded either as a metastable saturated solid solution of CaO in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$, or as $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ with four molecules of CaO of crystallization, rather than as a stable phase in the strict sense of the word.

UNIVERSITY OF MICHIGAN, ANN ARBOR

LOW TEMPERATURE DISTILLATION OF LIGNITE COAL

By H. K. BENSON AND L. L. DAVIS

Received August 6, 1917

The use of lignite coal for the production of paraffin and illuminating oils by destructive distillation has been developed to a considerable extent in the Saxonia-Thuringia lignite belt of Germany.¹ For this purpose soft, friable "wax coals" were distilled at about 200°C . under a slight vacuum for 24 hours, yielding the following products: tar, 6 to 8 per cent; coke, 32 to 36 per cent; tar water, 46 to 50 per cent; and gas, 10 to 12 per cent. From the distillation and refining of the crude oils were obtained a light lignite oil ("benzin"), distilling under 150°C ., with a specific gravity of 0.780 to 0.810 and a flash point of 25 to 30°C .; a burning oil ("solaröl"), boiling below 250°C ., with a specific gravity of 0.825 to 0.830 and a flash point of 50°C .; a solvent oil ("putzöl") boiling up to 280°C ., with a specific gravity 0.850 to 0.860 and flash point, 100°C .; together with paraffin oil, soft and hard paraffin and creosote oil. Ammonia may be recovered from the tar water, though it is generally used directly as a fertilizer. The coke does not "cake" as does that of ordinary coking coals, but shrinks slightly during distillation and is generally briquetted for use as a fuel. In 1908, 12 factories, employing 1221 workmen, were engaged in refining lignite oils.²

Inasmuch as a large portion of the coals of Washington and of the West in general are of a lignite character a study of a representative Washington lignite coal was made to determine the yield of oil from the coal and the relation of the temperature of distillation to the nature of the products obtained.

DESCRIPTION OF THE SAMPLE

The coal used was a representative sample of black lignite from the Hannaford No. 1 Mine, Tono, Washington. It is black in color, with a brown streak, is slightly banded in structure and breaks with a conchoidal fracture. The coal slacks on exposure to air, but may be shipped some distance without weathering if placed in closed cars. The only use made of the coal at the present time is as a steam coal in specially designed locomotives. The proximate analysis of the coal is given in Table I:

TABLE I—PERCENTAGE COMPOSITION OF TONO LIGNITE

PERCENTAGES	CAR SAMPLE		LABORATORY SAMPLE	
	(U. S. Geol. Survey, Bull. 474, 75)		As Received	Air Dry
Moisture	30.2	14.5	...	12.3
Volatiles	31.5	33.5	44.0	40.8
Fixed Carbon	39.9	43.9	56.0	39.8
Ash	8.4	9.05	...	7.1
Sulfur	0.52	0.56	0.73	0.3
Nitrogen	1.06	1.14	1.49	1.60
B. t. u.	9,280	9,940	13,000	9,650

APPARATUS USED

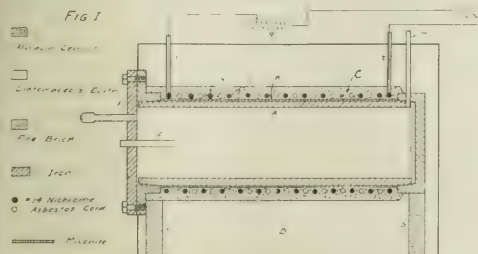
The retort used in distilling the coal was constructed as in Fig. 1. A piece of standard black 3-in. pipe (A) 18 in. long was closed at one end with a cap and at the other with a companion flange and blind flange. The blind flange was bolted to the face with two

¹ Dammer, "Handbuch der Chemischen Technologie," 4, 135-148, Ludwig Medicus, "Lehrbuch der Chemischen Technologie," 965-977, Fischer, "Handbuch der Chemischen Technologie," 141-153.

² Z. angew. Chem., 1909, 2072.

$\frac{3}{4}$ -in. bolts, the companion flange being threaded to receive the bolts. The face plate was turned smooth in a lathe to obtain a tight fit. The flange was made perfectly air-tight by means of an asbestos gasket, well rubbed with flake graphite and oil. The face plate was tapped for the outlet pipe (F) and a pyrometer socket (P). A $\frac{1}{8}$ -in. pipe (M) was tapped in the cap at the back of the retort and connected to a manometer for measuring the pressure in the retort. The heating element was of nichrome wire.

Fig. I



The pipe was first insulated with two layers of miconite (B): 40 ft. of No. 14 nichrome wire (N) was then wound on, the individual turns being separated with asbestos cord (I). The heating unit was then covered with alundum cement (C). The retort was then placed in a metal lined box, on fire-brick supports (S) and was packed with powdered diatomaceous earth (D) as a heat insulator. The nichrome wire was brought out in leads through porcelain tubes (I) and was connected to the 110-volt alternating current lighting circuit. The temperature was controlled by means of a resistance rheostat (R) having a capacity of 50 amperes. A copper advance couple and millivoltmeter was used for temperature measurements.

Fig. II

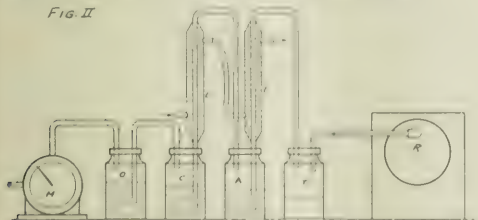


Fig. II gives a diagrammatical sketch of the set-up. The distillation gases passed from the retort (R) to the tar extractor (T), thence through the Liebig condensers (L) to the wash bottles (A), (C) and (O), and finally through the gas meter (M) to the exhaust pump.

The tar extractors and washers consisted of 16-oz. wide-mouth bottles. The first washer (A) was for ammonia and contained slightly acidified water, the second (C) was for cyanides and contained a suspension of ferrous carbonate in water. The third washer (O) was an oil scrubber and was filled with a high flash lubricating oil.

The retort was heated to the desired temperature and weighed wash bottles were put in place. One kilogram of coal was then placed in the retort, the apparatus closed, and the exhaust started. A run

lasted 24 hours, during which time the temperature was held constant and the pump so regulated that the pressure within the retort was atmospheric. At the completion of a run the hot coke was drawn out and placed in an air-tight can to cool. The wash bottles were removed and clean bottles put in their places and a new charge of coal placed in the retort. Gas samples were drawn from the system at intervals and analyzed.

The coal was prepared for distillation by passing through a jaw crusher. The coal which passed through a 4-mesh and remained on a 40-mesh sieve was used.

YIELD OF RAW PRODUCTS

The yields of raw products at different temperatures are recorded in Table II.

TABLE II—YIELDS OF DISTILLATION PRODUCTS

Temp. ° C.	Total Distillate Per cent	Dry Tar Per cent	Aqueous Solution Per cent	Core Per cent	Gas Cu. ft. per ton
100	12.3	...	12.3	87.7	
200	22.1	...	22.1	77.3	200
250	24.9	3.6	21.3	63.8	1900
250	25.2	3.5	21.7	63.8	1700
330	27.1	4.9	22.2	56.0	3800
330	26.8	4.9	21.9	57.2	4000
380	27.3	5.4	21.4	54.2	4100
380	27.1	5.1	22.0	53.8	4200
380	27.4	5.4	22.0	54.4	4400
415	26.7	4.6	22.1	53.9	6100
415	26.2	4.4	21.8	53.7	5800
450	25.6	4.2	21.4	52.6	7500
450	25.8	4.2	21.6	52.6	7800
490	25.0	4.1	20.9	51.2	8700
490				51.4	
490	25.2	4.0	21.2	51.1	8000
550	24.9	3.8	21.1	50.1	9600
550	25.0	3.9	21.1	49.8	9800
600	24.6	3.4	21.2	48.8	9800
600	24.4	3.5	20.9	48.9	9700

GAS

The washed gas was measured in a Sargent wet test meter. The yields are indicated by Fig. III. The gases were sampled and analyzed in a Moorehead gas apparatus and the percentage compositions are given in Table III.

TABLE III—PERCENTAGE COMPOSITIONS OF GASES

° C.	CO ₂	H ₂	CH ₄	C ₂ H ₆	H ₂	A-H ₂	N ₂
300	82.4	0.0	0.0	12.2	0.0	0.0	5.4
350	52.1	0.0	1.2	13.4	0.0	0.0	33.3
330	38.2	0.0	1.8	13.3	8.2	1.4	36.1
380	14.6	0.8	1.1	13.1	18.1	17.2	35.1
415	10.2	0.8	3.2	13.2	20.0	17.0	35.6
450	4.8	1.0	0.8	13.6	17.6	21.8	31.9
490	4.4	0.8	1.4	15.4	14.8	23.2	30.4
550	3.6	1.2	1.6	17.2	15.8	24.2	27.0
600	3.0	1.6	2.2	19.6	15.4	24.4	24.8

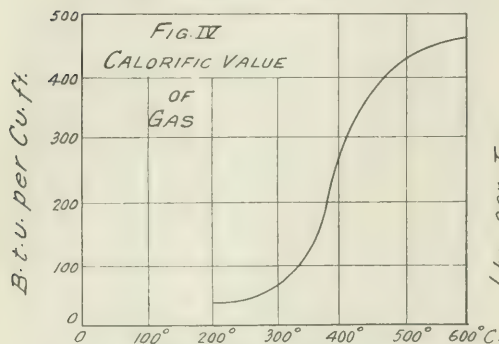
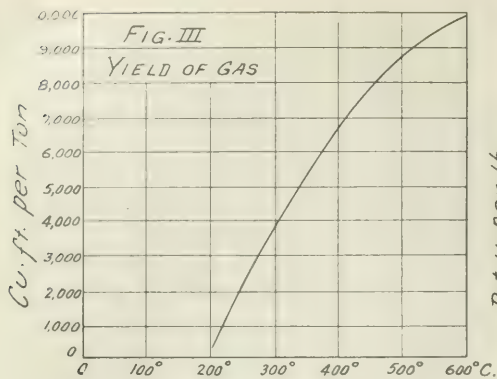
The calorific values calculated by Lunge's method¹ are plotted against the temperature of distillation in Fig. IV.

LIGNITE RESIDUE ON COKE

The coke or residue differs from that obtained from coking coals. It is dull black in color and retains the size and shape of the original particles. Its composition is given in Table IV, showing the yields per ton of coal and Fig. V shows the increase in calorific value with increase of temperature.

TABLE IV—ANALYTICAL DATA ON COMPOSITION OF LIGNITE RESIDUE

Temp. ° C.	Coke Lbs.	Yield Per cent	Ash Per cent	Sulfur Per cent	H. C. (Btu.)
100	1.754	46.6	9.3	0.8	11,000
200	1.546	43.1	9.3	0.8	11,000
250	1.276	34.1	9.3	0.8	11,000
330	1.130	28.5	9.3	0.8	11,000
380	1.092	14.0	13.0	0.8	11,000
415	1.068	8.8	13.1	0.8	12,740
450	1.058	8.4	13.1	0.8	12,740
490	1.054	8.4	13.1	0.8	12,740
550	1.050	8.4	13.1	0.8	12,740
600	1.046	8.4	13.1	0.8	12,740



AMMONIACAL LIQUOR

The aqueous distillate was tested for ammonia and cyanides. The latter were present only in traces at the higher temperatures but the yield of ammonia in lbs. per ton is given in Fig. VI.

LIGNITE OILS

The oily portion of the crude distillate was extracted with ether and the latter distilled off at 50° C. The

TABLE V. COMPOSITION OF LIGNITE OIL.

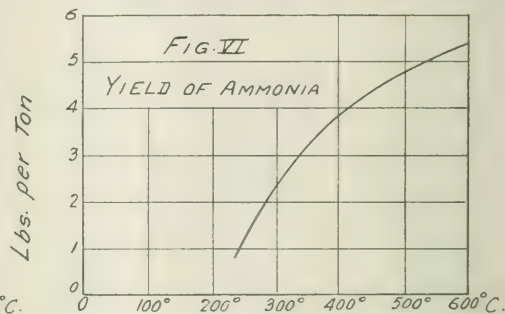
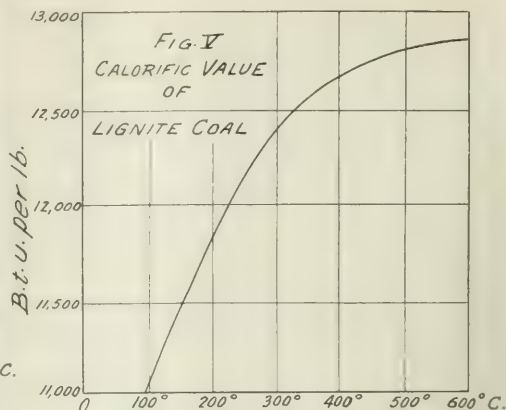
Temp.	Light Oil	Medium Oil	Paraffin Oil	Coke	Gas
250° C.	23.4	28.6	41.1	4.0	2.9
330	23.8	28.4	41.4	4.4	2.0
380	23.9	27.4	42.4	4.2	2.0
415	22.5	27.5	41.3	6.2	2.4
450	24.4	33.3	28.8	6.1	2.5
490	24.2	26.4	20.9	26.7(a)	2.0
550	19.0	28.2	18.8	31.8	1.8
600	19.2	24.5	18.2	36.1	2.2

(a) At 490° the character of the tar so changed that a crystalline paraffin mass could not be obtained by distillation and the residue resembled ordinary coal tar pitch.

TABLE VI. YIELD OF OILS IN POUNDS PER TON OF COAL.

Temp.	Raw Tar	Light Oil	Medium Oil	Paraffin	Paraffin Oil
250° C.	72	16.8	20.6	3.8	25.8
330	98	23.3	27.6	5.6	34.9
380	108	25.8	29.3	6.9	38.9
415	92	20.7	25.3	5.5	32.5
450	84	24.1	28.0	3.5	20.6
490	82	19.9	11.7	17.2	14.3
550	76	14.4	21.5	14.3	12.4
600	68	13.0	16.7		

crude oil thus resulting was dark brown in color and was solid at ordinary temperatures. Its specific gravity at 15° C. was 0.985 to 0.995. At 550° C. the oil was black with a gravity of 1.000 and at 600° C. it was slightly heavier than water. The oils were



distilled in small glass retorts and the percentage yields are given in Table V. In Table VI the yields per ton of coal are given, including also the paraffin separated by Eisenlohr's method.¹

CHEMICAL PROPERTIES OF LIGNITE OILS

The light oils were washed with sodium hydroxide and sulfuric acid, 32 per cent being soluble in alkali. The washed oils were treated with concentrated nitric and sulfuric acids in a reflux condenser but no evidence of the formation of nitro derivatives was obtained. The cresols obtained from the alkali washings were tested with bromine water but no phenols were isolated. The specific gravities of the oils were obtained by means of a pipette pycnometer, made by blowing a small bulb in a capillary tube. The gravities of the various fractions are given in Table VII.

TABLE VII.—SPECIFIC GRAVITIES OF LIGNITE OILS

Temp.	Light Oil	Medium Oil	Paraffin Oil
250° C.	0.812	0.868	0.920
330	0.810	0.884	0.946
380	0.815	0.900	0.960
415	0.854	0.900	0.968
450	0.876	0.912	0.972
490	0.870	0.922	0.985
550	0.868	0.918	0.986
600	0.864	0.925	0.988

CONCLUSIONS

I—The maximum yield of lignite oils is obtained by distilling at 380° C.

¹ *Z. angew. Chem.*, 1897, 300-326, 332-336.

II—About 5.5 per cent of the coal may be obtained as raw oils.

III—These raw oils are more similar to petroleum and shale oil than to coal tar, there being no benzol or benzol derivatives present.

IV—Lignite raw oils will give valuable solvents, burning oils, engine fuel oils, and lubricating oils.

V—About seven pounds of paraffin wax per ton of coal may be obtained.

VI—The gas resulting from the low temperature distillation of lignites is of low heat value and is small in volume.

VII—Small quantities of ammonia can be obtained from lignite tar water.

VIII—The residue from lignite distillation is a valuable fuel having a calorific value of over 12,000 B. t. u. per lb.

IX—Due to the small unit used it is impossible to determine the commercial feasibility of lignite distillation, but sufficient data have been obtained to warrant a semi-commercial test to be made upon the Tono lignites.

LABORATORY OF INDUSTRIAL CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON

THE DETERMINATION OF SULFUR DIOXIDE

By O. R. SWEENEY, HARRY E. OUTCAULT, AND JAMES R. WETHEROW

Received May 31, 1917

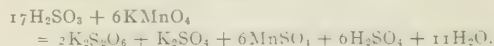
The accurate determination of sulfur dioxide in gas mixtures is a matter of great importance at the present time. The control of sulfuric acid plants, the investigation of air charged with fumes from smelters, the regulation of community nuisances from high pressure sulfuric acid concentration in unreasonable proximity to residential districts, and the analysis of the products from the explosion of gunpowder are some of the cases where such a determination is necessary.

Since the sulfur dioxide is nearly always accompanied by sulfur trioxide, those methods which oxidize the dioxide and weigh it as barium sulfate are not suited to this kind of work. The nature of such investigations generally requires a volume of determinations and therefore speed of method is strongly desired.

The titration of the sulfur dioxide with standard iodine solution has been developed into a satisfactory method by the "Selby Smelter Commission" and is described in the Bureau of Mines *Bull.* 98. The objections to this method are that it uses an iodine solution which must be frequently standardized and is so sensitive to the action of light that a blank must be run during the determination.

Potassium permanganate is known to be an oxidizing medium for sulfurous acid. Since its solution is more stable than that of iodine, and can be used without an indicator, it is a more inviting reagent to use. In applying permanganate, however, it was found that the reaction did not give results which would be expected if the sulfurous acid were oxidized completely to sulfuric acid. There was fair agreement among the

results themselves, however. Dymond and Hughes,¹ who studied this reaction exhaustively, found that a part of the sulfurous acid was oxidized to the dithionate accordingly to the equation



This explained our failure to get results in accordance with a complete oxidation to sulfuric acid.

They also found that this reaction is not modified by the concentration of sulfuric acid present, the temperature, or by the dilution of the solution. Our results confirmed all of this, except that the concentration of the sulfuric acid must be within certain wide limits, and there must always be an excess of permanganate present.

A very considerable amount of experimenting was necessary before the proper conditions for making titrations were obtained. It is necessary to record here only the conditions which were finally found to give proper results.

It was found that 0.005 *N* potassium permanganate was the best strength to use. Under proper conditions the effect of one drop could be observed, and the low normality made a high degree of accuracy possible. One drop of such a solution corresponds to 0.000009 g. SO_2 . Should the concentration of sulfur dioxide be very large a stronger solution should be used.

The solution was prepared by diluting the laboratory stock solution, and, after standing for several days, was standardized. Satisfactory results were obtained by using thiosulfate, but in order to duplicate more nearly the conditions of the actual analysis sodium sulfite was used. Both Dymond and Hughes, and the Selby Smelter Commission used sodium sulfite for their standard. The sodium sulfite was purified by a series of recrystallizations from water, after which it was dried. Weighed quantities were dissolved in water and definite portions were pipetted out and titrated. Measured volumes of pure sulfur dioxide gas were also dissolved in water and portions were titrated and found to check the sulfite method as did other methods of standardizing.

As was stated above, the permanganate must always be present in excess. For this reason it was impossible to titrate the sulfurous acid directly. Recourse was had to the scheme of the Selby Smelter Commission. A certain amount of the permanganate was run into dilute sulfuric acid solution, and, after mixing, was divided into two equal parts. The sulfur dioxide was dissolved in one of the parts and standard permanganate was then added from a burette until the color again matched that of the other portion. Of course, such an amount of permanganate was added as would convert the sulfur dioxide and still be in excess.

Experiments showed that the best color in match was produced by adding to one of approximately equal *N* permanganate solutions of water. It was observed that after the permanganate was added, the color in both solutions did not exactly match the original, but had a slightly redder hue. If, however,

the solution was reduced and oxidized once or twice, before dividing the solution, then the color could be easily matched. In fact, when a series of analyses are made it is best to mix the two portions after each determination, divide them again, and use the same portion over and over for color check.

The solution should contain from 25 to 50 cc. of approximately 2 *N* sulfuric acid. Less than this amount gives a reddish colored solution which is difficult to match; more than this amount acts on the permanganate. Even when large amounts of sulfur trioxide accompany the sulfur dioxide it is generally safe to use 25 cc. of the double normal acid.

The reaction is complete in the cold and the titration is made at ordinary temperature. It was found that merely shaking the permanganate solution in the sample bottle, free from sulfur dioxide, caused no loss of color; hence it was not necessary to run a blank but merely to match color accurately. A little practice in color matching brings accuracy and speed.

The apparatus used was similar to that described in the Bureau of Mines Bull. 98, but since no blank was necessary, less apparatus was required; some of the parts were also simplified.

APPARATUS

One 24-liter, or larger, bottle such as a carboy provided with a two-holed, properly cleaned, rubber stopper containing a large stopcock and a plug, is used as a sample bottle.

Two 500-cc. glass bottles of uniform clear glass are necessary for titrating. To facilitate the color matching, these should be free from waves. One of the bottles should be provided with a two-holed rubber stopper containing a tube which will reach to the bottom of the bottle.

A white background is necessary for titrating and is provided by a box with a partition, to prevent color reflection, the inside being painted white.

One 1000-cc. bottle is needed for diluting and mixing the permanganate solution.

A 25-cc. burette is best, since the readings can be made with greater accuracy.

Two Nessler tubes should be provided for very accurate work.

A suction pump is necessary for evacuating the sample bottle and a manometer tube or gauge is required to obtain the amount of evacuation.

METHOD OF PROCEDURE

The large sample bottle is evacuated and the pressure within the bottle is noted and the temperature taken. When the sample is to be taken, the end of the stopcock is put in communication with the gases to be analyzed and the stopcock opened. The vessel is then closed and the temperature and the barometric pressure are noted. From this data the volume of the sample can be calculated.

About 475 cc. of water are placed in the 1000-cc. bottle and 30 cc. of 2 *N* sulfuric acid are added, after which 10 cc. of the recently standardized 0.005 *N* permanganate are run in. After mixing, the solution is divided about equally into the two 500-cc. bottles.

Sodium sulfite solution, or sulfurous acid, is added to one of the bottles until the color is very faint, after which the color is roughly restored with permanganate. The solutions are now mixed and again divided. The burette is filled with standard permanganate solution and the position of the meniscus is noted. Such an amount of the solution is added to one of the bottles as will prevent the sulfurous acid from completely decolorizing the solution if this is likely to happen. The two-holed rubber stopper and tube are now placed in the permanganate bottle. The gas sample bottle is inverted and the end of its stopcock pushed just through the free hole of the permanganate stopper.

On opening the stopcock, removing the plug and inverting the sample bottle, the solution runs into the same. If the stopcock tube be bent at a right angle the sample bottle can be laid on its side and the liquid run by swinging the permanganate bottle through a half circle. After agitating the sample bottle and its contents for some time, the solution is run back into the small bottle and is titrated with permanganate until the color matches the other portion of the solution. It is again run into the sample bottle as before and then run out and matched closely with the other portion. This matching should be done against a white background, and for very close work portions can be compared in Nessler tubes. The total amount of permanganate run from the burette gives the amount of sulfur dioxide in the sample. The details of manipulation are the same as those so thoroughly worked out for the iodine method by the Selby Commission (*Loc. cit.*).

The following results were obtained by using known amounts of gas, or solutions of known sulfur dioxide content. These results are typical of a large number of analyses made.

GRAMS SO ₂ PRESENT	GRAMS SO ₂ FOUND BY AUTHORS' METHOD			
	No. 1	No. 2	No. 3	No. 4
0.001234	0.001120	0.001306	0.001230	0.001306
0.002468	0.002314	0.002407	0.002407	0.002388
0.00370	0.003373	0.003373	0.003373
0.001897	0.001866	0.001875	0.001904
0.001379	0.001381	0.001388	0.001381

The accuracy of this permanganate method is good, when the dilution of the gas is considered, and it compares favorably with the best results obtained by other methods. It was found very satisfactory for the determination of sulfur dioxide in the atmosphere about the plant in which we were interested.

CONCLUSIONS

This work has shown that permanganate is to be preferred to iodine for SO₂ determination for the following reasons:

- I—It gives as great accuracy.
- II—It is as easy to prepare.
- III—It can be more easily manipulated.
- IV—It can be operated on small traces of SO₂ as well as large amounts.
- V—It is more stable to light.
- VI—It gives a color as easy or easier to match than the starch-iodine end-point.
- VII—It requires no simultaneous blank, and hence less apparatus to be transported in the field.

THE SEPARATION OF ALUMINUM FROM IRON BY MEANS OF ETHER

By SAMUEL PALEIN

Received June 16, 1917

Various methods¹ for the separation of aluminum from iron have been proposed. None of these, however, have found extensive use in analysis. As the method of separation herein proposed is based on the use of organic solvents, only such processes as have a direct bearing on this method will be discussed in this paper.

It had been noted by Gladysz² that hydrous aluminum chloride was very slightly soluble in strong hydrochloric acid, while ferric chloride was readily soluble in that medium.

Gooch and Havens³ utilized the observation of Gladysz, but introduced the use of ether to reduce the solubility of aluminum chloride. They precipitated this salt from a mixture of equal parts of concentrated hydrochloric acid and ether saturated with hydrochloric acid gas at 15° C.

It appears that the method of Gooch and Havens is the only one on record which utilizes any organic solvent (one-half aqueous hydrochloric acid and one-half ether).

Frankforter⁴ in studying the action of aluminum chloride on aliphatic ethers found that the presence of moisture caused precipitation of a compound of this salt with water and hydrochloric acid from an ether solution of the anhydrous aluminum chloride. This precipitate, however, was not constant in composition. He utilized this reaction as a qualitative test for water in ether.

The method proposed in this paper, like the Gooch and Havens method, depends on the insolubility of hydrated aluminum chloride in solvents as contrasted with that of iron, but may be more closely compared with the qualitative observation of Frankforter, as it neither uses a mixture of water and ether, nor requires saturation of the medium with hydrochloric acid gas. It is primarily the latter feature in the Gooch and Havens method which is troublesome and objectionable for ordinary laboratory procedure, as in each determination, hydrochloric acid gas must be passed through the solution at low temperature (15° C.) to saturation (a point rather difficult to determine with certainty) and the precipitate washed with ether-water mixture, itself saturated with HCl gas. In the proposed method, the medium is entirely organic solvent, except for traces of moisture introduced by the solvents.

The essentials of the method are as follows:

The dried mixed chlorides of aluminum and iron are taken up in a small amount of hydrochloric acid alcohol solution and evaporated to crystallization of the salts. The residue is then again acidified with alcoholic HCl. Ether (C. S. P.), which contains a trace of water, is gradually added, and the aluminum

is precipitated as a hydrated chloride, varying in composition, while the iron chloride remains in solution.

EXPERIMENTAL

EFFECT OF MOISTURE—It was observed in preliminary experiments that anhydrous aluminum chloride was readily soluble in absolute alcohol and absolute ether, but that the presence of a trace of moisture, introduced as such or by means of wet alcohol or wet ether, caused an immediate precipitate. An excessive amount of moisture, however, invariably caused the formation of a second layer of a viscous gelatinous mass. It was necessary, therefore, to determine the limits of water tolerance and the best means of introducing that water.

A series of experiments was performed in which water was introduced in varying amounts using, at first, strong aqueous HCl, as that acid was found necessary to keep the iron in solution. This manner of introducing the water was found impracticable as the amounts of HCl necessary caused, in many cases, an excessive amount of water to be introduced. An alcoholic solution of HCl was, therefore, prepared and water was introduced by means of the ether used. The following facts were observed:

1—When an insufficient amount of water was present as obtained by dissolving the salt in a small quantity of alcohol and using largely absolute ether, the precipitate came down in an exceedingly finely divided condition, colloidal or semi-colloidal, practically impossible of filtration. When filtered, the precipitate was exceedingly hygroscopic, behaving somewhat like finely powdered (dried) calcium chloride: the physical state of the precipitate was such that a clean separation from the iron would be impossible even if the precipitation were complete. It was, in fact, found that up to an alcoholic content of about 4 per cent, the precipitation was complete, when the suspension was filtered several times.

2—When an excessive amount of water was present, which depended on the amount of salt present to take care of it and the amount of water introduced with the ether, it was found that a gelatinous layer of the salt was formed.

EFFECT OF ALCOHOL—An excessive amount of alcohol had a tendency similar to that observed in the case of insufficient water, namely, to precipitate the aluminum chloride in a very finely divided state. In addition, the precipitation is incomplete when alcohol is present beyond certain limits, depending upon the amount of water present.

EFFECT OF HYDROCHLORIC ACID—The oxygen was introduced in the form of an alcoholic solution. Aside from the fact that HCl was required to keep the iron in solution, it was found that a slight acidity was essential for two reasons: (1) to make the precipitation complete; (2) to modify the physical state of the precipitate so that it may be filtered. On the other hand, excessive amounts of acid caused it to tend toward formation of a gelatinous body, even in the case of excessive water.

¹ W. W. Scott, "Standard Methods of Chemical Analysis," 1917, pp. 4-5.

² Ber., 16 (1883), 447.

³ Am. J. Sci. [4] 11 (1896), 416.

⁴ J. Am. Chem. Soc., 37 (1915), 550.

A large number of experiments were performed to observe the effect of these various factors. Table I contains a few which show in a quantitative way the results obtained.

TABLE I—SEPARATION OF ALUMINUM CHLORIDE FROM MIXTURES OF VARIOUS PROPORTIONS OF ALCOHOL, HCL (U. S. P.) AND ABSOLUTE ETHER, AND IN THE PRESENCE OF FERRIC CHLORIDE

No.	Mg. Used AlCl ₃	Absolute ReCl ₃	Alcoholic Ce	HCl 35%	Ether U. S. P.	Ether Condition Absolute of Ce	Filtrate	Residues as AlCl ₃
1	100		2		50	Clear		Mg
2	100		2	2 drops	50	Clear		0.2
3	100	1	5	0.5 cc.	50	Clear		0.1
4	100		1	1 cc.	50	Clear		0.0
5	50		2	2 drops	50	Clear		0.1
6	50		1.5	0.5 cc.	50	Clear		0.1
7	50		1.5	0.5 cc.	25	25	Clear	0.3
8	500		2.5	2.5 cc.	250		Clear	0.3
9	10		1.5	0.5 cc.	25	25	Clear	0.2
10	500		1.5(a)	0.5 cc.	40	40	Clear	0.2(b)
11	500		1.5	0.5 cc.	40	40	Clear	0.2
12	10	500	1	1 cc.	50		Clear	0.2
13	10	50	1	1 cc.	50		Clear	0.2
14	10	50	1	1 cc.	50		Clear	0.2

(a) Approximate (b) Total residue on bath

As indicated in the outline of the method given above, the chlorides of aluminum and iron, after driving off nearly all of the moisture in an oven, are taken up in alcoholic HCl and absolute alcohol, evaporated to a viscous semi-crystalline mass and then definite amounts of HCl, alcohol and ether are added. It was deemed advisable to see how much, approximately, HCl and alcohol remained after evaporating to a viscous mass. An experiment was performed using 0.5 g. anhydrous aluminum chloride (the maximum amount of combined salts permitted in the proposed method) adding absolute alcohol and HCl-alcohol, heating until salts completely dissolved and evaporating to viscous mass. The total was weighed before and after, and the difference found to be about 0.62 g., that is, both HCl and alcohol. In the actual method, 0.5 cc. alcoholic HCl is then added. The total volume could not exceed 1.5 cc. in that case (to which is then added the requisite quantities of ether). It is evident, as illustrated in Table I, that the amount of aluminum chloride remaining in solution is practically negligible. This fact is borne out by later experiments on actual separation of known quantities of the salts as shown in Table II.

TABLE II—RESULTS OBTAINED BY APPLICATION OF PROPOSED METHOD

No.	AlCl ₃ used Ce solution	Amount FeCl ₃ used	Grams AlCl ₃ Found Calculated	Grams FeCl ₃ Found Calculated
1	50 A	20 mgs.	0.0068	0.2069
2	50 A	700 mgs.	0.0204	0.0207
3	25 A	0.1336	0.1036	0.1035
4	50 A	700 mgs.	0.0207	0.0207
5	25 A-A	300 mgs.	0.1007	0.1004
6	50 A-A	10 mgs.	0.0204	0.2007
7	50 A	50 cc 1	0.0212	0.0207
8	25 A	25 cc 1	0.1041	0.1035
9	50 A	5 cc 1	0.2070	0.2069
10	50 A	Spilled 1	0.0085	0.0083
11	50 A	2 cc 1	0.2071	0.2069
12	50 B	10 cc 11	0.1995	0.2001
13	50 B	25 cc 11	0.0099	0.1001
14	25 B	25 cc 11	0.1001	0.1001
15	25 B	25 cc 11	0.1004	0.1001
16	25 C	25 cc 11	0.1036	0.1027
17	25 C	25 cc 11	0.1027	0.1027
18	25 C	25 cc 11	0.1030	0.1027
19	25 C	25 cc 1V	0.1029	0.1027
20	25 C	25 cc IV	0.0084	0.0082
21	25 C	25 cc IV	0.0086	0.0082
22	50 D	25 cc IV	0.0100	0.2008
23	50 D	25 cc IV	0.2008	0.2008
24	50 D	25 cc IV	0.2009	1.2008

In the experiments for the quantitative separation of aluminum from iron, alcoholic solutions were made up of C. P. (Kahlbaum's) aluminum chloride and C. P. ferric chloride, respectively, in which 50 cc. were ap-

proximately equivalent to 0.5 g. of salt. Aliquots were pipetted at definite temperature both for determination of metal content of solution (blank) and for actual separation by the proposed method.

In the determination of iron, subsequent to the separation from aluminum by the proposed method, experiment has shown that the iron residue offers considerable difficulty of oxidation even with nitric and sulfuric acids, due to the formation of resinous condensation products of which the organic solvent is the source. Precipitation of the hydroxide is therefore not recommended. A satisfactory procedure was found in conversion of the iron chloride to sulfate and direct ignition.

The method was submitted to Messrs. C. D. Wright, H. E. Buckbinder, E. K. Nelson and W. F. Kunke, of the Bureau of Chemistry, for cooperation. Residues of mixtures of iron and aluminum chloride obtained by evaporation of definite volumes of solution were submitted to each individual. The results obtained appear in Table III.

TABLE III—COÖPERATIVE RESULTS BY BUREAU OF CHEMISTRY WORKERS

ANALYST	SOLUTION TAKEN		Grams		Grams	
	AlCl ₃ Ce.	FeCl ₃ Ce.	Found	Calc.	Found	Calc.
C. D. Wright.....	2 B	25 II	0.0078	0.0080	0.2411
	25 B	25 II	0.1007	0.1001	0.1205
	50 B	25 II	0.1998	0.2001	0.0098
H. E. Buckbinder....	25 C	25 III	0.1031	0.1027	0.1229	0.1227
E. K. Nelson.....	25 D	25 IV	0.1009	0.1014	0.1251	0.1251
W. F. Kunke.....	25 C	25 IV	0.1023	0.1027	0.1246	0.1251

PROPOSED METHOD

The chlorides of iron and aluminum (not over 0.5 g. total) are evaporated to dryness on the steam bath in a 150 cc. Erlenmeyer flask (preferably lipped). The residue is stirred occasionally with a glass rod to allow better exposure of the salts to drying. The rod is allowed to remain in the flask. The residue is then further dried in an oven at about 120° C. for one-half hour, stirring occasionally as before. When dry, the residue is moistened with 0.5 cc. to 1 cc. absolute alcoholic HCl solution¹ (25 to 35 per cent HCl), warmed on the steam bath and stirred to convert any oxides that have been formed to chlorides; about 3 or 4 cc. absolute alcohol are added and the flask is heated on the steam bath until all salts have gone into solution.²

When this has been accomplished the flask is allowed to remain on the steam bath until salts begin to crystallize out and the resulting residue is quite viscous but not solid. About 0.5 cc. alcoholic hydrochloric acid is now added, the flask again warmed and the residue stirred to have the mass uniformly impregnated with the HCl. The flask is then removed and 30 cc. U. S. P. ether (sp. gr. 713 to 716 at 25° C.) are added gradually with stirring. The hydrated aluminum chloride should come down as a uniform, granular, white precipitate, leaving the supernatant liquid clear. Forty cc. absolute ether are then added,

¹ The alcoholic HCl is prepared by passing HCl gas through absolute alcohol, the gas being conveniently generated by the action of concentrated H₂SO₄ on anhydrous calcium chloride.

² When AlCl₃ is present to the extent of nearly 1/5 g., and very little iron is present, it is sometimes very difficult to get all salts in solution. With small amounts of iron present the last traces of AlCl₃ need not pass into solution.

with stirring, and the flask allowed to stand. The solution, when the precipitate has settled, is filtered through a Gooch crucible, using a bell jar arrangement, into a 250 to 300 cc. Erlenmeyer flask. The crucible is fitted preferably with a small circular filter paper (cut to size) instead of asbestos. The flask should be washed with wash-ether (100 parts absolute ether and 2 parts alcoholic HCl) while filtering so as not to allow any ferric chloride to dry on the white precipitate or on the crucible. The usual precautions of washing the flask, crucible and funnel are taken to insure complete transfer of iron. It is not necessary, however, to transfer all of the aluminum chloride precipitate to the Gooch crucible. The aluminum precipitate is removed with the paper from the crucible by tapping it into a 25 cc. beaker and then washing with water to remove adhering particles. The original flask is also washed to transfer completely any adhering aluminum precipitate. The aluminum chloride solution is diluted to approximately 100 cc., about 5 g. ammonium nitrate are dissolved in it, and made just alkaline¹ with ammonia (using methyl red as indicator, preferably), boiled, filtered and the precipitate is washed in the usual way. The precipitate is ignited in a covered crucible² and weighed as Al_2O_3 . The ether solution of iron is distilled or evaporated to remove the ether. The residue is transferred with a little water and HCl to a weighed platinum dish, using as little water as possible, and evaporated to dryness on the steam bath, moistened with 1 cc. concentrated H_2SO_4 , warmed on the steam bath gently to expel most of the HCl, and then slowly over a flame by placing the dish on a triangle which in turn is put on an asbestos gauze (to prevent too rapid heating), and heated until all the ferric chloride is converted to sulfate and no further fuming of sulfuric acid takes place. The dish is then heated over a free flame and finally over a blast to entirely convert the sulfate to ferric oxide. This is then cooled and weighed as oxide in the usual manner.

BUREAU OF CHEMISTRY
DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

A METHOD FOR THE COLORIMETRIC ESTIMATION OF SMALL AMOUNTS OF ANILINE

By ELLIS BLUM

Received August 17, 1917

In the sanitary examination of air in industrial establishments where aniline is employed, the detection and estimation of aniline vapors is quite important. A method for this purpose has been worked out by Hebert and Horn.³ According to these authors, the aniline vapors are collected by holding a liter of the air through a suitable absorption bulb containing 10 cc. of water acidified with sulfuric acid. For

ascertaining the presence of aniline, the calcium hypochlorite test is employed. The quantitative determination is carried out by precipitating the aniline as tribromoaniline with bromine water. The precipitate is caught on a tared filter paper, dried *in vacuo*, and weighed.

In this connection, it occurred to the writer that it might be possible to work out, for estimating the aniline, a colorimetric method based on the qualitative test with hypochlorite. If this were possible, it certainly would be desirable, for not only would considerable time and effort be saved but probably a considerably smaller sample than 10 liters would be sufficient and quantitative measurements could also be applied in cases where the amount of aniline in the samples available, or that can be conveniently collected, is too small for the gravimetric determination. A detailed study of the hypochlorite test for aniline was therefore undertaken.

THE HYPOCHLORITE TEST FOR ANILINE

The hypochlorite test for aniline is described by various authors in rather indefinite language. Thus Blyth¹ in describing this test simply states that an aqueous solution of aniline or its salts is colored blue by "a little" chloride of lime or hypochlorite of soda. Heffter,² although stating that an excess of the reagent should be avoided, does not give any information as to the proper strength of the hypochlorite solution or what amount of it to use for a given volume of the solution to be tested. All the information given is contained in the statement that on adding to the aqueous solution of aniline, chloride of lime or sodium hypochlorite solution, a purplish violet coloration appears which later changes to a dirty red. That the proportion of hypochlorite to aniline and the degree of their concentration are, however, important factors and hence should be taken into consideration in applying this test, appears conclusively proven by the following results:

EFFECT OF VARYING THE PROPORTION OF HYPOCHLORITE

That the proportion of hypochlorite used for a given amount of aniline is an important factor in the test, even when the concentration of the aniline remains the same, and that in certain cases it may even cause a change in the result from negative to positive, is shown by the results obtained in the following experiment. To each of two beakers 100 cc. there was added 0.1 cc. of a 1 to 100,000,000 solution of aniline. No. 1 was then mixed with 1 cc. of a sodium hypochlorite solution of available chlorine of which was about 1 per cent. No. 2 was similarly treated with 0.1 cc. of a sodium hypochlorite solution, the available chlorine of which was only about 0.1 per cent. Immediately after mixing, No. 1 developed a pronounced, brilliant purplish color, but No. 2 appeared? absolutely colorless.

¹ *Trans. Chem. Soc. London*, 1890, 69, 101, p. 102.

² *Monatsh. Chem. Phys.*, 1891, 22, 111.

³ *Engineering Chemistry*, 1916, 1, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100.

¹ W. Blum, "The estimation of ammonium chloride," *Technical Papers of the Bureau of Chemistry*, No. 286.

² The difficulties involved in the accurate determination of chlorine are not generally known and the reader is referred to the examination made by Doctor Blum on this subject.

³ *Eng. Chem. Anal.*, 21, 335-340 (1911); *Anal. Chem.*, 6, 1911, 1912.

EFFECT OF VARYING THE CONCENTRATION

That simply varying the concentration of the hypochlorite and aniline, even without changing the proportion of either, also has a decided effect on the results obtained, may be seen from the following experiment. To each of two tubes there was added 1 cc. of a 0.1 per cent aqueous solution of aniline. No. 1 was diluted to 2 cc. with distilled water while No. 2 was diluted to 20 cc. with the same water. Each was then mixed with 0.5 cc. of a calcium hypochlorite solution, the available chlorine of which was about 1 per cent. Immediately after mixing, a very decided purplish color developed in No. 1 while in No. 2 no purplish color appeared but a yellow¹ color developed.

The reason why the hypochlorite test for aniline has not heretofore been made the basis of a colorimetric method for estimating small amounts of aniline is probably to be found in the fact that the purplish color ordinarily obtained is very unstable and hence cannot well be made the basis of a quantitative method. Also the solution often acquires more or less turbidity and thus still further complicates the problem. It was found, however, that none of these difficulties is encountered with the yellow color obtained under the conditions of the above experiment (sol. No. 2), since this color does not possess the very fugitive character of the purplish color but is sufficiently stable to admit of its being utilized for quantitative purposes; nor is reading of the colors made difficult on account of turbidity, since under the conditions which favor the formation of the yellow color, the solution remains clear, at least sufficiently long so as not to interfere with the readings. These results, therefore, indicated the feasibility of making the hypochlorite test the basis of a colorimetric method for estimating small amounts of aniline, provided the conditions were chosen which would yield the yellow color instead of the purplish.

SENSITIZING EFFECT OF ADDED ALKALI

It was found that the addition of alkali to the mixed solutions of aniline and hypochlorite, which were mixed under the conditions referred to above as yielding the yellow colors, has the effect of sensitizing the reaction, so that a distinct yellow color is obtained even with an amount of aniline which is too small to show any color in the absence of this treatment, as may be seen from the following experiment. To each of two tubes there was added 0.1 cc. of a 0.1 per cent aqueous solution of aniline and sufficient distilled water to make 20 cc. Each was then mixed with 1 cc. of calcium hypochlorite solution, the available chlorine of which was about 0.1 per cent. On letting these solutions stand the usual period of 10 minutes, no appreciable color developed. On now mixing, however, one of these solutions with 1 cc. of

N NaOH, a decided yellow color developed in a few minutes while the solution which did not receive this treatment remained practically colorless in comparison.

TIME OF ADDING ALKALI

It appears also that in order for the added alkali to act as sensitizer, it is necessary to add it *after* the aniline solution has been mixed with the hypochlorite reagent, as may be seen from the following experiment. To each of two tubes there was added 0.1 cc. of a 0.1 per cent aqueous solution of aniline and each was diluted to 20 cc. with distilled water. No. 1 was mixed first with 1 cc. of the calcium hypochlorite solution¹ and after standing about a minute was then mixed with 1 cc. of *N* NaOH while No. 2 was mixed first with 1 cc. of the *N* NaOH and after standing about a minute was then mixed with 1 cc. of the same hypochlorite solution. After the final mixing with the 1 cc. *N* NaOH, No. 1 began to develop color and had a very decided yellow color after it had stood about 10 minutes, but No. 2 appeared practically colorless in comparison, in spite of the fact that, excepting for the reverse order in which the reagents were added, it had received exactly the same treatment as No. 1.

SENSITIVENESS OF THE TEST

Since the hypochlorite test for aniline, in one or other of its modifications, is probably the most characteristic of the various color tests for aniline which have been proposed, it seemed desirable in this connection to determine its sensitiveness by the improved procedure here described. According to Dragendorff,¹ 1 part aniline in 6,000 parts water is the minimum concentration which will yield a positive test with calcium hypochlorite. According to Jacquemin,² the sensitiveness of the test can be increased so as to detect 1 part aniline in 10,000 parts water by substituting sodium hypochlorite in place of the calcium hypochlorite employed by Dragendorff. It was found, however, that by basing the test on the yellow color instead of the purplish and taking advantage of the above described sensitizing effect of added alkali, even as little as 0.01 mg. in 20 cc., or 1 part in 2,000,000, could be readily detected.

PROCEDURE ADOPTED

The following procedure was finally adopted. A preliminary test was carried out on the solution to be examined, with the object of obtaining an idea as to the approximate amount of aniline present. If this indicated that its concentration was more than 1 part in 200,000, the solution was diluted³ with distilled water so as to make it come within the range of the standards (1 pt. in about 285,000 to 1 pt. in 2,000,000)

¹ Containing 0.1 per cent available chlorine.

² See Jacquemin, *Compt. rend.*, **83** (1876), 226.

³ This fact, besides enabling one to utilize this test for quantitative purposes, as is shown in this paper, can help also to make the hypochlorite test for aniline more characteristic, for, when the regular purplish color is obtained, the result could be confirmed on another portion of the same sample by varying the concentration, as shown above, so as to obtain the yellow color; and then the result could be still further confirmed by showing that this yellow color is much increased by adding alkali, as is shown in another part of this paper.

⁴ Instead of diluting the solution to be examined, one may also prepare a set of standards with correspondingly higher aniline concentrations. For example, a series of standards may be prepared having ten times the concentration of those used in this work and reading 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 and 0.7 mg., respectively. In using such a higher series of standards, however, it appears more advantageous to adopt a little longer interval than 10 minutes for the tubes to stand before being read, when one has occasion to use the higher end of the series.

used; 20 cc. of this solution was then mixed with 1 cc.¹ of calcium hypochlorite solution,² the available chlorine of which was 0.1 per cent. After standing 2 minutes, it was mixed with 1 cc. of N NaOH and allowed to stand 10 minutes.³ The color of this solution was then compared with those of standards, which were obtained by treating similarly known amounts of a standard aniline solution. The mixing with the reagents and the final reading of the color was carried out in the same tube, the narrow form 50 cc. Nessler tubes having been found convenient for this purpose. The mixing of the unknown solution and the standards with the reagents was effected nearly simultaneously with the aid of bulbed glass rods, by means of which it was found comparatively very easy to mix thoroughly the contents of four or five tubes practically simultaneously. The standards were prepared from a stock solution of pure aniline in distilled water, which contained 1 gram aniline in 1,000 cc. of solution. The regular⁴ standards contained 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06 and 0.07 mg. aniline, respectively, and the volume of each, exclusive of the reagents, was 20 cc.

RESULTS OBTAINED

The following results were obtained by the above procedure when working with aqueous solutions of aniline, the amount of aniline in which was unknown⁵ to the writer at the time the work was done.

MILLIGRAMS ANILINE IN 20 CC.			
No.	Given	Found	Error
1.....	0.04	0.04	0.00 (0.000)
2.....	0.02 (0.024)	0.02 (0.023)	0.00 (-0.001)
3.....	0.18	0.17	-0.01 (-0.010)
4.....	0.11	0.11 (0.105)	0.00 (-0.005)
5.....	0.03 (0.032)	0.03 (0.032)	0.00 (0.000)
6.....	0.01 (0.014)	0.02 (0.017)	+0.01 (+0.003)
AVERAGE.....			0.003 0.003

As will be noted, the amounts of aniline are expressed to the nearest one hundredth of a milligram, which is

¹ Since it is important that the unknown solution and the standards be mixed with the reagents as nearly simultaneously as possible, it is well to use pipettes or burettes with comparatively large outflow openings, so as to consume as little time as possible for the adding of the reagents.

² This solution was prepared by suitably diluting with water a stock solution, the available chlorine of which was about 3 per cent, which was obtained by shaking thoroughly for 10 minutes 29 g. of a sample of commercial chlorinated lime with 100 cc. water and then filtering. This stock solution should not be prepared from a chlorinated lime which has lost much of the available chlorine that it originally had, since it might leave too much calcium in the final reagent and thus cause a precipitate or turbidity when the excess alkali is added.

³ In the case of the standard containing the smallest amount of aniline (0.01 mg.), reducing this time of standing to 5 minutes appears advantageous.

⁴ For most practical purposes these standards are probably sufficient, since in case the color of the unknown solution happens to fall between two of the above standards, one can, especially after some experience, judge which of the two standards it approaches nearer and assign it a proper intermediate value which will probably be close enough for most practical purposes. When dealing with the middle and especially the lower end of the above series of standards, however, since there would be greater possibilities for a larger percentage error, it is advisable to confirm any such assumed value by actually preparing the corresponding standard and one a little above and another a little below that value and repeating the simultaneous treatment with the reagents. In order to enable one to prepare quickly and easily such intermediate standards, it is advisable to have on hand a more dilute solution of aniline than the above mentioned stock solution. Such a solution was prepared by diluting 10 cc. of the stock solution to 1000 cc. with distilled water, which has also the advantage that the volume used in the preparation of any standard, expressed in cc., gives also the value of that standard in hundredths of a milligram of aniline. By keeping some of this dilute solution in an appropriate burette, any desired intermediate standard was quickly and easily prepared.

⁵ These solutions were submitted to the writer as "unknowns" by Dr. A. Seifell, of this laboratory.

probably close enough for most practical purposes, and also to the thousandth of a milligram (the figures in the parentheses) where the amount given or found was not in even hundredths. The average error (neglecting the algebraic signs) was practically the same (0.003 mg.) whether we accept the figures expressing the amounts of aniline to the nearest hundredth of a milligram or to the thousandth of a milligram. These results further confirm the general principle that from the point of view of percentage accuracy it is well to work with as large amounts as possible within the given range, since an error of only 0.003 mg. in the case of No. 6 shows up as a much greater percentage error than even over three times this amount (0.010 mg.) in the case of No. 3.

Finally, when we recall that by the ordinary application of the hypochlorite test for aniline even the solution with the highest of the above amounts of aniline (No. 3) would not show even qualitatively the presence of any aniline while the proposed method measures such small amounts quantitatively, and the further fact that this method does not require elaborate apparatus but is very simple and quickly and easily carried out, its advantages when one has occasion to detect and estimate such small amounts of aniline, become very apparent.

HYGIENIC LABORATORY
U. S. PUBLIC HEALTH SERVICE
WASHINGTON, D. C.

A MODIFICATION OF THE PRICE METHOD FOR THE SEPARATION OF THE PERMITTED COAL-TAR COLORS TO INCLUDE TARTRAZINE

By E. H. INGERSOLL

Received July 2, 1917

Food Inspection Decision 70, issued by the U. S. Department of Agriculture in 1907, enumerated seven coal-tar colors that could be used in foods under certain restrictions. Price¹ in 1911 described a method for the separation of these colors when they occurred in mixtures. Recently, under Food Inspection Decision 164, there has been another coal tar dye added to the seven previously permitted, namely, Tartrazine. The including of this additional color among the permitted ones makes it necessary for the analyst to have available a method whereby these eight coal-tar dyes may be separated and identified in cases where they occur in mixtures. Ewins² has stated the necessity for such a method and gives a modification of the method described by Price to include this additional color. By this method Amaranth is separated from Tartrazine by saturating the aqueous solution of these two dyes with sodium chloride; however, it has been observed that when but small amounts of dye have been taken out of the original mixture in extraction with the ammonium sulfate reagent, the separation is very difficult at all attainable. Furthermore, while some Tartrazine, like Naphthal Yellow 5, is soluble in saturated ammonium sulfate solution, the larger part is not extracted by the reagent, if the Price direc-

¹ U. S. Department of Agriculture, D. A. T. Circular 180.

² Food Inspection, 10 (1916), 135-136.

tions to wash until the washings are no longer red are adhered to, but remains insoluble on the filter.

As the method of separation described by Estes proved unsatisfactory in the hands of the author, work was undertaken to devise a method which would be entirely satisfactory. In undertaking this work, it was thought best to take the Price method as a basis, and, if possible, so to modify it as to include all of the eight permitted coal-tar colors. The method described below is a result of this work and is given only after it has been tried by several analysts working independently and with satisfactory results on samples of unknown mixtures of coal-tar colors.

Rub from 0.1 to 0.2 g. of the dye sample, depending upon the amount of foreign salts in the mixture, with 25 cc. of saturated ammonium sulfate solution in a mortar and filter through a dry filter. If the filtrate comes through red, wash the color residue in the mortar and on the filter with successive 10 to 15 cc. portions of the ammonium sulfate solution until the washings are no longer colored red. The filtrate and washings contain the greater part of the Amaranth together with some Naphthol Yellow S and also some Tartrazine. Combine the filtrate and washings and shake with successive portions of acetic ether until the acetic ether is no longer colored yellow. The acetic ether removes that portion of the Naphthol Yellow S which was dissolved by the ammonium sulfate solution and may be discarded, since the greater part of this dye is recovered later in the scheme. Shake the ammonium sulfate solution containing Amaranth and some Tartrazine with acetone to remove these colors; discard the ammonium sulfate solution, dilute the acetone portion with an equal volume of water and drive the acetone off on a steam bath. Saturate with sodium chloride, add 10 cc. of alumina cream, agitate, warm, settle, filter and wash with warm saturated sodium chloride solution until the washings are no longer colored yellow. To recover the Amaranth, suspend the alumina cream precipitate in saturated ammonium sulfate solution and shake with acetone.

The filtrate contains Tartrazine and is to be discarded, or, when dealing with small amounts, if desired, can be saved and the Tartrazine identified with the greater portion of this color separated further in the scheme.

Dissolve the portion of the original sample not dissolved by ammonium sulfate, in water, acidify with acetic acid and shake with successive portions of ethyl ether until the ether is no longer colored. The ether contains erythrosine, which it is very essential to remove completely from the other dyes before proceeding further. Wash the ether solution several times with water and finally extract the erythrosine from the ether with dilute ammonia solution. Remove the ammonia by evaporation on the steam bath and observe if this solution, when very dilute, has any fluorescence which might indicate the presence of prohibited colors having similar reaction. Remove the ether from the acetic acid aqueous solution by warming on a steam bath, saturate with sodium chloride at steam bath temperature and add sodium chloride

in excess; cool and filter through a dry filter. Wash with saturated sodium chloride solution until the washings are colorless. When a bulky precipitate is obtained here, which is difficult to wash, it may be time-saving to redissolve the precipitate and excess salt in water and repeat the salting and washing process, adding the filtrate and washings to those of the first saturation. The combined filtrate and washings contain Light Green S F Yellowish, Naphthol Yellow S, Tartrazine, traces of Orange 1, and possibly Amaranth, since the latter dye may not be entirely removed by the first extraction of the dry sample with the ammonium sulfate reagent.

To separate the Naphthol Yellow S, extract with successive portions of acetone until the acetone fails to remove any more color. Combine the acetone extracts and wash with several portions of saturated sodium chloride solution to remove traces of Tartrazine and Light Green S F Yellowish from the acetone. Add to the acetone solution an equal volume of water and drive off acetone on the steam bath. Acidify the water solution and shake with amyl alcohol to remove traces of Orange 1 that may be present; discard this amyl alcohol solution. Drive off all the amyl alcohol mechanically held in the aqueous solution by warming on the steam bath and test this solution for Naphthol Yellow S.

To separate the Light Green S F Yellowish from the Tartrazine, remove the acetone from the aqueous salt solution by heating on the steam bath, and add fuller's earth in the proportion of 0.5 g. to each 10 cc. of warm dye solution. After mixing well and heating, allow to settle; filter and wash with water. The Light Green S F Yellowish remains on the filter and can be dissolved in strong, hot acetic acid and further identified. If Tartrazine was present in the original mixture, the filtrate from the precipitation of the Light Green S F Yellowish will be yellow or golden yellow, not decolorized by hydrochloric acid. Imperfect removal of Naphthol Yellow S, previously, would result in a yellow filtrate here which could be decolorized by hydrochloric acid. The Tartrazine can be further isolated from a possible trace of Amaranth by adding 10 cc. of alumina cream to each 100 cc. of solution, mixing, warming and filtering, when the Tartrazine will be found in the sodium chloride filtrate. To isolate from the salt, evaporate and redissolve in alcohol.

Dissolve the precipitant containing Orange 1, Ponceau 3R and Indigo Disulfo Acid, together with excess sodium chloride on the filter paper, in water and extract with three successive portions of acetic ether. Orange 1 is taken up by acetic ether. Combine the acetic ether extracts and wash with saturated sodium chloride solution, until no more color is removed. Extract the acetic ether solution with water to obtain the Orange 1 in an aqueous solution and free from acetic ether by warming on the steam bath.

Warm the water solution containing Ponceau 3R and Indigo Disulfo Acid from which the greater part of the Orange 1 has been removed, on the steam bath until free from acetic ether, cool, add 10 g. gran-

ulated calcium chloride, allow to stand 15 minutes and then add 15 cc. of a freshly prepared stannous chloride solution containing the equivalent of 3 per cent metallic tin and 12 per cent of hydrochloric acid (sp. gr. 1.19). Mix well and allow to stand until the solution shows no blue color. If Ponceau 3R is present, it will be precipitated. Filter immediately, wash the precipitate twice with 25 per cent calcium chloride solution to remove all the reduced Indigo Disulfo Acid, dissolve the remaining residue in dilute ammonia solution and test for Ponceau 3R.

To the filtrate, which should be practically colorless, add 3 per cent hydrogen peroxide solution. A deep blue coloration indicates the presence of Indigo Disulfo Acid.

MEAT INSPECTION LABORATORY
WASHINGTON, D. C.

DETECTION OF ADDED WATER IN MILK BY MEANS OF A SIMPLIFIED MOLECULAR CONCENTRATION CONSTANT¹

By LESLIE W. FERRIS
Received May 31, 1917

It is a known fact that the osmotic pressure of the blood serum of a healthy cow is practically constant, and naturally the osmotic pressure of the milk must be regulated by that of the blood. The bulk of the osmotically active substances in the milk are lactose and soluble salts, chiefly the chlorides of the alkali metals. Since the quantity of lactose in milk varies considerably the chlorides would be expected to vary inversely to the lactose. Therefore, a figure that would represent both lactose and chlorides in isotonic equivalence ought to be fairly constant.

Mathieu and Ferre² have embodied this principle in the calculation of a simplified molecular concentration constant which they use as the basis of a method for the detection of added water in milk. Giving 1 g. of sodium chloride the isotonic equivalence of 11.9 g. of crystallized lactose they obtain an apparent constant by adding the grams of lactose per liter of milk to the grams of sodium chloride per liter $\times 11.9$. They then correct this apparent constant for the volume of the fat and casein, using 0.94 as the specific gravity of fat and 1.35 as the specific gravity of casein. Mathieu and Ferre conclude that this simplified molecular constant varies between 74 and 79 for genuine milk and falls below 73 if the milk contains 5 to 8 per cent added water.

Since the completion of this work it is noted that Mathieu³ has found values between 70 and 82 for 15 out of a new series of 93 samples taken in summer.

Monier Williams⁴ has calculated the Mathieu and Ferre constant for a number of samples of milk from individual cows. After eliminating certain samples that were known to be of abnormal character he found values for the constant varying from 70.0 to 78.1.

The object of this work was to test the procedure upon different grades of American milk. The molecular concentration constant was determined upon 31 samples of milk, representing complete milkings from several breeds of cows. The different samples of milk varied considerably in quality, as is shown by the fact that the percentage of solids-not-fat ranged from 7.63 to 9.52.

On all of the samples analyzed fat was determined by the Babcock Method, casein by the Official Method of the Association of Official Agricultural Chemists, and the specific gravity taken with the lactometer. Sodium chloride was determined by the Volhard Method on a copper sulfate serum, as used by Poetschke,⁵ with the exception that it was found best to weigh instead of measure the sample of milk. Lactose was determined in the copper sulfate serum by the Munson and Walker Method. No correction was made for the volume of the precipitate produced by the copper sulfate, since this error was found to be well within the error of the manipulation. Duplicate determinations of lactose and sodium chloride were made on 30 samples and the two corresponding figures for the molecular concentration constant calculated, as shown in Table I. The greatest difference was 0.6 (Sample 16) and the average experimental error on the 30 samples was 0.22.

Fig. 1—Relation of Lactose and Sodium Chloride

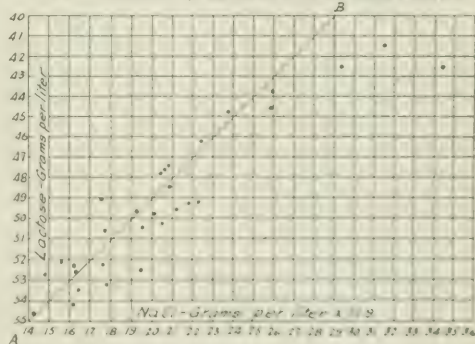


Fig. 1 shows that within certain limits the per cent of sodium chloride gradually rises as the lactose decreases. The grams per liter of lactose are represented as ordinates and the grams per liter of sodium chloride multiplied by 11.9 as abscissas. When the experimental results are plotted it is seen that they approach a constant represented by the line A-B.

Table I gives the analysis of the samples of milk with the three figures that are used as a basis for the detection of added water, the percentage of solids-not-fat, the reduction and vol. of the solid serum, and the molecular concentration constant. The values for the molecular concentration constant vary between 73.1 and 82.0. The two high figures for the constant in Table I, samples 8 and 20, case No. 2, were obtained from milk that was abnormally high in fat. Case No. 1 was near the end of the lacta-

¹ Published by permission of the Secretary of Agriculture, read at the meeting of the American Chemical Society, New York City, September 25 to 30, 1916.

² *Ann. Ind. 7* (1914) 12-21.

³ *Ind. 9* (1916) 48-8.

⁴ Report of the Food Government Board, Great Britain, No. 22 (1914).

⁵ *Eng. Trans.* 1 (1906) 150.

TABLE I.—ANALYSES OF MILK OF INDIVIDUAL COWS (SAMPLES ARRANGED TO SHOW PRECEDING VALUES OF LACTOSE)

Sample No.	Breed	Cow No. (a)	Age of Cow Yrs.	Time since Calving	Milk-ing Time	Milk Lbs.	Lac-tometer Reading	Per cent				Sour Red. at 20° C.	SRUM Ash, g. per 100 cc.	Per cent (28.0) per Solids-not-fat	Mol. Wt. Const.
								Fat	Casein	Lactose	NaCl				
1	Grade Holstein	12	7	3 mos.	Night	13.5	31.4	4.15	2.31	5.31	0.117	44.1	0.69	8.84	73.8
2	Thoroughbred Holstein	13	■	2 1/2 mos.	Noon	26.1	30.7	4.00	1.97	5.27	0.132	44.2	0.75	8.57	73.5
3		13	■	2 1/2 mos.	Morning	30.2	31.8	3.05	2.10	5.20	0.134	43.0	0.73	8.52	74.4
4		6	4	5 wks.	Night	14.8	32.3	4.25	2.63	5.19	0.132	42.8	0.79	9.20	73.4
5		13	8	2 1/2 mos.	Night	21.0	31.4	3.45	2.08	5.12	0.121	42.8	0.75	8.49	76.4
6		2	3	9 mos.	Noon	15.2	31.0	3.90	2.36	5.11	0.133	41.3	0.69	8.77	71.7
7		4	7	..	Morning	17.2	33.8	2.40	2.66	5.12	0.159	40.2	0.76	9.14	73.2
8		2	3	9 mos.	Night	12.5	33.0	3.25	2.49	5.09	0.131	41.5	0.78	8.95	76.0
9	Grade Holstein	10	9	2 mos.	Morning	18.0	32.6	3.90	2.70	5.07	0.143	42.3	0.82	8.84	75.6
10	Thoroughbred Holstein	11	3	4 mos.	Night	10.0	32.3	3.30	2.43	5.05	0.129	44.9	0.72	9.00	72.7
11	Grade Holstein	10	9	2 mos.	Night	18.5	31.4	5.05	2.64	4.91	0.144	41.1	0.81	8.85	74.7
12	Thoroughbred Holstein	11	3	4 mos.	Morning	13.0	30.6	3.55	2.48	4.89	0.159	42.8	0.73	8.70	74.3
13		2	3	9 mos.	Morning	15.0	32.9	3.20	2.74	4.88	0.168	44.9	0.78	8.98	74.2
14		4	7	..	Night	13.2	32.6	3.30	2.71	4.83	0.163	41.3	0.77	9.08	74.3
15		6	4	5 wks.	Morning	18.1	30.3	4.20	2.33	4.85	0.157	41.0	0.75	8.51	74.1
16	Grade Durham	15	6	5 mos.	Night	6.5	33.3	4.60	3.15	4.78	0.171	43.1	0.87	9.52	73.7
17		9	8	3 mos.	Morning	19.2	30.4	2.55	2.07	4.82	0.172	42.8	0.74	8.09	76.1
18	Thoroughbred Holstein	5	3	5 mos.	Morning	13.2	30.0	3.50	1.99	4.75	0.184	40.4	0.77	8.03	76.7
19	Grade Jersey	14	8	5 wks.	Night	13.0	30.4	4.45	2.12	4.81	0.175	40.3	0.78	8.18	75.5
20	Thoroughbred Holstein	5	3	5 mos.	Night	10.4	29.7	3.30	2.00	4.76	0.142	39.7	0.75	8.04	71.1
21	Grade Holstein	9	■	3 mos.	Night	17.4	28.5	4.30	1.70	4.69	0.171	39.0	0.75	7.78	73.2
22	Grade Jersey	16	2 1/2	8 mos.	Night	4.3	31.5	6.65	3.00	4.65	0.168	39.0	0.75	7.78	73.1
23	Grade Jersey	17	18	1 mo.	Night	13.0	28.8	3.90	1.85	4.64	0.166	42.4	0.86	9.10	72.7
24	Thoroughbred Holstein	7	7	2 1/2 mos.	Morning	15.0	28.3	3.40	1.91	4.62	0.171	39.5	0.74	7.80	75.4
25		7	7	2 1/2 mos.	Night	17.6	29.4	3.50	2.28	4.50	0.181	39.5	0.80	8.00	72.6
26	Grade Holstein	8	7	1 1/2 mos.	Morning	24.8	29.1	3.20	1.90	4.35	0.193	39.4	0.84	7.71	72.2
27	Thoroughbred Holstein	1	5	11 mos.	Morning	11.8	30.4	3.20	2.44	4.34	0.212	40.7	0.86	8.39	74.1
28	Grade Holstein	3	9	6 mos.	Morning	10.0	28.1	3.70	2.11	4.25	0.211	38.3	0.80	7.83	74.3
29	Thoroughbred Holstein	1	5	11 mos.	Noon	9.9	30.1	3.50	2.46	4.15	0.281	43.2	0.82	8.67	73.5
30	Grade Holstein	3	9	6 mos.	Night	7.1	27.9	3.60	2.08	4.14	0.238	39.6	0.77	7.63	73.6
31	Thoroughbred Holstein	1	5	11 mos.	Night	8.4	30.9	3.25	2.48	4.09	0.294	42.2	0.93	8.54	81.2
32	Composite Sample of Herd Milk						31.0	3.85	2.44	4.93	0.155	8.73	76.1
	with 5 per cent Added Water						30.6	3.70	2.40	4.72	0.144	8.41	76.2
	with 8 per cent Added Water						29.5	3.55	2.28	4.54	0.140	8.20	70.2
33	Market "Fresh" Milk						31.3	3.70	2.31	4.79	0.166	40.5	0.79	(8.59)*	67.7
	with 5 per cent Added Water						29.0	3.45	2.21	4.55	0.156	38.9	0.74	(7.94)*	74.1
	with 8 per cent Added Water						28.2	3.25	2.10	4.42	0.150	37.9	0.71	(7.70)*	69.7
34	Market "Fresh" Milk						29.5	3.90	2.31	4.67	0.146	40.5	0.77	(8.16)*	70.2
	with 5 per cent Added Water						28.2	3.75	2.21	4.45	0.140	39.9	0.72	(7.90)*	66.7
	with 8 per cent Added Water						28.0	3.60	2.08	4.29	0.136	38.0	0.70	(7.72)*	64.3

(a) No. of cows as used in paper by J. T. Keister, THIS JOURNAL, 9 (1917), 862. * Figures in parentheses obtained by the Babcock formula.

tion period and gave a very small amount of milk which would have little effect in raising the salt content of a sample of mixed milk. Therefore, the constant obtained on market milk would naturally have a narrower range than that shown by milk of individual cows.

To show the effect of added water 5 per cent and 8 per cent of distilled water were added to 3 samples of milk (Samples 32, 33 and 34 of Table I). The lowest figures found on the above authentic samples were: for solids-not-fat, 7.63; for refraction of sour serum, 38.3; and for ash of sour serum, 0.69. The corresponding figures on the samples containing 5 per cent added water were well above these results. When 8 per cent water was added, the solids-not-fat and the ash of the sour serum were both above and the refraction of the sour serum only slightly below the minima found for genuine milk. On the samples containing

5 per cent added water the molecular concentration constant was near or below 70 and was considerably below 70 in each case where 8 per cent water was added. From these figures it is evident that the molecular concentration constant is a better means of detecting added water than either the solids-not-fat, the refraction of the sour serum or the ash of the sour serum.

To show the effect of the age of milk upon the constant, several samples of market milk were kept under different conditions and the constant and acidity determined, as shown in Table II. These samples were not authentic and it is evident from the figure 64.6 that No. 37 contained added water. As the acidity of the milk increased the lactose diminished, thus having the same effect upon the constant as the addition of water. Since this effect is not constant for different conditions of souring, it does not seem

practical to calculate the lactose originally present in the milk that has soured from the apparent lactose and the acidity. However, there is little or no loss of lactose if the acidity of the sample is not above 0.2 per cent, and milk that contains a larger amount of acid is not generally considered fresh.

TABLE II—EFFECT UPON THE MOLECULAR CONCENTRATION CONSTANT OF THE ACIDITY AND OF USE OF FORMALDEHYDE AS A PRESERVATIVE

Sample No.	DESCRIPTION OF SAMPLE	Held before Analysis	Per cent Lactic Acid	Per cent Lactose	Mol. Conc. Constant
35	Market "Fresh" Milk	0	0.14	4.85	73.2
	Kept on ice	3 days	0.15	4.84	73.0
	3 days on ice then at 15° C.	1 day	0.18	4.78	72.5
		2 days	0.42	4.45	68.8
36	Market "Fresh" milk	0	0.15	4.78	72.6
	Kept at 15° C.	2 days	0.16	4.77	72.7
	Warmed to 25° C., then on ice	1 day	0.34	4.54	70.2
37	Market "Fresh" Milk	0	0.18	4.30	64.6
	Kept on ice	1 day	0.21	4.30	64.6
		2 days	0.24	4.25	64.0
		3 days	0.27	4.23	63.8
38	Market "Fresh" milk	0	0.16	4.68	72.8
	Kept on ice	1 day	0.18	4.71	73.1
		2 days	0.19	4.65	72.5
		3 days	0.22	4.63	72.3
39	Market "Fresh" milk	0	0.15	4.86	75.2
	Kept on ice	3 days	0.17	4.83	74.8
		6 days	0.20	4.79	74.4
40	0.2 per cent formaldehyde added to sample No. 39 while fresh	0	0.15	4.83	75.0
	Kept on ice	3 days	0.16	4.84	75.0
		7 days	0.18	4.83	74.8
		9 days	0.18	4.85	75.1
41	Market "Fresh" milk	0	0.15	4.88	71.3
	Added formaldehyde, 1 part to 2500; on ice	5 days	0.18	4.81	70.6
		8 days	0.18	4.81	70.6
42	Market "Fresh" milk	0	0.15	4.85	71.4
	0.1 per cent formaldehyde added, then kept at room temp. (22° C.)	1 day	0.18	4.85	71.4
		3 days	0.18	4.87	71.7
	Kept at room temperature	5 days	0.18	4.85	71.4
		9 days	0.18	4.85	71.1
		12 days	0.18	4.84	71.5

If a sample of milk cannot be analyzed while it is fresh, it should be preserved with formaldehyde. The results of Nos. 40, 41 and 42 of Table II show that the amount of formaldehyde necessary to preserve a sample of milk at room temperature for 12 days will not affect the determination of the molecular concentration constant.

The freezing point of the samples of milk in Table I was determined by J. T. Keister.¹ The effect produced by a given amount of added water is about the same in each case, but since the freezing point has a smaller variation than the molecular concentration constant, the former method is more accurate for the detection of a small amount of added water. However, the molecular concentration constant is determined by a simple chemical analysis, and, since a sample can be preserved for some time and the constant still be determined, the method should be a valuable aid in the detection of watered milk.

SUMMARY

I—The thirty-one samples analyzed showed values for the molecular concentration constant between 71.1 and 82.6.

II—The development of acidity has the same effect upon the constant as the addition of water, however, the use of formaldehyde as a preservative is permissible.

III—On the three samples to which 8 per cent of water was added in each case this method showed the presence of added water.

IV—If a sample of milk can be examined while fresh the freezing-point method is more accurate, but, if it is desired to preserve the sample, the determination of the molecular concentration constant is better for the detection of added water in milk.

DAIRY LABORATORY AND LABORATORY OF FOOD CONTROL
BUREAU OF CHEMISTRY, WASHINGTON, D. C.

A METHOD FOR THE DETERMINATION OF THE VOLATILE OIL CONTENT OF CITRUS FRUITS

By C. P. WILSON AND C. O. YOUNG

Received April 4, 1917

In the course of the investigation of the by-products of citrus fruit it was found necessary to devise a method for determining the total volatile oil contained in the peel.

Several attempts were made to extract this oil from the ground peel by means of various organic solvents, such as alcohol, ether, benzol, gasoline, chloroform, and carbon tetrachloride. It was found that invariably a large amount of water became mixed with the solvent, even when benzol, carbon tetrachloride and similar solvents were used. No practical method was found to drive off this water without loss of oil.

In order to avoid this difficulty the ground peel was dehydrated with anhydrous copper sulfate or sodium sulfate and the mixture extracted as before. Trouble was experienced, however, on account of the large amount of dehydrating material required, which caused packing or caking in the thimble and prevented complete extraction. Even when extraordinary care was exercised in carrying out this method it was found impossible to remove the last traces of solvent without loss of oil. Results were always low, as can be seen by comparing the figures obtained by the steam distillation of peel and by extraction with absolute ether of another sample of the same peel previously dehydrated by mixing with anhydrous copper sulfate.

TABLE I—COMPARISON OF STEAM DISTILLATION METHOD AND EXTRACTION METHODS OF DETERMINING LEMON OIL

Determinations made on Peel Calculated to Entire Fruit	Per cent Oil in Fruit
Method	
Steam Distillation	0.81
Extraction, Ether	0.31
Extraction, Ether	0.28

The extraction method not being very satisfactory, steam distillation was tried. After a number of experiments the following procedure has been evolved and has been used for a large number of determinations:

METHOD FOR THE DETERMINATION OF VOLATILE OIL IN CITRUS FRUIT OR PEEL

PREPARATION OF SAMPLE—Peel the entire sample of whole fruit three times through a fine cutting food grinder and mix thoroughly.

DETERMINATION—Weigh thirty after grinding sample 200 g. of the sample into a 1/2 liter flask and mix with 100 cc. of water. Attach the flask to a 3 ft. straight condenser by means of a kiddlebock joint. Connect with a ground glass tube, place a small amount under flask and draw the sample rapidly in a current

¹ THIS JOURNAL, 9 (1917), 862.

of steam until the oil ceases to come over. About 200 cc. of distillate are usually sufficient.

The distillate is received in a special oil flask through a long stem funnel, the latter being used to avoid clogging in the neck of the flask with subsequent loss by overflow. The special flask is shown in Fig. 1. It is made similar to a Babcock milk test bottle: the body has a capacity of 200 cc. and the neck 2 cc., the latter being graduated in $1/10$ cc.

As soon as the distillation is complete, bring the oil into the graduated neck of the flask by the addition of water and whirl in a centrifuge until all of the oil has collected in a clear layer. Note the volume of the oil, reading the extreme of the meniscus at the top as well as at the bottom of the column. Calculate the weight of the oil from its volume and specific gravity by the following formula:

$$W = V \times 0.849 \times 0.996$$

where V is volume of the oil obtained, 0.849 the average specific gravity of California lemon oils, and 0.996 the factor correcting for determinations made at $25^\circ/25^\circ$ C. in air. In exact work the specific gravity of the oil should be predetermined for the particular kind of fruit used and an average of a number of determinations on distilled oil taken. The volume reading should be made at the same temperature as that at which the specific gravity determinations are made.

For oil distilled from California lemons the specific gravity factor at $25^\circ/25^\circ$ C. determined in air with brass weights is 0.849.

If preferred the oil may be weighed directly by drawing it into a tared weighing pipette, such as was described by Mertes,¹ and weighed directly. This method is not as accurate as the first method given, owing to the difficulty in transferring all of the oil to the pipette without admixture of water.

By the steam distillation method, calculating weight of oil from its volume and specific gravity, a number of determinations may be run simultaneously and results are satisfactory. Duplicate determinations should not vary more than 0.1 cc. on a volume of 1.5 cc. and the weights of the oil should check within 0.05 per cent.

TABLE II COMPARATIVE RESULTS OF OIL DETERMINATIONS ON THE SAME FRUIT, OIL, DETERMINATION BEING MADE ON INSIDE GROUND FRUIT, THE OTHER ON THE GROUND PEEL

The Percentage of Oil in Both Cases Is Calculated to the Entire Fruit Oil Is Fruit		PEEL		OIL IN PEEL		CALC. FROM PEEL	
By Dist. of Whole Fruit	Per Cent	Per Cent	Per Ton	Per Cent	Per Cent	Per Cent	Lbs. per Ton
No.	Percent	Lbs. per Ton	cent	Percent	Percent	Lbs. per Ton	cent
1057...	0.67	13.4	32.7	1.02	0.33	6.6	
1058...	0.74	14.8	29.2	1.13	0.33	6.6	
1060...	0.67	13.4	27.3	0.89	0.24	4.8	
1061...	0.68	13.6	29.3	1.78	0.52	10.4	

While it is possible to distil the ground peel alone instead of the whole fruit, and calculate back to the

entire fruit from the percentage of peel, the results obtained are usually low. This is shown by Table II.

Low results on the ground peel are attributed to loss of oil in the peeling and grinding operations, when considerable free oil is exposed to the air and there is every chance for volatilization.

In the earlier work all determinations were made by weighing the oil in the special pipette. It was found difficult, however, to remove all of the oil from the bottle without taking a small amount of water with it, and this occasioned considerable error. It was thought likely that the specific gravity of the distilled oil would vary within such narrow limits that by reading the volume of the oil and applying a factor, more accurate results would be obtained than by weighing the oil direct.

With a view to determining this factor for California distilled lemon oil the specific gravities of a number of samples of oil were taken. The determinations were made at $25^\circ/25^\circ$ C. using brass weights in air, as the oil when removed from the centrifuge was usually within two or three degrees of that temperature. Samples of lemons of the different varieties grown in California and also from different localities were used to determine whether or not the specific gravity of the oil in any case varied greatly from the average. The results are shown in Table III:

TABLE III SPECIFIC GRAVITIES OF DISTILLED LEMON OILS AT $25^\circ/25^\circ$ C.

VARIETY	No.	Date Rec'd	at Lab.	WHERE GROWN	Sp. Gr.
Eureka.....	639	12/ 6/15		Santa Paula	0.8489
	646	12/13/15		Whittier	0.8494
	678	12/29/15		San Fernando	0.8449
	696	1/18/16		Arlington Heights	0.8476
	713	1/26/16		Whittier	0.8502
	717	1/31/16		San Fernando	0.8502
	726	2/ 5/16		Carpinteria	0.8504
	935	6/16/16		Whittier	0.8495
	957	6/16/16		Claremont	0.8462
	998	7/ 6/16		Carpinteria	0.8494
Average.....					0.8487
Lisbon.....	637	12/ 1/15		Chula Vista	0.8506
	662	12/21/15		Chula Vista	0.8511
	692	1/12/16		Corona	0.8482
	693	1/15/16		Corona	0.8506
	706	1/24/16		Whittier	0.8468
	806	3/11/16		Arlington Heights	0.8454
	826	3/24/16		Escondido	0.8501
	833	3/25/16		Whittier	0.8479
	851	4/ 6/16		Chula Vista	0.8506
	880	4/24/16		Whittier	0.8475
Average.....	915	5/18/16		San Dimas	0.8434
	920	5/22/16		Bonita	0.8503
					0.8484
Villa Franca.....	675	12/27/15		Bonita	0.8508
	883	4/24/16		Bonita	0.8489
	921	5/22/16		Bonita	0.8485
Average.....					0.8494
GENERAL AVERAGE.....					0.8487

It will be seen from Table III that the average of all the determinations is 0.8487. This table shows the averages for Eureka and Lisbons to be practically the same, and that for the Villa Francas to be a little higher. In the latter case, however, all the samples are from the same tree and may not represent the average for the variety.

Table IV gives a comparison of the oil yield obtained by direct weighing and by calculating, using the factor 0.846. $0.849 \times 0.996 = 0.846$.

The largest volume of oil obtained in the determinations is 1.81 cc., and the lowest 0.96 cc. Taking this largest volume (1.81 cc.) and calculating the weight

¹ THIS JOURNAL, 7 (1915), 236.

TABLE IV.—COMPARISON OF LEMON OIL DETERMINATIONS BY DIRECT WEIGHING OF DISTILLED OIL AND BY CALCULATION OF WEIGHT OF OIL FROM VOLUME AND SPECIFIC GRAVITY AT 25°, 25° C.

No.	Per cent Oil	Direct Weight	Oil from 200 g.	Weight of Oil	Oil per Ton	Direct Weight	Oil per Ton
				× 0.846		By Calculation	
637.....	0.69	1.73	1.464	13.8	14.6		
639.....	0.43	1.06	0.897	8.6	9.0		
646.....	0.48	1.22	1.032	9.6	10.3		
662.....	0.66	1.64	1.387	13.2	13.9		
675.....	0.70	1.70	1.438	14.0	14.4		
678.....	0.60	1.48	1.252	12.0	12.5		
692.....	0.71	1.73	1.464	14.2	14.6		
693.....	0.81	1.81	1.531	15.0	15.3		
696.....	0.54	1.36	1.151	10.8	11.5		
706.....	0.55	1.44	1.218	11.0	12.2		
713.....	0.42	1.09	0.922	8.4	9.2		
717.....	0.37	1.40	1.184	11.4	11.8		
726.....	0.45	1.11	0.939	9.0	9.4		
806.....	0.38	1.46	1.235	11.6	12.4		
826.....	0.49	1.23	1.041	9.8	10.4		
833.....	0.37	0.96	0.807	7.4	8.3		
851.....	0.43	1.12	0.948	8.6	9.5		
880.....	0.38	1.00	0.846	7.6	8.5		
883.....	0.58	1.42	1.201	11.6	12.0		
915.....	0.46	1.19	1.007	9.2	10.1		
920.....	0.49	1.21	1.024	9.8	10.2		
921.....	0.62	1.54	1.303	12.4	13.0		
955.....	0.47	1.22	1.032	9.8	10.3		
957.....	0.45	1.15	0.973	9.0	9.7		
998.....	0.40	0.99	0.838	8.0	8.4		

of oil from the specific gravity, using the largest, smallest and average values for specific gravity, we have:

$$1.81 \times 0.8511 \times 0.996 = 15.34 \text{ lbs. per ton}$$

$$1.81 \times 0.8434 \times 0.996 = 15.20 \text{ lbs. per ton}$$

$$1.81 \times 0.8490 \times 0.996 = 15.31 \text{ lbs. per ton}$$

The greatest difference is only 0.14 lb. per ton, which is well within the limits of experimental error. For determinations involving smaller volumes of oil the possible error involved through use of the factor is of course reduced. The yield of oil, pounds per ton, obtained by use of the factor is in every case a trifle higher than that obtained by direct weighing.

It is the intention to continue the work and determine the specific gravities of the distilled oils of other California citrus fruit in order to arrive at a factor similar to that applied to lemon oils. That an idea may be had of the oil content of the fruit the data already obtained is given.

TABLE V. PERCENTAGES OF OIL IN VALENCIA ORANGES, TANGERINES AND GRAPEFRUIT BY DISTILLATION METHOD.

No.	Oil dist. from 200 g.	Per cent Oil	Sp. Gr. of Oil 25°, 25° C.
Valencia Oranges(a)...	1.80	0.71	0.8411
1901	1.7	0.70	0.8410
1002	2.49	0.99	0.8411
1004	3.53	1.29	0.8434
Tangerines	1.35	0.52	0.8438
	1.70	0.67	0.8488
	1.78	0.69	0.8418
Grapefruit	1.61	0.70	0.8420

(a) In a recent article by Hood [THIS JOURNAL, 8 (1916), 709] data are given on the oil content of Florida Valencia. Amounts were found not exceeding 0.84 per cent. This fruit was peeled and the determinations made on the peel. In our experience, as above stated, this practice invariably yields low results.

SUMMARY

I. The steam distillation method is the most practical one thus far developed for the determination of the volatile oil content of citrus fruit.

II. A special calibrated receiving flask has been designed to meet the needs of this determination.

III. For rapid and reasonably accurate work the weight of the oil distilled from lemons may be calculated by multiplying the volume of the distilled oil at 25° C by 0.846.

CITRUS BY-PRODUCTS LABORATORY
BUREAU OF AGRICULTURE
LOS ANGELES, CAL.

THE DETERMINATION OF AVAILABLE OXYGEN IN PYROLUSITE

By O. L. BARNEBEY

Received April 12, 1917

Pyrolusite is the principal manganese ore. The ore has value for the available oxygen and the manganese contained therein. Hence the determination of these two elements in the ore evaluate it for the industries. Various methods for the determination of manganese have been studied by many chemists, but the methods in use for the determination of available oxygen have received but little attention.¹

Results for the percentage of manganese dioxide obtained by various responsible chemists have given differences of as much as five per cent on a carefully prepared sample, while differences of a per cent or two are quite common.² This paper contains the results of a detailed study as to the causes of such discrepancies and recommends two accurate methods for the analysis of oxidized manganese ores.

Three methods have been in general use for the determination of available oxygen in pyrolusite: the oxalic acid method,³ the ferrous sulfate method⁴ and the chlorine evolution method.⁵ Of these methods the oxalic acid method is perhaps the most universally applied for this determination. Bunsen's method is seldom used due to the inconvenience of distilling the chlorine, which process becomes very time consuming when a large number of ores are to be analyzed.

THE OXALIC ACID METHOD

The oxalic acid method consists in dissolving a weighed portion of pyrolusite in a known quantity of oxalic acid in the presence of dilute sulfuric acid, heating the solution to facilitate reaction. The excess of oxalic acid is then titrated with standard permanganate and the per cent of manganese dioxide or available oxygen computed.⁶

Any discrepancy existent in the analyses of an ore should be evident when samples of the ore are analyzed under such conditions that the factors involved in the determination are alternately kept constant and made variable. Thus one can maintain a constant weight of sample, constant volume, constant amount of oxalic acid, constant temperature and make variable the sulfuric acid concentration. Two such series of results are given in Table I. As approximately N/4 oxalic acid solution was prepared and standardized from time to time against standard permanganate of approximately N/10 strength, the

¹ See Bibliography at the end of this Summary of Manganese, Talbot and Brown, Smithsonian Institution, Washington, D. C., 1902.

² See also Carlbom, *Anal. Chem.*, 1914, 1, 100; *Anal. Chem.*, 1915, 1, 100; *Bureau of Standards*, 1916, 1, 100.

³ *Handbook of Analytical Chemistry*, 1916, 1, 100; *Handbook of Analytical Chemistry*, 1917, 1, 100.

⁴ *Handbook of Analytical Chemistry*, 1916, 1, 100; *Handbook of Analytical Chemistry*, 1917, 1, 100.

⁵ *Handbook of Analytical Chemistry*, 1916, 1, 100; *Handbook of Analytical Chemistry*, 1917, 1, 100.

⁶ *Handbook of Analytical Chemistry*, 1916, 1, 100; *Handbook of Analytical Chemistry*, 1917, 1, 100.

⁷ *Handbook of Analytical Chemistry*, 1916, 1, 100; *Handbook of Analytical Chemistry*, 1917, 1, 100.

⁸ *Handbook of Analytical Chemistry*, 1916, 1, 100; *Handbook of Analytical Chemistry*, 1917, 1, 100.

⁹ *Handbook of Analytical Chemistry*, 1916, 1, 100; *Handbook of Analytical Chemistry*, 1917, 1, 100.

¹⁰ *Handbook of Analytical Chemistry*, 1916, 1, 100; *Handbook of Analytical Chemistry*, 1917, 1, 100.

¹¹ *Handbook of Analytical Chemistry*, 1916, 1, 100; *Handbook of Analytical Chemistry*, 1917, 1, 100.

¹² *Handbook of Analytical Chemistry*, 1916, 1, 100; *Handbook of Analytical Chemistry*, 1917, 1, 100.

¹³ *Handbook of Analytical Chemistry*, 1916, 1, 100; *Handbook of Analytical Chemistry*, 1917, 1, 100.

¹⁴ *Handbook of Analytical Chemistry*, 1916, 1, 100; *Handbook of Analytical Chemistry*, 1917, 1, 100.

¹⁵ *Handbook of Analytical Chemistry*, 1916, 1, 100; *Handbook of Analytical Chemistry*, 1917, 1, 100.

permanganate was standardized against pure sodium oxalate, ferrous ammonium sulfate and electrolytic iron. The volume of extraction solution was 200 cc. in this series. The temperature was maintained at about 75° until the residue was very light-colored and siliceous in character. After the ore had been completely dissolved the excess of oxalic acid was titrated with the permanganate. Samples 6, 7 and 8 were diluted with hot water before titration to lessen the concentration of the sulfuric acid somewhat. Series II differed from Series I in that the temperature was higher, being just below boiling. The results of Series II indicate that better uniformity is obtained at the higher temperature, due to the fact that reaction occurs much more rapidly at the elevated temperature, thus diminishing the time necessary to dissolve the ore.

TABLE I—RESULTS ON 0.5-GRAM WEIGHTS OF SAMPLES 104 AND 105

Expt. No.	Normality of Sulfuric Acid	PERCENTAGES OBTAINED			
		Series I—Sample 104	Manganese Dioxide	Series II—Sample 105	Manganese Dioxide
1.....	0.4	14.09	76.58	13.18	71.45
2.....	0.8	13.90	75.80	12.97	70.39
3.....	1.6	13.92	75.65	12.92	70.17
4.....	2.4	13.81	75.05	12.91	70.15
5.....	3.2	13.76	74.83	12.91	70.15
6.....	4.0	13.77	74.80	12.89	70.02
7.....	8.0	13.73	74.59	12.87	69.92
8.....	12.0	13.51	73.44	12.84	69.78
Maximum Difference.....	0.58		3.14	0.34	1.67

A series of analyses was performed keeping the amount of sulfuric acid added constant and varying the volume, with the other factors the same as in the two previous series. The results were similar to those tabulated in Table I, the lower the acid concentration the higher the per cent of manganese dioxide obtained.

Another series of experiments was performed varying the weight of samples taken for analysis. In another series the amount of excess of oxalic acid was varied. In still another series phosphoric acid was substituted for sulfuric acid. In each series varying results were obtained. One of the most interesting features observed was that as long as one maintains as nearly identical conditions of experimentation as possible the operator can usually obtain quite closely agreeing results. By changing conditions somewhat, again closely agreeing results are obtained, but these results are different from the previous series. This shows the method to be highly empirical.

The chemical nature of the reactions involved in this determination suggests several possible errors: I—Imperfect titration of oxalic acid to carbonic acid; II—Decomposition of oxalic acid during the heating period; III—Escape of oxygen during interaction of the pyrolusite and the oxalic acid; IV—Decomposition of the oxalic acid into water, carbon monoxide and carbon dioxide. These possibilities have been studied in the order named.

I—TITRATION OF OXALIC ACID BY PERMANGANATE

Constant amounts of oxalic acid were titrated with permanganate in constant volumes of solutions (200 cc.) containing variable concentrations of sulfuric acid and the solutions heated to constant temperature (85°) preceding titration (see Table III).

The conclusion from this series of experiments is that oxalic acid can be titrated accurately in dilute hot sulfuric acid solution but when the hot solution becomes too concentrated in acidity a single drop of the permanganate in excess of that required for the reaction with the oxalic acid will not give a recognizable tinge of color to the solution. In the concentration of sulfuric acid greater than about 8 *N*, titrating at 80°, the end-points are indistinct, the pink color imparted by a drop of the standard permanganate fading very rapidly. With less than 8 *N* acidity the end-points become more definite with diminishing acidity to 0.8 *N*.

The previous observation regarding acid concentrations explains the reason for the exceptionally low percentage of manganese dioxide obtained in Expt. 8 of Series I and could easily account for a large difference than exists between Expts. 7 and 8 of Series II.

II—DECOMPOSITION OF OXALIC ACID IN HOT AQUEOUS SOLUTION

It has been known for a long period of time that oxalic acid decomposes slowly. A number of authors¹⁻¹⁵ have called attention to this decomposition and have attributed the cause to fungus growths, oxidation by the air, action of the light, molecular rearrangement, etc. Jorissen and Reicher^{14,15} studied the rate of decomposition of oxalic acid in the presence of various substances over long periods of time (1-140 days) at temperatures varying from room temperature to 55°. These authors conclude that "the oxidation of oxalic acid is accelerated in diffused light in the presence of sulfuric acid, boric acid, sodium fluoride, sulfates of manganese, iron (ferrous and ferric), cerium (cerous and ceric), thorium, and erbium and also manganous acetate, butyrate, benzoate and oxalate. In sunlight the acceleration increased with the amount of catalyzer added and was much greater than in diffused light. The acceleration is dependent upon the composition of the catalyzer." They obtained decomposition effects as great as 4.6 per cent per day with manganous sulfate present. DeBries,¹ Lemoine,² and Lemoine and Poitevin³ found that ferric salts in the light caused oxidation of oxalic acid.

Unaware of Jorissen's work at the lower temperatures, the author studied in a detailed manner the decomposition of oxalic acid at a more elevated temperature and obtained some interesting results directly applicable to the determination of available oxygen in pyrolusite.

¹ Wittstein, *J. anal. Chem.*, **1** (1862), 495.

² Neubauer, *Ibid.*, **9** (1870), 392.

³ Bizio, *Ibid.*, **9** (1870), 52.

⁴ Downes and Blunt, *Chem. News*, **36** (1877), 279; *Jahresb.*, **1870**, 643; *C. C.*, **1870**, 50.

⁵ Richardson, *J. Chem. Soc.*, **65** (1894), 450, 453.

⁶ Hartley, *Chem. News*, **37** (1878), 9.

⁷ Fleury, *J. Pharm. Chem.*, [5] **7**, 388.

⁸ DuClaux, *Compt. rend.*, **103** (1886), 1011.

⁹ Wurlburg, *Untersuch. botan. Inst. Tübingen*, **2** (1886-87), 117.

¹⁰ Wehmer, *Bot. Zis.*, **1891**, 41.

¹¹ Gign, *C. C.*, **1** (1893), 11.

¹² Gerland, *J. Soc. Chem. Ind.*, **10** (1891), 25.

¹³ Reigler, *J. anal. Chem.*, **35** (1896), 522.

¹⁴ Jorissen, *Z. angew. Chem.*, **1899**, 521.

¹⁵ Jorissen and Reicher, *Z. phys. Chem.*, **31** (1899), 142.

TABLE II—ACCURACY OF PERMANGANATE TITRATION OF OXALIC ACID

Exp. No.	Sulfuric Acid	NORMALITY OF OXALIC ACID		GRAMS
		Present	Found	
1	0.8	0.2504	0.2504	
1a	0.8	0.2504	0.2503	
2	1.6	0.2504	0.2503	
2a	1.6	0.2504	0.2505	
3	4.0	0.2504	0.2503	
4	6.0	0.2504	0.2505	
5	8.0	0.2504	0.2506	
5a	8.0	0.2504	0.2505	
6	10.0	0.2504	0.2510*	
7	12.0	0.2504	**	
8	18.0	0.2504	**	
9	28.0	0.2504	**	

* End-point rather indefinite.

** End-point very indefinite.

TABLE III—DECOMPOSITION OF OXALIC ACID IN HOT AQUEOUS SOLUTION (1) Effect of Heating with H_2SO_4

Exp. No.	Sulfuric Acid	NORMALITY OF OXALIC ACID		GRAMS
		Present	Found	
1	0.4	0.2502	0.2504	
2	0.8	0.2502	0.2498	
3	1.6	0.2502	0.2497	
4	2.4	0.2502	0.2504	
5	3.2	0.2502	0.2503	
6	4.0	0.2502	0.2503	
7	8.0	0.2502	0.2504	
8	2.4	0.2502	0.2503	
9	2.4	0.2502	0.2502	
10	2.4	0.1668	0.1670	
11	2.4	0.2502	0.2503	
12	2.4	0.3336	0.3333	
13	2.4	0.5004	0.4996	
14	2.4	0.6672	0.6654	
15	2.4	0.8340	0.8324	

(2) Effect of Manganous Sulfate

Exp. No.	Sulfuric Acid	NORMALITY OF MANGANESE SULFATE		GRAMS
		Present	Found	
1	2.4	0.02	0.2502	0.2459
2	2.4	0.04	0.2502	0.2433
3	2.4	0.06	0.2502	0.2337
4	2.4	0.10	0.2502	0.2321
5	2.4	0.20	0.2502	0.2301
6	2.4	0.40	0.2502	0.2310
7	2.4	0.80	0.2502	0.2280
8	2.4	1.20	0.2502	0.2263
9	2.4	1.60	0.2502	0.2327
10	2.4	2.00	0.2502	0.2292
11	2.4	0.2502	0.2502

(3) Effect of Sunlight

Exp. No.	Sulfuric Acid	NORMALITY OF MANGANESE SULFATE		GRAMS
		Present	Found	
1	2.4	0.02	0.2184	0.1973
2	2.4	0.04	0.2184	0.1970
3	2.4	0.06	0.2184	0.1951
4	2.4	0.10	0.2184	0.1965
5	2.4	0.20	0.2184	0.1956
6	2.4	0.40	0.2184	0.1967
7	2.4	0.00	0.2184	0.2155
8	0.0	0.00	0.2184	0.2175
9	0.8	0.06	0.2184	0.1994
10	1.6	0.06	0.2184	0.1994
11	2.4	0.06	0.2184	0.1995
12	3.2	0.06	0.2184	0.2008
13	4.0	0.06	0.2184	0.2027
14	0.0	0.06	0.2184	0.2104
15	2.4	0.20	0.2502	0.2177
16	2.4	0.20	0.2502	0.2124

(1) The effect of heating oxalic acid solution with varying and constant concentrations of sulfuric acid in diffused daylight was studied. Constant portions of standard oxalic acid were measured into beakers and 16 N sulfuric acid added in varying amounts followed by sufficient water to make 200 cc. in each case. The solutions were then heated for six hours at 85° in diffused light, after which the oxalic acid was titrated with standard permanganate [see Table III (1)]. In Expts. 8 and 9 the oxalic acid was titrated as soon as the solutions had reached 80° and these titrations served as a standard with which to compare the other titrations. In Expts. 10 to 15 the normality of the sulfuric acid was maintained constant and the oxalic acid concentration progressively increased. In these last five experiments the heating period was 4 hours and in the first seven experiments 6 hours. This series shows that the loss occasioned by heating in diffused sunlight oxalic acid solutions acidified with dilute sulfuric acid is very slight indeed, in fact negligible over the short periods of time when application to analytical chemistry is considered.

(2) The effect of the addition of the products of reaction in the determinations was then studied. Potassium sulfate and acid sulfate were found to have no particular influence. Manganous sulfate, however, exerted a striking effect. In consequence of this effect a more detailed study was taken up with the manganese, typical results being quoted in Table III (2). In this series of experiments the volume was 200 cc. and the heating period was 4 hours at a temperature of about 80°. A 4 N manganese sulfate solution was used as the source of the manganese. Table III (2) shows manganese sulfate to have a tendency to accelerate the decomposition of oxalic acid very markedly. In general, the above series of results indicates that the decomposition increases as the amount of manganese increases. In Expts. 7, 8, 9 and 10 difficulty was experienced in obtaining an end-point due to the pink coloration imparted to the solution by the rather large amounts of manganese sulfate.

Another series of experiments was performed under similar conditions to those of Table III (2) except that the concentration of manganese sulfate was kept constant, 0.06 N, and the sulfuric acid concentration was varied from 0.4 N to 12.0 N. In all cases there was decomposition of the oxalic acid

during the heating period, the results showing somewhat irregularly from 4 to 8 per cent loss of oxalic acid.

In the previous series the experiments were performed in beakers covered with watch glasses. A series of experiments was performed using Erlenmeyer flasks fitted with Bunsen valves, thus allowing the steam to displace the air in the flask. The decomposition of the oxalic acid proceeded in the same general manner as before only to a lesser degree. Other series were performed with flasks fitted with Bunsen valves, removing the air by carbon dioxide before fitting on the valve. This method of procedure diminished the decomposition but did not completely prevent it. To remove the source of difficulty, the effect of boiling was also tried, with results similar to those obtained by use of carbon dioxide.

(3) In some preliminary experiments sunlight was found greatly to accelerate the decomposition of oxalic acid. These experiments were followed by a systematic study of the light effect. Table III (3) contains the results of heating in direct sunlight oxalic acid solutions containing variable amounts of manganese sulfate. The concentrations of oxalic acid, sulfuric acid, the volume (200 cc.) and the temperature (90°) were kept constant in Expts. 1-7, inclusive. In Expts. 9-13, inclusive, the manganese sulfate was maintained constant with the other factors and the acidity made the variable. Expts. 1-8, 9-14, and 15-16 were performed on three different days. The sunlight was quite strong on the first two days and very bright on the third day. The time of heating in the sunlight was 3 hours in every case.

In Expts. 1-6 a somewhat constant loss occurred—approximately 10 per cent of the oxalic acid. With no manganese sulfate present (7) the decomposition was much less and also with no sulfuric acid present (8) the loss was still less than in the previous cases. Increase in acidity in Expts. 9-13 gave a gradually increased percentage of the oxalic acid although at no time was the loss small in amount. With no sulfuric acid present (14 and 15) the decomposition was not quite so large as when it was present. However, more experimentation should be carried out to prove this point definitely. Experiments 15 and 16 were conducted over 4-hour periods instead of 3 in very bright sunlight. In Expt. 15 the solution

was contained in an Erlenmeyer flask closed with a Bunsen valve and 16 was contained in a beaker covered with a watch glass. It is to be noted that in Expt. 16 the percentage loss during the heating period attained over 15 per cent.

This work proves definitely that manganese sulfate in the presence of the light at a temperature of 80–90° causes oxalic acid in sulfuric acid solution to decompose rapidly.

In this study of the decomposition of oxalic acid the time intervals were made 3 to 4 hours in order to give greater accuracy to the work than a shorter time would give. Only occasionally will such a length of time be required to dissolve a pyrolusite ore sample provided the ore is pulverized to pass a 200-mesh silk bolting cloth. When the ore samples are passed through a 100-mesh sieve or less such a length of time for the decomposition using a temperature of 80° will frequently be necessary. If the solution is heated to boiling, the time is greatly reduced. If the time of heating can be diminished, as in the case of some ores, to a few minutes and the operation be conducted in diffused daylight, or still better in the dark, especially if conducted in an atmosphere free from oxygen, the error due to decomposition of oxalic acid in the determination of available oxygen in pyrolusite is reduced to a minimum. However, so great is the decomposition of oxalic acid in hot sulfuric acid solutions containing bivalent manganese that no exact analytical method can be formulated without preventing this decomposition effect. Inasmuch as bivalent manganese is an end-product in the determination of available oxygen in pyrolusite the task of preventing the effect is a difficult one. All attempts to counteract the decomposition completely have thus far failed.

There is another possible cause for the decomposition of oxalic acid in solution and that is the possibility of oxalic acid undergoing rearrangement or decomposition, or both, forming other organic compounds which are not titratable with permanganate to the extent of the full equivalent amount of the original oxalic acid. This point has not been investigated.

III—ESCAPE OF OXYGEN DURING INTERACTION OF MANGANESE DIOXIDE AND OXALIC ACID

The possibility suggested itself that oxygen may be evolved in small amounts when manganese dioxide and oxalic acid react in sulfuric acid solution. The probability of such an effect seemed all the more plausible in the light of the experiments of Richardson,¹ who calls attention to the formation of hydrogen peroxide when oxalic acid decomposes.

To test the above point the following experiments were performed: 50 grams of manganese dioxide suspended in 2.5 liters of pure water were placed in a 3-liter balloon flask. The water was prepared by distilling, first from alkaline permanganate, then from potassium acid sulfate. A reflux condenser was attached

to the flask, and to the condenser was attached a U-tube containing ammoniacal manganese chloride solution. The U-tube was protected from the air by a second U-tube likewise containing ammoniacal manganese chloride solution. The suspension was heated to boiling for some time to insure as complete removal of air from the system as possible; then the U-tubes were connected and the heat continued to prove a negative effect of manganese dioxide alone. Then 80 g. of oxalic acid contained in 1 : 4 sulfuric acid, previously boiled to remove any dissolved air, were added through a separatory funnel fitted through a second hole in the rubber stopper which makes the connection between the flask and the condenser. Boiling was continued for some time but no appreciable oxidation of the manganese to manganese dioxide occurred in the test U-tube. Cuprous chloride was also employed with similar results.

IV—DECOMPOSITION OF OXALIC ACID INTO WATER, CARBON MONOXIDE AND CARBON DIOXIDE

Any direct decomposition of oxalic acid should result in the formation of carbon monoxide, carbon dioxide and water. If the decomposition reaction is due to oxidation only then no carbon monoxide would be found as an end-product of the reaction. To ascertain if any carbon monoxide is formed by heating dilute sulfuric acid solutions of oxalic acid a number of experiments were performed. A solution of 80 g. of crystallized oxalic acid in two liters of 1.5 *N* sulfuric acid was heated in flask *a* of Fig. 1. To *a* was connected



Fig. 1

a reflux condenser, *b*, containing a trap, *c*, which returned any water carried over mechanically back to the flask *a* through the tube *d*. The tube *e* conducted the gas to the wash bottle *f*, which contained concentrated sulfuric acid which removed the water from the gas. The gas then entered the tube *g* which contained a charge of I_2O_5 which completely filled 8 in. of the tube *h*. The I_2O_5 was prepared from HIO_3 by dehydration at 160°. Plugs of glass wool were inserted in the tube to support the iodine pentoxide and also to act as filters for the gas. The second plug was tamped rather snugly to prevent any mechanical carrying over of the pentoxide. The pentoxide tube was heated at 130 to 135° by the carbon electric light *j* in the copper

bath *k*. The gas passed from *g* to the suction flask *l* which contained a dilute solution of KOH. The suction flask was connected to a suction pump by means of the tube *m*; *n* is a tower filled with soda lime and *o* is a U-tube half filled with glass wool.

The solution was heated by means of the electric hot plate and the gases formed by the decomposition removed by drawing air through the system at the rate of about 5 liters per hour. The gas passed through the heated iodine pentoxide. Any carbon monoxide present in the gas then reacted with the pentoxide, liberating iodine which was absorbed in the potassium hydroxide. At the end of the decomposition period the potassium hydroxide solution was made distinctly acid with hydrochloric acid, potassium iodide added, then the iodine titrated with 0.1 *N* thiosulfate (see Table IV).

TABLE IV—DECOMPOSITION OF OXALIC ACID AT 90-95° C.

Exp. No.	Light	Time Hrs.	Total cc. 0.1 <i>N</i> Na ₂ S ₂ O ₄	Cc. Na ₂ S ₂ O ₄ required per hr.
1	Diffused Sunlight	4	0.56	0.14
2	Darkness	12	1.20	0.10
3	Direct Sunlight	4	0.68	0.17
4	Added 100 cc. of 4 <i>N</i> MnSO ₄	4		
5	Diffused Sunlight	5	0.36	0.07
6	Darkness	17	1.10	0.06
7	Direct Sunlight	4	0.60	0.12
8	With pure water in Flask <i>a</i>	4	0.00	0.00
9	Diffused Sunlight	4	0.00	0.00
10	Direct Sunlight	4	0.00	0.00

The results of Table VII show that very small amounts of carbon monoxide are continuously evolved from heated 1.5 *N* sulfuric acid solutions of oxalic acid. Expts. 1, 2 and 3 performed without the addition of manganese gave more carbon monoxide than did Expts. 4, 5 and 6, which contained manganese sulfate. This indicates that the manganese facilitates the oxidation of carbon monoxide by the air before it is evolved from the solution. Expts. 7 and 8 were performed as blanks on the effectiveness of the apparatus and to determine what, if any, amount of decomposition of the iodine pentoxide was caused by the heat alone in the intervals of time of experimentation. The results showed no decomposition in the absence of oxalic acid from Flask *a*.

These experiments prove that only very slight amounts of carbon monoxide are evolved by heating oxalic acid in dilute sulfuric acid solution. Hence the major portion of the decomposition of the oxalic acid in such solutions is undoubtedly that of air oxidation of the oxalic acid in the heated solution, the manganese sulfate acting as a carrier and the light accelerating this action.

THE FERROUS SULFATE METHOD

The ferrous sulfate method, like the oxalic acid method, has been in use for a long time and is described in many of our text books¹ dealing with quantitative analysis. In brief, the method now used consists in dissolving the pyrochlore in an excess of ferrous sulfate or ferrous ammonium sulfate in the presence of sulfuric acid, and after the ore is completely decomposed the excess of ferrous iron is titrated with permanganate.

¹ "Treadwell-Hall, "Analytical Chemistry," Vol. II, 1911, Ed., p. 624.
Olsen, "Quantitative Analysis," 1916-19, p. 326.

Manganese salts have been shown by the author¹ to act as oxygen carriers between the air and ferrous salts in fluoride solutions, but in sulfate solutions no such effect was obtained, at least the effect was found to be so small that it was negligible during a moderate period of time. However, the study was conducted in diffused daylight. In order to ascertain if any effect of this kind is caused in sulfuric acid solutions in the presence of direct sunlight the experiments of Table V were performed. Sample 8 was titrated

TABLE V—EFFECT OF DIRECT SUNLIGHT AND MANGANESE SULFATE ON THE OXIDATION OF FERROUS SULFATE IN SULFURIC ACID SOLUTION

Experiment No.	Normality of H ₂ SO ₄	Normality of MnSO ₄	Grams Taken	Grams Iron Found
1	2.4	0.20	0.5301	0.5294
2	2.4	0.40	0.5301	0.5298
3	2.4	0.20	0.5301	0.5300
4	2.4	0.15	0.5301	0.5300
5	2.4	0.10	0.5301	0.5298
6	2.4	0.05	0.5301	0.5300
7	2.4	0.00	0.5301	0.5298
8	2.4	0.00	0.5301	0.5300

immediately without heating. Samples 1-7, inclusive, were contained in a volume of 200 cc. and were heated to about 80° in the direct sunlight for 4 hours. The solutions in 1, 2 and 6 were contained in beakers covered with watch glasses, and 3, 4, 5 and 7 were contained in Erlenmeyer flasks likewise covered with watch glasses.

This series shows conclusively that the oxidation due to atmospheric oxygen must be very slight indeed in solutions sufficiently acid with sulfuric acid.

The effect of pulling air by suction through solutions similar to those of Table VIII heated to about 80° was studied. These experiments were performed in diffused daylight. The solutions were contained in Erlenmeyer flasks and were heated by an electric hot plate. Sample 4 was titrated immediately. The

TABLE VI—EFFECT OF PASSING A CURRENT OF AIR THROUGH FERROUS SULFATE SOLUTIONS CONTAINING MANGANESE SULFATE

Experiment No.	Normality H ₂ SO ₄	Normality MnSO ₄	Time Hrs.	Grams Taken	Grams Iron Found
1	0.8	0.2	3	0.5301	0.5290
2	0.8	0.2	3	0.5301	0.5300
3	0.8	0.0	3	0.5301	0.5298
4	0.8	0.0	3	0.5301	0.5300

results of Table II show that manganese sulfate does not materially increase the rate of oxidation of ferrous sulfate by the oxygen of the air in solutions sufficiently acid with sulfuric acid.

The fact that ferrous sulfate solutions are far more stable in the presence of manganese salts than are oxalic acid solutions, especially when sunlight is involved, suggests the elimination of oxalic acid and the substitution of ferrous sulfate in all possible cases involving the presence of manganese sulfate or sunlight where a period of time of heating is involved.

To ascertain what errors, if any, are inherent in the ferrous sulfate method, several series of experiments were performed along the same general lines as those involved in the study of the oxalic acid method.

In Table VII are given the results obtained with 0.1 g. samples of pyrochlore. The ferrous sulfate solution contained 50 g. of concentrated ferrous sulfate and 100 cc. of sulfuric acid sp. gr. 1.841 in 8 liters. The solution was accurately standardized previously to give 0.0010 permanganate with one drop.

ardized against electrolytic iron and ferrous ammonium sulfate: 50 cc. of the ferrous sulfate were originally added to the sample contained in an Erlenmeyer flask followed by the sulfuric acid and the manganese sulfate, if any of the last named salt was added. The flask was then covered with a watch glass and heated. The flask was occasionally agitated to facilitate solution of the ore. When decomposition was complete each solution was diluted somewhat with water and the cooled solution titrated with permanganate to determine the excess of ferrous sulfate.

TABLE VII—ANALYSIS OF PYROLUSITE FOR MnO_2 CONTENT BY FeSO_4 METHOD

Experiment No.	Normality H_2SO_4	Normality MnSO_4 added	Per cent MnO_2 Found
1.....	0.0	0.0	70.72
2.....	0.4	0.0	70.40
3.....	0.8	0.0	70.45
4.....	2.4	0.0	70.32
5.....	4.0	0.0	70.30
6.....	8.0	0.0	70.18
7.....	0.8	0.2	70.20
8.....	1.6	0.2	70.18
9.....	4.0	0.2	70.10
10.....	0.8	0.0	70.18
11.....	1.6	0.0	70.20

Expt. 1 (and also 2 and 3 to a lesser degree) gave a high result due in all probability to an insufficient quantity of sulfuric acid to prevent the ferrous sulfate from oxidizing. Only the sulfuric acid contained in the 50 cc. of standard ferrous iron solution was present in the experiment. The end-points of Expts. 6, 7, 8 and 9 were somewhat indistinct. Greater dilution, thus diminishing the manganese concentration in 7, 8 and 9 and of sulfuric acid in 6, would have made the end-points clearer. The results from 4 to 11, inclusive, show a good agreement under different solution conditions, which is not the case with the use of oxalic acid solutions.

Other samples were analyzed under the same conditions as those given in the preceding series to test the general application of the procedure. Some typical results are given in Table VIII along with results obtained by the direct iodimetric and chlorine distillation methods on the same samples. Hence this series gives not only a test as to the accuracy of the ferrous sulfate method but a comparison of the three methods as well.

TABLE VIII—COMPARATIVE RESULTS OF FERROUS SULFATE, DIRECT IODIMETRIC AND DISTILLATION METHODS

Sample No.	Normality H_2SO_4	PER CENT MnO_2 FOUND		
		Ferrous Sulfate Method	Direct Iodimetric Method	Chlorine Distillation Method
101.....	0.8	69.67	69.87	69.60
101.....	1.6	69.64	69.70	69.68
101.....	2.4	69.63
102.....	0.8	80.05	80.10	80.10
102.....	1.6	80.07	80.04	80.20
102.....	2.4	80.06
103.....	0.8	84.82	84.90	85.00
103.....	1.6	84.83	84.92	84.80
103.....	2.4	84.83
104.....	1.6	75.22	75.17	75.04
104.....	2.4	75.30	75.20	75.20
105.....	0.8	70.44	70.18	70.40
105.....	1.6	70.47	70.32	70.36
105.....	2.4	70.44
106.....	1.6	78.20	78.20	78.32
106.....	2.4	78.20	78.18	78.28

In Table VIII the column "Ferrous Sulfate Method" contains the results obtained by the ferrous sulfate method as previously outlined. The column "Direct Iodimetric Method" contains the percentage obtained by use of the author's direct iodimetric method.¹

¹ J. Am. Chem. Soc., 39 (1917), 607.

In the column "Chlorine Distillation Method" are contained the results obtained by Bunsen's distillation method.¹ The results show a very good agreement among the three methods.

The following outline is recommended for the analysis of pyrolusite by the ferrous sulfate method.

PREPARATION OF SOLUTIONS

The following data are calculated per liter of each solution but the solutions are best made up in large volumes.

FERROUS SULFATE SOLUTION—200 cc. of sulfuric acid (sp. gr. 1.84) are slowly added to 900 cc. water with stirring and while the solution is still warm 90 grams of crystallized ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) are added, stirring until solution is effected. The solution should be at room temperature before use. This solution is standardized just preceding use against the standard solution of permanganate.

PERMANGANATE SOLUTION—10 g. of permanganate are dissolved per liter of water and the solution allowed to stand several weeks before use. This solution is approximately of the same equivalent strength as the ferrous sulfate solution prepared as above. The permanganate is standardized by means of any reliable standardizing agent, such as electrolytic iron, ferrous ammonium sulfate or sodium oxalate.

PROCEDURE

A sufficient quantity of the well mixed sample is ground to pass a 200-mesh sieve and dried at 100–105° to constant weight. Some samples when dried in this manner have a tendency to take on water during weighing and consequently such samples should be weighed by difference from a glass-stoppered weighing bottle. Other samples do not have this tendency and may be weighed directly on a watch glass.

A 0.5 gm. sample is placed in a 250 cc. Erlenmeyer flask: 50 cc. of the standard ferrous sulfate solution are added, the flask is covered with a watch glass and the solution heated to boiling until solution of the ore is accomplished. The solution is then diluted to about 150 cc. and the excess of ferrous iron titrated with standard permanganate.

In consequence of the preceding work the ferrous sulfate and direct iodimetric methods are to be recommended for the analysis of pyrolusite for its available oxygen or manganese dioxide content. In the laboratory, which requires a large number of determinations each day, the ferrous sulfate method will be found most appropriate as the use of any iodimetric method will be found expensive, due to the present cost of iodides. Where a smaller number of analyses are to be made either method will be found applicable.

CONCLUSIONS

I—The oxalic acid method for the determination of available oxygen in pyrolusite has been found to be inaccurate.

¹ *See, etc.*

II—The inaccuracy is due to the decomposition of the oxalic acid during the heating period required for the solution of the ore.

III—Manganese salts and the sunlight greatly accelerate the decomposition of oxalic acid.

IV—Some carbon monoxide is evolved from dilute sulfuric acid solutions (1.5 *N*) containing oxalic acid, but the amount of this decomposition is very small.

V—No appreciable quantity of oxygen is evolved when manganese dioxide and oxalic acid react in dilute sulfuric acid solution.

VI—The ferrous sulfate method is not subject to the errors of the oxalic acid method enumerated in I, II and III.

VII—The ferrous sulfate and the direct iodimetric methods are to be recommended for the determination of the available oxygen in pyrolusite.

This investigation was carried out for and in cooperation with the C. F. Burgess Laboratories of Madison, Wisconsin, and it is with their approval that the foregoing publication is made.

MADISON, WISCONSIN

A CONTRIBUTION TO THE THEORY OF EMULSIFICATION BASED ON PHARMACEUTICAL PRACTICE—II¹

By WILLIAM G. CROCKETT AND RALPH E. OESPER

Received June 12, 1917

In a previous article² the existence of "critical points" of emulsification was pointed out. Depending on the method of determination, these critical values have been defined as either (a) the minimum quantity of emulsifying agent, say acacia, that can produce permanent emulsification of a given quantity of oil in a fixed quantity of water, or, (b) the minimum quantity of water that can bring about stable emulsification of a definite quantity of oil by a fixed quantity of emulsifier, say soap. Given standard conditions, these points are quite definite, for while permanent emulsions are produced by these critical amounts, the use of a few milligrams less of emulsifier or of a small fraction of a cubic centimeter of water less than these quantities results in imperfect, temporary emulsification or none at all. Although quantities in excess of the critical value do bring about emulsification, the resulting emulsions do not possess the stability or general excellence of those prepared from the critical proportions. The character of the emulsion depends in no small degree upon the procedure followed in its preparation and it was found that the emulsifier is most efficiently used when it is hydrated all at one time and in the presence of the internal phase.

This work has been extended to other systems whose critical points have been determined and the conclusions drawn from our previous experiments have been supported by these later results. It was found that the size and shape of the vessel in which the emulsion is prepared has a distinct influence on

the critical point and an extended study of this factor which probably involves a consideration of viscosity, surface tension, etc., is planned. A preliminary report of the combined influence of several emulsifiers on the critical point is included.

EXPERIMENTAL

MATERIALS USED AS INTERNAL PHASES

- 1—Carbon tetrachloride, B. P. 76.4–76.8°.
- 2—Chloroform, B. P. 61.3–61.8°.
- 3—Benzene, B. P. 80°.
- 4—Oil of Turpentine, U. S. P., sp. gr. 0.86.
- 5—Oil of Almonds, expressed U. S. P., sp. gr. 0.912.
- 6—Mineral Oil, sp. gr. 0.853.

Nos. 1, 2 and 3 were dried over calcium chloride for 18 hrs. and fractionally distilled.

EMULSIFIERS USED

- 1—Powdered acacia.
- 2—Powdered tragacanth.
- 3—Extract of Irish moss; prepared by boiling the moss with water, straining and evaporating the filtrate to dryness. The residue was then rubbed to a fine powder in a mortar.
- 4—Soft soap, Squibb's; alcoholic solution, containing 25 g. in sufficient alcohol to measure 50 cc.

TABLE I—TRAGACANTH EMULSIONS

INTERNAL PHASE	MIXTURE No.	Tragacanth Gram	Size of Globules, Microns	EMULSION	CRITICAL POINT
Chloroform	A 1	0.085	20	Very thick	0.070 to
	2	0.080	20	Very thick	0.075 gram
	3	0.075	30	Good	Tragacanth
	4	0.070	..	None	..
Benzene	B 1	0.040	15–20	Very thick	0.015 to
	2	0.030	25	Good	0.020 gram
	3	0.020	30–35	Thin	Tragacanth
	4	0.015	..	None	..
Carbon tetrachloride	C 1	0.070	20	Thick	0.055 to
	2	0.060	25–30	Good	0.060 gram
	3	0.055	..	None	Tragacanth
	4	0.050	..	None	..
Oil of Turpentine	D 1	0.08	..	None	..
	2	0.10	..	None	..
	3	More than 0.10 g.	forms thick, unmanageable mass
	4	0.07	60	Thick, but separates	..
Almond Oil	E 1	0.07	60	Thick, separates in 3 mins	..
	2	0.05	..	Thick, separates in 3 mins	..
	3	More than 0.07 g.	forms unmanageable mass
	4	0.05	..	Thick, separates in 3 mins	..

SPECIAL CASES AND REMARKS

- A (a) 10 cc. chloroform plus 0.08 g. tragacanth and water added in 0.8 cc. portions, shaking after each addition, required a total of 10 cc. water for emulsification, and the emulsion thus formed showed a separation of 28 per cent its volume after 12 hrs. Emulsions 1 and 2 show no such separation.
- (b) 10 cc. chloroform, when shaken with a mucilage previously prepared from 0.08 g. tragacanth and 7.5 cc. water gave no emulsion 10 cc. chloroform formed no emulsion when shaken with mucilages containing 0.10 and 0.20 g. tragacanth, respectively, in 7.5 cc. of water.
- (c) and (d) emphasize the necessity of hydrating the emulsifier all at once and in the presence of the internal phase.
- (e) If chloroform is allowed to stand in contact with the tragacanth for 15 hrs. before the water is added the critical point is not changed.
- (f) The globules of the chloroform emulsions showed a motion similar to the Brownian movement, the benzene and carbon tetrachloride emulsions with tragacanth do not.
- B (a) The critical point is not influenced if the benzene is allowed to stand in contact with the tragacanth for 15 hrs. before adding the water.
- (b) If dry, distilled carbon tetrachloride is allowed to stand in contact with the tragacanth for 15 hrs. before adding the water, the critical point is unaffected. If brown, carbon tetrachloride which had previously stood in contact with water for 1 hr. and was then allowed to dry and remove the water without being dried it gave the following discordant results:
 - 10 cc. plus 0.1 g. tragacanth plus 1 cc. water gave no emulsion.
 - 10 cc. plus 0.05 g. tragacanth plus 1 cc. water gave no emulsion.
 - 10 cc. plus 0.02 g. tragacanth plus 1 cc. water gave no emulsion.
 - 10 cc. plus 0.01 g. tragacanth plus 1 cc. water gave no emulsion.
- This experiment was repeated three times with the same result.
- C If 10 cc. Tragacanth was added to the mixture, followed by a quantity which showed definite tendency to emulsify, and then 10 cc. of water, inferior to emulsion if there are to be considered by having. This has shown that 0.1 g. tragacanth when the critical point is reached is employed.

¹ The work reported in this article constitutes the basis of a thesis submitted by William H. Crockett to the Faculty of the Graduate School of New York University in partial fulfillment of the requirements for the degree of Master of Science.

² Room and Oesper, THIS JOURNAL, 9 (1917), 156.

TABLE II—IRISH MOSS EMULSIONS

INTERNAL PHASE	MIXTURE No.	Extract Irish Moss Gram	Size of Globules Microns	Emulsion	CRITICAL POINT
Chloroform	A 1	0.09	15-20	Good	0.06 to
		0.08	20	Fair	0.07 gram
		0.07	25-30	Thin	Irish Moss
		0.06		None	
Benzene	B 1	0.20	15	Good	0.04 to
		0.10	20-25	Good	0.05 gram
		0.05	30	Thin	Irish Moss
		0.04		None	

REMARKS AND SPECIAL CASES

- A (a) Emulsions 1, 2 and 3 are immediately cracked by the addition of 1 drop of soap solution, but the addition of 3 drops more causes re-emulsification. However, 4 drops of soap solution alone will not bring about emulsification of 10 cc. of chloroform in 7.5 cc. water.
- (b) 10 cc. chloroform plus 0.07 g. extract Irish moss plus 1 drop soap gave no emulsion on addition of 7.5 cc. water; nor did this mixture emulsify after ageing for 15 hrs.; however, the addition of glycerine in portions, shaking after each addition, brought about emulsification when a total of 12 cc. had been added.
- (c) Mixture A4 plus 2 drops of soap gave a temporary emulsion which became permanent when 2 more drops were added.
- (d) Emulsion 2 cracked by the addition of 1 drop of soap, was re-emulsified by adding 10 cc. glycerine and shaking. If 10 cc. glycerine is added to Emulsion 2, and then 1 drop of soap solution, the emulsion does not crack.
- (e) Mixture A4 plus 17 cc. glycerine gave no emulsion.
- B (a) Emulsions 1, 2 and 3 are instantly cracked when shaken with 1 drop of soap solution; addition of more soap causes re-emulsification; addition of glycerine likewise causes re-emulsification.
- (b) Emulsion 2 plus 10 cc. glycerine is not cracked by 1 drop soap solution.
- (c) Emulsions 1 and 2 are not cracked by the addition of 1 cc. of alcohol but they become much whiter. The subsequent addition of 1 drop of soap solution cracks them, but they may be re-emulsified by the addition of glycerine.
- (d) Mixture 4 is emulsified by the addition of 14 cc. of glycerine added in portions.
- (e) Mixture 4 is emulsified by the addition of 3 drops soap solution. 4 drops of soap solution are not sufficient to emulsify 10 cc. benzene and 7.5 cc. of water.

The emulsions were prepared by shaking in 125-cc. oil bottles, the procedure being: 10 cc. of the internal phase and the desired weight of emulsifier were placed in the bottle and well shaken to insure intimate mixture; 7.5 cc. of water were then added *all at once* and the bottle vigorously shaken for 1 min. If the amount of emulsifier present equals or exceeds the critical value, emulsification takes place after a few seconds shaking, but if less than the critical amount is used the emulsion does not form even after prolonged agitation. The operator soon becomes accustomed to the behavior of the material and after a little experience a few vigorous shakes will enable him to predict whether emulsification will ensue, *i. e.*, whether or not the critical amount of emulsifier is present.

The effect of the shape of the container on the critical point is shown in Table II. Mixtures A were shaken in corked 40 cc. test tubes, while mixtures B were shaken in 125 cc. oil bottles. Some experiments were also carried out on the influence of soap upon the emulsifying power of acacia.

CONCLUSIONS

I—Critical points have been established using tragacanth and Irish moss as emulsifying agents.

II—Better tragacanth emulsions are obtained by adding the proper amount of water to the previously mixed internal phase and emulsifier and shaking immediately, than by adding the water in portions, shaking after each addition.

TABLE III—ACACIA EMULSIONS

INTERNAL PHASE	MIXTURE No.	Acacia Grams	Size of Globules Microns	Emulsion	CRITICAL POINT
Chloroform	A 1	0.90	15	Thick	0.42 to
		0.55	15	Good	0.43 gram
		0.43	20	Good	Acacia
		0.42		None	
Chloroform	1	1.00	10	Thick	0.95 to
		0.98	10	Good	0.96 gram
		0.97	15	Good	Acacia
		0.96	20	Good	
Mineral Oil	C 1	2.50	18	Very thick brown mass	
		1.20	35	Thin white	Perhaps
		0.40	50	Thin white	0.01 to 0.02
		0.07	70	Thin white	Acacia
Turpentine Oil	D 1	0.02	100	Very thin white	
		0.01		None	
		0.20	15	Apparently good	
		0.10	25-30	Apparently good	Uncertain
Almond Oil	E 1	0.05	35	Thin	
		0.03		None	
		0.20	25	Good	
		0.25	40	Apparently good	Uncertain
	4	0.23	55	Apparently good	
		0.18		None	

REMARKS AND SPECIAL CASES

- A (a) Mixture A4 formed only a temporary emulsion on the addition of 10 drops soap solution, while 10 cc. chloroform plus 0.42 g. acacia plus 1 drop soap solution and then 7.5 cc. water gave a good emulsion, showing the influence of hydrating both emulsifiers all at once in the presence of the internal phase.
- (b) 10 cc. chloroform plus 0.41 gram acacia (less than critical value) plus 3 drops soap solution and then 7.5 cc. water gave a good emulsion.
- (c) The addition of soap solution did not crack these acacia emulsions.
- C (a) The critical point for mineral oil-acacia emulsion, when prepared by trituration, was reported in the previous article as 2.2 to 2.3 g. acacia, but our later experience with the preparation of emulsions in a mortar has indicated that the critical points thus obtained are not as sharp as those obtained by shaking volatile oils in bottles. In general, the results with viscous oils are far less definite than those obtained with the less viscous ones.
- (b) Emulsions 2-5 were very white and thin and the globules were relatively large. In these respects they differ from No. 1 which is thick and brown. Although they all closely resemble each other, they differ great from No. 6 and this leads us to believe that the critical point lies near 0.01 to 0.02 g.
- D (a) The critical point is less clearly defined than is that of mineral oil. Roan and Oesper were unable to find a definite critical point for oil of turpentine with acacia, and Pickering has stated that it does not emulsify with soap as do other oils, a part always remaining unemulsified while the line of demarcation is not distinct.
- (b) No. 1 appears at first to be a good emulsion, but after 4 hrs. it creams upward from the bottom and shows a slight clear layer on top. No. 2 likewise appears to be beyond the critical point, but creams upward and shows a clear layer on top at the end of 5 min. 3 is very thin, does not wet the sides of the bottle and separates into 3 layers in from 3-5 minutes.
- E (a) The critical point with this oil is likewise indistinct, but falls within narrower limits than those shown by oil of turpentine.
- (b) Emulsions 2 and 3 appear to be good at first, but separate within 24 hrs.

III—If the water and the critical amount of tragacanth are made into a mucilage and this then shaken with the internal phase, no emulsion is formed.

IV—The critical points are not affected by allowing the dried internal phase to stand in contact with the emulsifying agent before the addition of water.

V—Irish moss emulsions are not affected by small quantities of alcohol, but are instantly cracked by the addition of a trace of soap, whether this be added before the addition of the water or after emulsification has been completed. More than a trace, however, is not detrimental but aids the Irish moss in producing emulsification.

VI—Glycerine serves to re-emulsify emulsions cracked by soap and emulsions to which glycerine has previously been added are not cracked by a trace of soap. It does not directly aid Irish moss as an emulsifying agent.

VII—Acacia emulsions are not cracked by the addition of a trace of soap. If less than the critical amount of acacia is used, a trace of soap added before the addition of the water supplements the acacia and emulsification ensues; if, however, emulsification is attempted by shaking the internal phase with water and an insufficient quantity of acacia and then adding

the soap, it is found that no emulsion is produced—by not only the quantity of soap previously used, but even by many times that quantity.

VIII—Critical points are less distinct with more viscous than with the less viscous oils.

IX—Tragacanth is not suited for the emulsification of fixed oils in water under the foregoing conditions, for it forms a thick, ungovernable mass.

X—Critical points vary with the shape of the container in which the emulsions are made.

HAVEMEYER CHEMICAL LABORATORY
NEW YORK UNIVERSITY, NEW YORK CITY

LABORATORY AND PLANT

THE USE OF TEXTILE FIBERS IN MICROSCOPIC QUALITATIVE CHEMICAL ANALYSIS

By E. M. CHAMOT AND H. I. COLB

Received July 9, 1917

I—THE DETECTION OF ALKALINITY AND ACIDITY BY MEANS OF FIBERS DYED WITH LITMUS

The employment of animal and vegetable fibers as carriers of reagents in microscopic qualitative analysis is so old that it is impossible to trace back through the literature and ascertain when and by whom this method of qualitative testing was first applied. No really systematic work was done, however, until Emich,¹ in 1901, studied the preparation of silk fibers impregnated with litmus and called attention to the use of such fibers in testing for acidity and alkalinity in tiny drops of liquid.

In 1904 Donau² showed that fibers, specially treated, could be used for the detection of gold in minute amounts of material. Three years later Emich³ published an extensive article on the application of the textile fibers to the analysis of a number of inorganic compounds. In this paper he gives a method for the detection of boron by means of cotton or linen fibers dyed with turmeric and for the detection of the heavy metals by means of zinc sulfide fibers.

In trying to apply Emich and Donau's methods in practice, so many difficulties were encountered that it appeared desirable to undertake a systematic study of the whole question of the preparation and use of fibers as carriers of reagents in qualitative analysis.

The preparation of these impregnated fibers involved a study of the kind of fiber to be employed, the preliminary treatment of the fiber, the method of dyeing and the character of the dye to be used.

Fibers from flax, cotton, viscose silk (cellulose xanthate), lustron silk (cellulose acetate), gelatin silk, wool, mohair and true silk were tested in a great variety of ways as to their permeability and were dyed with litmus in neutral, in acid and in alkaline solutions. Of these fibers, silk was found to possess the highest adsorptive power for a satisfactory indicator dye and was also most desirable because of its transference

sensitiveness, uniformity of color and depth of adsorption of the dye.

The raw silk of commerce consists of the filaments from 2 to 15 cocoons united to form a thread, cemented together by the sericin. The individual filaments (bave) are made up of two exceedingly fine threads (brins) cemented together by the silk glue or sericin. This sericin can be removed by boiling water, soap solutions or alkalis.

The raw or partially purified silk fibers (having part of the sericin removed) adsorb more litmus but are not as sensitive as the completely purified litmus silk fibers. Donau suggested using partially purified silk fibers, but in the case of most silks the complete purification of the fiber is to be preferred.

To determine whether the sensitiveness varied with the kind of silk used, twenty different varieties, four China, eleven Japan, one Italian, two Tussah and two American wild silks [from cocoons of *Samia cecropia* (Lin.) and of *Telea polyphemus* (Cramer)] were tried. While the size of the brins varied with the variety of the silk, the actual sensitiveness of the resulting litmus fiber was practically the same, irrespective of the variety or source of the sample, providing the purified brins were colorless. Tussah and polyphemus silks are brownish.

Difficulty was experienced at first, however, in obtaining great enough adsorption of the dye by the silk. A preliminary treatment of the raw silk with a 10 per cent solution of sodium hydroxide at room temperature for a hour and subsequent washing was found to increase markedly the adsorptive powers of the silk. Dyeing of the treated silk in a 1 per cent solution of purified litmus solution with a pH of 7.0 (a mixture of 100 cc. of 1.0 N. NaOH and 100 cc. of 1.0 N. HCl) produced a fiber of the proper color intensity. In order to test the effect properly, the acid litmus solution was used. It is recommended to keep the silk fibers constant and instead of washing with neutralized distilled water, wash with sodium hydroxide solution and again washed thoroughly. If red silk fiber is used, the silk can be washed with neutral distilled water, may be treated with strong caustic and be used for weak to strong alkaline solutions. The acid litmus solution is recommended for routine work.

¹ *Monatsh.* **22** (1901) 600; **23** (1902) 27.

² *Ibid.* **25** (1904) 74.

³ *Ibid.* **30** (1909) 436.

The sensitiveness of the litmus silk depends upon the degree of adsorption of the dye, the degree of purification of the raw silk and the degree of purification of the litmus.

If too little dye is adsorbed the color change is not distinct enough. If too much dye is adsorbed the fiber becomes less sensitive and the color is so deep that it renders the fiber opaque.

The greater the degree of purification of the litmus the more sensitive the dyed fiber, though this factor is not as important as the two former ones.

The following procedure (essentially Wartha's¹ method) is suggested for obtaining an exceedingly pure litmus. Commercial litmus "cubes" are extracted with 95 per cent alcohol until the alcoholic extract no longer has a reddish tinge. They are then repeatedly extracted with water until the greater part of the coloring matter is removed, a current of air being blown through the solution to prevent reduction. The filtered solution is carried to a thick syrup in an evaporator on the water bath. The mass is then evaporated several times with portions of absolute alcohol acidified with acetic acid in order to destroy carbonates and the residue is extracted repeatedly with absolute alcohol as long as the alcohol has a reddish color by *reflected* light. The residue is dissolved in water, concentrated to a thick syrup and treated with absolute alcohol. The pasty mass is stirred with absolute alcohol until the portions poured off no longer contain any red coloring matter. The final residue is dissolved in distilled water, concentrated to a thick syrup and poured into absolute alcohol. The semi-solid gummy precipitate is spread on a plate and dried at 70 to 80° C. The pigment as thus obtained forms a hard tenacious mass, easily soluble in water and yields an indicator of great sensitiveness, changing at once to red or blue with acid or alkali.

The silk fibers may also be used as a carrier for lacmoid, but this indicator was found to be less satisfactory than litmus and far less sensitive.

The following procedure is recommended for testing a drop of solution for acidity or alkalinity. Place upon an object slide a drop of the solution to be tested. Insert into it a litmus silk fiber 5 mm. long for only part of its length. Move the preparation on the stage of the microscope until a portion of the fiber, both in and out of the drop, falls within the field of view. Note the change of color, if any. Acid turns the neutral (violet-tinted) fiber red; alkali turns it blue. Since the portion of the fiber outside the drop is not acted upon, the color change is readily recognized.

In order to express numerically the sensitiveness of the litmus silk fibers, the following method was adopted. Solutions of decreasing normalities of alkali and acid were used. A constant sized drop was obtained by means of a platinum loop, 3 mm. in diameter. The drops delivered by this loop contained from 0.145 to 0.150 cc. Starting with a solution producing a decided color change in the fiber, decreasing concentrations were tested until one was reached which failed

to give a color change. The most dilute solution, one drop of which will produce a positive color change in the fiber within one minute, gives the sensitiveness. This limit may be expressed either in terms of normality, in milligrams per liter or as the absolute amount contained in the drop used. In the last case, if a drop containing 0.148 cc. is used, and the limit of sensitiveness of hydrochloric acid is a $N/4500$ solution, then the absolute amount of hydrochloric acid contained in the drop is

$$0.148 \times \frac{36.5}{4500 \times 1000} \times 1000 = 0.001 \text{ mg. HCl.}$$

Sulfuric, nitric or hydrochloric acid produces a positive color change in the fiber in solutions as dilute as $N/4500$; acetic acid $N/100$. With red litmus fibers, ammonium, sodium or potassium hydroxide solution reacts in concentrations down to $N/200$; the neutral litmus fibers are more sensitive but the color change is not so readily discerned in this case.

EFFECT OF VARIOUS METHODS AND DEGREES OF PURIFICATION OF THE SILK ON THE ADSORPTION OF THE DYE

Five different degrees of purification were used on five different varieties of silk:

- 1—Raw silk as obtained from the manufacturer.
- 2—Raw silk which had been boiled in water for 30 minutes and then washed and dried.
- 3—Raw silk treated successively with 95 per cent alcohol and ether. This removes a slight amount of wax.
- 4—Raw silk immersed in cold 10 per cent sodium hydroxide for 4 hours, according to Donau. This removes all of the glue and wax but makes the fiber very weak and friable.
- 5—Raw silk boiled for 1 hour in a 2 per cent "Ivory" soap solution.

TABLE I

No.	VARIETIES OF SILK	Sensitiveness to	
		Acid	Alkali
1	Doppioni Gold Chicken 35 40 Rather rough silk Japan Silk No. 1344. Verv fine brins. China Silk.	$N/4500$	$N/100$
2	Blue Dragon Extra S1802. Good fibers. China Silk.	$N/4000$	$N/100$
3	1st Five Girls S510. Japan Silk	$N/4500$	$N/150$
4	Iris. Japan Silk	$N/4500$	$N/150$
5	Filature Extra—Japan Silk	$N/4000$	$N/150$
6	Filature Double Extra—Japan Silk Good heavy silk well dyed	$N/4000$	$N/250$
7	Filature Grand Double Extra. Very good fiber—Japan Silk.	$N/4500$	$N/300$
8	Filature No. 1. Japan Silk	$N/4500$	$N/300$
9	Filature Best No. 1—Japan Silk	$N/4500$	$N/300$
10	Japan Special Battleship 18/20—Japan Silk	$N/4500$	$N/300$
11	Filature Double Extra Special—Japan Silk	$N/4500$	$N/300$
12	Tussah S99 Black Double Magpie No. 1. Natural color interferes	$N/4500$	$N/250$
13	S1800 (used as standard) China Silk	$N/4500$	$N/300$
14	Italian Yellow Gin 20 22	$N/4500$	$N/300$
15	No. 1 Factory China Steam Filature 10/16—China Silk	$N/4500$	$N/300$
16	Japan Best No. 1 Maple 13 15	$N/4000$	$N/250$
17	Best Tussah Spinning Girl	$N/4500$	$N/250$
18	American Native Silk from <i>Samia cecropia</i> (Lin.)	$N/4000$	$N/250$
19	American Native Silk from <i>Telea polyphemus</i> (Cramer)	$N/4000$	$N/250$

Silk dyed after Treatments 1, 2 and 3 exhibited no differences in their sensitiveness, the limit with acids being $N/4000$ and with alkalis $N/100$; but after Treatments 4 and 5 a marked increase in sensitiveness followed, Treatment 5 yielding a more

sensitive fiber than Treatment 4 and increasing the alkali sensitiveness to $N/350$.

DETERMINATION OF THE BEST SILK FOR LITMUS SILK FIBERS

Twenty different samples of silk were tested in the following experiments. The raw silks were purified in the soap solution before being used. Equal portions of silk were placed in equal amounts of 10 per cent Merck litmus and evaporated almost to dryness. The silks were washed, neutralized and dried and then examined microscopically and tested as to their sensitiveness. No marked deviation from the standard was observed. The results obtained are shown in Table II:

TABLE II—SENSITIVENESS OF LITMUS SILK TO VARIOUS ACIDS AND ALKALIES

Test Solution	Sensitiveness to	
	Normality of Test Solution	Absolute Amount in Test Drop $\text{mg.} \times 10^{-5}$
HCl.....	$N/4500$	5.5
H ₂ SO ₄	$N/4500$	15
NH ₄ OH.....	$N/300$	80
NaOH.....	$N/300$	90
KOH.....	$N/300$	120

Table III shows that purified silk cannot be very satisfactorily dyed in alkaline or neutral solution, but can be in a concentrated acid solution of litmus.

TABLE III—DETERMINATION OF THE BEST CONCENTRATION OF LITMUS FOR DYEING PURIFIED SILK

Reaction of Litmus	Time of Dyeing Min.	Concentration of Dye Per cent	FINISHED PRODUCT
Neutral	30	2	Color too light. Unsatisfactory
Neutral	30	10	Color too light. Unsatisfactory
Neutral	30	20	Color rather light. Fairly satisfactory
Neutral	90	2	Color too light. Unsatisfactory
Neutral	90	10	Color too light. Unsatisfactory
Neutral	90	20	Color rather light. Fairly satisfactory
Neutral	120	2	Color too light. Unsatisfactory
Neutral	120	10	Color too light. Unsatisfactory
Neutral	120	20	Color rather light. Fairly satisfactory
Alkaline	120	20	Color too light. Unsatisfactory
Acid	60	2	Color too light. Unsatisfactory
Acid	60	10	Color rather light. Fairly satisfactory
Acid	60	20	Color correct. Satisfactory

II—THE DETECTION OF ACIDITY BY MEANS OF FIBERS DYED WITH CONGO RED

The use of Congo Red has often been mentioned as an indicator for estimating mineral acids in the presence of organic acids, as the latter are supposed not to affect it. The application of a fiber dyed with Congo Red for use in microscopic qualitative analysis at once suggests itself.

Of the common textile fibers tested, silk and viscose silk were found to be the most suitable for the preparation of Congo Red fibers, the latter giving an even more sensitive fiber than the former.

The best concentration of the dye for the silk fibers was found to be a 2 per cent solution, made alkaline with sodium hydroxide. For the preparation of the Congo Red viscose silk fibers a somewhat more concentrated solution is advisable. Dyeing in a 2 per cent alkaline solution of Congo Red for 15 minutes, washing thoroughly and then drying by pressing between filter papers, was found to yield an eminently satisfactory fiber.

Congo Red fibers can be used in the red form only, as the blue form is unstable in the air. For the detection of acidity they compare favorably with the litmus silk fibers, having the same degree of sensitiveness.

Contrary to our expectations, however, the Congo Red viscose silk fibers were found to be altogether too sensitive to the organic acids to be used as a means of differentiating organic from mineral acids. A large number of organic acids were tested and the greater proportion of them gave a positive color change in the Congo Red fiber in concentrations ranging from 1 g. to 0.1 g. per liter. The mineral acids give this color change in concentrations as low as 0.01 g. per liter.

SUMMARY

I—A method for the detection of alkalinity and acidity in minute drops of liquid has been described.

II—The litmus silk fibers can be used for the detection of either acid or alkali, while the Congo Red viscose silk fibers can be used for the detection of acidity only.

III—Acidity due to mineral acids can be detected in exceedingly dilute solutions, a $N/4500$ solution giving a positive reaction. The indicator fibers are not quite so sensitive to alkali.

IV—The sensitiveness of these indicator fibers varies with the degree of adsorption of the dye, the degree of purification of the raw silk and the degree of purification of the litmus.

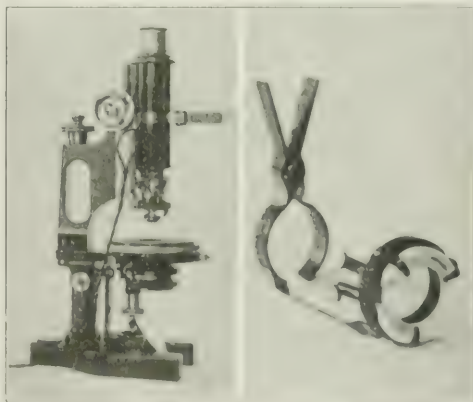
V—Congo Red fibers cannot be used to differentiate organic acids from mineral acids.

LABORATORY OF CHEMICAL MICROSCOPY
CORNELL UNIVERSITY, ITHACA, N. Y.

A NEW ILLUMINATOR FOR MICROSCOPES¹

BY ALEXANDER SILVERMAN

There has, for many years, been a demand for a satisfactory and convenient source of illumination for



ILLUMINATOR FOR MICROSCOPES

optique objectives designed for microscopic illumination. A device designed by the writer has been in use in this laboratory for some time. As it has been so

¹ U. S. PATENT OFFICE, 2,811,111, 2,811,112, 2,811,113, 2,811,114, 2,811,115, 2,811,116, 2,811,117, 2,811,118, 2,811,119, 2,811,120, 2,811,121, 2,811,122, 2,811,123, 2,811,124, 2,811,125, 2,811,126, 2,811,127, 2,811,128, 2,811,129, 2,811,130, 2,811,131, 2,811,132, 2,811,133, 2,811,134, 2,811,135, 2,811,136, 2,811,137, 2,811,138, 2,811,139, 2,811,140, 2,811,141, 2,811,142, 2,811,143, 2,811,144, 2,811,145, 2,811,146, 2,811,147, 2,811,148, 2,811,149, 2,811,150, 2,811,151, 2,811,152, 2,811,153, 2,811,154, 2,811,155, 2,811,156, 2,811,157, 2,811,158, 2,811,159, 2,811,160, 2,811,161, 2,811,162, 2,811,163, 2,811,164, 2,811,165, 2,811,166, 2,811,167, 2,811,168, 2,811,169, 2,811,170, 2,811,171, 2,811,172, 2,811,173, 2,811,174, 2,811,175, 2,811,176, 2,811,177, 2,811,178, 2,811,179, 2,811,180, 2,811,181, 2,811,182, 2,811,183, 2,811,184, 2,811,185, 2,811,186, 2,811,187, 2,811,188, 2,811,189, 2,811,190, 2,811,191, 2,811,192, 2,811,193, 2,811,194, 2,811,195, 2,811,196, 2,811,197, 2,811,198, 2,811,199, 2,811,200, 2,811,201, 2,811,202, 2,811,203, 2,811,204, 2,811,205, 2,811,206, 2,811,207, 2,811,208, 2,811,209, 2,811,210, 2,811,211, 2,811,212, 2,811,213, 2,811,214, 2,811,215, 2,811,216, 2,811,217, 2,811,218, 2,811,219, 2,811,220, 2,811,221, 2,811,222, 2,811,223, 2,811,224, 2,811,225, 2,811,226, 2,811,227, 2,811,228, 2,811,229, 2,811,230, 2,811,231, 2,811,232, 2,811,233, 2,811,234, 2,811,235, 2,811,236, 2,811,237, 2,811,238, 2,811,239, 2,811,240, 2,811,241, 2,811,242, 2,811,243, 2,811,244, 2,811,245, 2,811,246, 2,811,247, 2,811,248, 2,811,249, 2,811,250, 2,811,251, 2,811,252, 2,811,253, 2,811,254, 2,811,255, 2,811,256, 2,811,257, 2,811,258, 2,811,259, 2,811,260, 2,811,261, 2,811,262, 2,811,263, 2,811,264, 2,811,265, 2,811,266, 2,811,267, 2,811,268, 2,811,269, 2,811,270, 2,811,271, 2,811,272, 2,811,273, 2,811,274, 2,811,275, 2,811,276, 2,811,277, 2,811,278, 2,811,279, 2,811,280, 2,811,281, 2,811,282, 2,811,283, 2,811,284, 2,811,285, 2,811,286, 2,811,287, 2,811,288, 2,811,289, 2,811,290, 2,811,291, 2,811,292, 2,811,293, 2,811,294, 2,811,295, 2,811,296, 2,811,297, 2,811,298, 2,811,299, 2,811,300, 2,811,301, 2,811,302, 2,811,303, 2,811,304, 2,811,305, 2,811,306, 2,811,307, 2,811,308, 2,811,309, 2,811,310, 2,811,311, 2,811,312, 2,811,313, 2,811,314, 2,811,315, 2,811,316, 2,811,317, 2,811,318, 2,811,319, 2,811,320, 2,811,321, 2,811,322, 2,811,323, 2,811,324, 2,811,325, 2,811,326, 2,811,327, 2,811,328, 2,811,329, 2,811,330, 2,811,331, 2,811,332, 2,811,333, 2,811,334, 2,811,335, 2,811,336, 2,811,337, 2,811,338, 2,811,339, 2,811,340, 2,811,341, 2,811,342, 2,811,343, 2,811,344, 2,811,345, 2,811,346, 2,811,347, 2,811,348, 2,811,349, 2,811,350, 2,811,351, 2,811,352, 2,811,353, 2,811,354, 2,811,355, 2,811,356, 2,811,357, 2,811,358, 2,811,359, 2,811,360, 2,811,361, 2,811,362, 2,811,363, 2,811,364, 2,811,365, 2,811,366, 2,811,367, 2,811,368, 2,811,369, 2,811,370, 2,811,371, 2,811,372, 2,811,373, 2,811,374, 2,811,375, 2,811,376, 2,811,377, 2,811,378, 2,811,379, 2,811,380, 2,811,381, 2,811,382, 2,811,383, 2,811,384, 2,811,385, 2,811,386, 2,811,387, 2,811,388, 2,811,389, 2,811,390, 2,811,391, 2,811,392, 2,811,393, 2,811,394, 2,811,395, 2,811,396, 2,811,397, 2,811,398, 2,811,399, 2,811,400, 2,811,401, 2,811,402, 2,811,403, 2,811,404, 2,811,405, 2,811,406, 2,811,407, 2,811,408, 2,811,409, 2,811,410, 2,811,411, 2,811,412, 2,811,413, 2,811,414, 2,811,415, 2,811,416, 2,811,417, 2,811,418, 2,811,419, 2,811,420, 2,811,421, 2,811,422, 2,811,423, 2,811,424, 2,811,425, 2,811,426, 2,811,427, 2,811,428, 2,811,429, 2,811,430, 2,811,431, 2,811,432, 2,811,433, 2,811,434, 2,811,435, 2,811,436, 2,811,437, 2,811,438, 2,811,439, 2,811,440, 2,811,441, 2,811,442, 2,811,443, 2,811,444, 2,811,445, 2,811,446, 2,811,447, 2,811,448, 2,811,449, 2,811,450, 2,811,451, 2,811,452, 2,811,453, 2,811,454, 2,811,455, 2,811,456, 2,811,457, 2,811,458, 2,811,459, 2,811,460, 2,811,461, 2,811,462, 2,811,463, 2,811,464, 2,811,465, 2,811,466, 2,811,467, 2,811,468, 2,811,469, 2,811,470, 2,811,471, 2,811,472, 2,811,473, 2,811,474, 2,811,475, 2,811,476, 2,811,477, 2,811,478, 2,811,479, 2,811,480, 2,811,481, 2,811,482, 2,811,483, 2,811,484, 2,811,485, 2,811,486, 2,811,487, 2,811,488, 2,811,489, 2,811,490, 2,811,491, 2,811,492, 2,811,493, 2,811,494, 2,811,495, 2,811,496, 2,811,497, 2,811,498, 2,811,499, 2,811,500, 2,811,501, 2,811,502, 2,811,503, 2,811,504, 2,811,505, 2,811,506, 2,811,507, 2,811,508, 2,811,509, 2,811,510, 2,811,511, 2,811,512, 2,811,513, 2,811,514, 2,811,515, 2,811,516, 2,811,517, 2,811,518, 2,811,519, 2,811,520, 2,811,521, 2,811,522, 2,811,523, 2,811,524, 2,811,525, 2,811,526, 2,811,527, 2,811,528, 2,811,529, 2,811,530, 2,811,531, 2,811,532, 2,811,533, 2,811,534, 2,811,535, 2,811,536, 2,811,537, 2,811,538, 2,811,539, 2,811,540, 2,811,541, 2,811,542, 2,811,543, 2,811,544, 2,811,545, 2,811,546, 2,811,547, 2,811,548, 2,811,549, 2,811,550, 2,811,551, 2,811,552, 2,811,553, 2,811,554, 2,811,555, 2,811,556, 2,811,557, 2,811,558, 2,811,559, 2,811,560, 2,811,561, 2,811,562, 2,811,563, 2,811,564, 2,811,565, 2,811,566, 2,811,567, 2,811,568, 2,811,569, 2,811,570, 2,811,571, 2,811,572, 2,811,573, 2,811,574, 2,811,575, 2,811,576, 2,811,577, 2,811,578, 2,811,579, 2,811,580, 2,811,581, 2,811,582, 2,811,583, 2,811,584, 2,811,585, 2,811,586, 2,811,587, 2,811,588, 2,811,589, 2,811,590, 2,811,591, 2,811,592, 2,811,593, 2,811,594, 2,811,595, 2,811,596, 2,811,597, 2,811,598, 2,811,599, 2,811,600, 2,811,601, 2,811,602, 2,811,603, 2,811,604, 2,811,605, 2,811,606, 2,811,607, 2,811,608, 2,811,609, 2,811,610, 2,811,611, 2,811,612, 2,811,613, 2,811,614, 2,811,615, 2,811,616, 2,811,617, 2,811,618, 2,811,619, 2,811,620, 2,811,621, 2,811,622, 2,811,623, 2,811,624, 2,811,625, 2,811,626, 2,811,627, 2,811,628, 2,811,629, 2,811,630, 2,811,631, 2,811,632, 2,811,633, 2,811,634, 2,811,635, 2,811,636, 2,811,637, 2,811,638, 2,811,639, 2,811,640, 2,811,641, 2,811,642, 2,811,643, 2,811,644, 2,811,645, 2,811,646, 2,811,647, 2,811,648, 2,811,649, 2,811,650, 2,811,651, 2,811,652, 2,811,653, 2,811,654, 2,811,655, 2,811,656, 2,811,657, 2,811,658, 2,811,659, 2,811,660, 2,811,661, 2,811,662, 2,811,663, 2,811,664, 2,811,665, 2,811,666, 2,811,667, 2,811,668, 2,811,669, 2,811,670, 2,811,671, 2,811,672, 2,811,673, 2,811,674, 2,811,675, 2,811,676, 2,811,677, 2,811,678, 2,811,679, 2,811,680, 2,811,681, 2,811,682, 2,811,683, 2,811,684, 2,811,685, 2,811,686, 2,811,687, 2,811,688, 2,811,689, 2,811,690, 2,811,691, 2,811,692, 2,811,693, 2,811,694, 2,811,695, 2,811,696, 2,811,697, 2,811,698, 2,811,699, 2,811,700, 2,811,701, 2,811,702, 2,811,703, 2,811,704, 2,811,705, 2,811,706, 2,811,707, 2,811,708, 2,811,709, 2,811,710, 2,811,711, 2,811,712, 2,811,713, 2,811,714, 2,811,715, 2,811,716, 2,811,717, 2,811,718, 2,811,719, 2,811,720, 2,811,721, 2,811,722, 2,811,723, 2,811,724, 2,811,725, 2,811,726, 2,811,727, 2,811,728, 2,811,729, 2,811,730, 2,811,731, 2,811,732, 2,811,733, 2,811,734, 2,811,735, 2,811,736, 2,811,737, 2,811,738, 2,811,739, 2,811,740, 2,811,741, 2,811,742, 2,811,743, 2,811,744, 2,811,745, 2,811,746, 2,811,747, 2,811,748, 2,811,749, 2,811,750, 2,811,751, 2,811,752, 2,811,753, 2,811,754, 2,811,755, 2,811,756, 2,811,757, 2,811,758, 2,811,759, 2,811,760, 2,811,761, 2,811,762, 2,811,763, 2,811,764, 2,811,765, 2,811,766, 2,811,767, 2,811,768, 2,811,769, 2,811,770, 2,811,771, 2,811,772, 2,811,773, 2,811,774, 2,811,775, 2,811,776, 2,811,777, 2,811,778, 2,811,779, 2,811,780, 2,811,781, 2,811,782, 2,811,783, 2,811,784, 2,811,785, 2,811,786, 2,811,787, 2,811,788, 2,811,789, 2,811,790, 2,811,791, 2,811,792, 2,811,793, 2,811,794, 2,811,795, 2,811,796, 2,811,797, 2,811,798, 2,811,799, 2,811,800, 2,811,801, 2,811,802, 2,811,803, 2,811,804, 2,811,805, 2,811,806, 2,811,807, 2,811,808, 2,811,809, 2,811,810, 2,811,811, 2,811,812, 2,811,813, 2,811,814, 2,811,815, 2,811,816, 2,811,817, 2,811,818, 2,811,819, 2,811,820, 2,811,821, 2,811,822, 2,811,823, 2,811,824, 2,811,825, 2,811,826, 2,811,827, 2,811,828, 2,811,829, 2,811,830, 2,811,831, 2,811,832, 2,811,833, 2,811,834, 2,811,835, 2,811,836, 2,811,837, 2,811,838, 2,811,839, 2,811,840, 2,811,841, 2,811,842, 2,811,843, 2,811,844, 2,811,845, 2,811,846, 2,811,847, 2,811,848, 2,811,849, 2,811,850, 2,811,851, 2,811,852, 2,811,853, 2,811,854, 2,811,855, 2,811,856, 2,811,857, 2,811,858, 2,811,859, 2,811,860, 2,811,861, 2,811,862, 2,811,863, 2,811,864, 2,811,865, 2,811,866, 2,811,867, 2,811,868, 2,811,869, 2,811,870, 2,811,871, 2,811,872, 2,811,873, 2,811,874, 2,811,875, 2,811,876, 2,811,877, 2,811,878, 2,811,879, 2,811,880, 2,811,881, 2,811,882, 2,811,883, 2,811,884, 2,811,885, 2,811,886, 2,811,887, 2,811,888, 2,811,889, 2,811,890, 2,811,891, 2,811,892, 2,811,893, 2,811,894, 2,811,895, 2,811,896, 2,811,897, 2,811,898, 2,811,899, 2,811,900, 2,811,901, 2,811,902, 2,811,903, 2,811,904, 2,811,905, 2,811,906, 2,811,907, 2,811,908, 2,811,909, 2,811,910, 2,811,911, 2,811,912, 2,811,913, 2,811,914, 2,811,915, 2,811,916, 2,811,917, 2,811,918, 2,811,919, 2,811,920, 2,811,921, 2,811,922, 2,811,923, 2,811,924, 2,811,925, 2,811,926, 2,811,927, 2,811,928, 2,811,929, 2,811,930, 2,811,931, 2,811,932, 2,811,933, 2,811,934, 2,811,935, 2,811,936, 2,811,937, 2,811,938, 2,811,939, 2,811,940, 2,811,941, 2,811,942, 2,811,943, 2,811,944, 2,811,945, 2,811,946, 2,811,947, 2,811,948, 2,811,949, 2,811,950, 2,811,951, 2,811,952, 2,811,953, 2,811,954, 2,811,955, 2,811,956, 2,811,957, 2,811,958, 2,811,959, 2,811,960, 2,811,961, 2,811,962, 2,811,963, 2,811,964, 2,811,965, 2,811,966, 2,811,967, 2,811,968, 2,811,969, 2,811,970, 2,811,971, 2,811,972, 2,811

aminated by chemists, biologists and metallographers and pronounced satisfactory for both direct observation and microphotography, it is described here for those who may be interested.

As shown in the accompanying illustration, a small circular tube-lamp surrounds the objective and is attached to a holder which is clamped to the microscope tube. The design of both clamp and holder may be modified to fit a binocular microscope. For the present, the holder illustrated is used because of the variation in diameter and shape of objectives. The lamp shown is a 6-volt tungsten lamp operated by six dry cells. Modifications of the lamp are possible. The present one might be replaced by a nitrogen-filled tungsten, daylight tungsten, mercury or carbon dioxide lamp.

The advantages in the use of the new device lie in the fact that an object is illuminated by a circular source of light, so directed by the reflector on the upper wall of the tube that diffusion results. Further, the light is always in place and is raised and lowered with the microscope tube, thus obviating the necessity for readjustment experienced in using vertical illuminators. The lamp, fitting snugly about the objective, enables one to lower the light into hollow objects too deep to permit of the use of a vertical illuminator.

In microphotography the lamp has been used to good advantage. Satisfactory results have been obtained on specimens with a 5 mm. eyepiece and 8, 16 and 32 mm. objectives. It has heretofore been quite difficult to obtain good photographs in metallography with low-power objectives using older forms of illuminators. With the new illuminator excellent results were obtained. The time of exposure was, on an average, 6 minutes for the 8 mm., $2\frac{1}{2}$ minutes for the 16 mm., and $1\frac{1}{2}$ minutes for the 32 mm. objective.

SCHOOL OF CHEMISTRY
UNIVERSITY OF PITTSBURGH
PITTSBURGH, PA.

A NEW MODEL OF THE BURRELL AND OBERFELL APPARATUS FOR THE ANALYSIS OF ILLUMINATING GAS

By J. R. SUYDAM, JR.

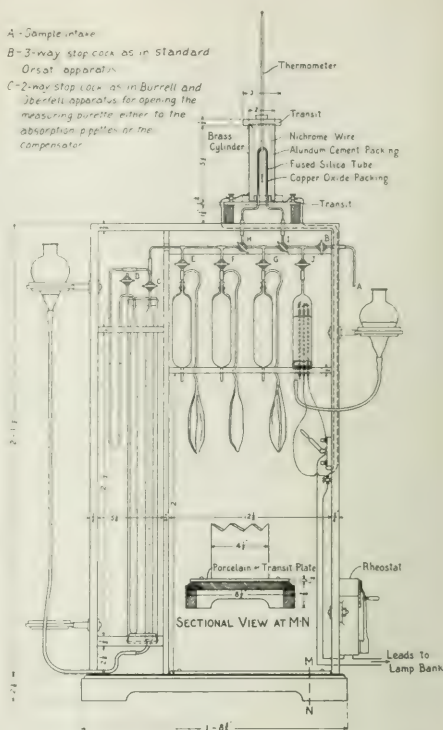
Received May 21, 1917

The apparatus shown herewith is practically identical with the apparatus described by Burrell and Oberfell in *THIS JOURNAL* for March, 1916, page 228, except that it has been put in a more compact stand which gives more protection to the glass parts than that shown by the above writers, and that a silica tube has been substituted for the glass one used by them as a container for the copper oxide.

The silica tube, which was made by the Hanovia Chemical Company of Newark, N. J., was more than paid for by the saving of the expense for repairing the glass tube, which broke very frequently.

The procedure for the analysis is identical with that given by Burrell and Oberfell.

The apparatus has given excellent results and is recommended as being more satisfactory for the



analysis of illuminating gas than the standard forms of apparatus now on the market.

DEPARTMENT OF CHEMICAL ENGINEERING
COLUMBIA UNIVERSITY, NEW YORK CITY

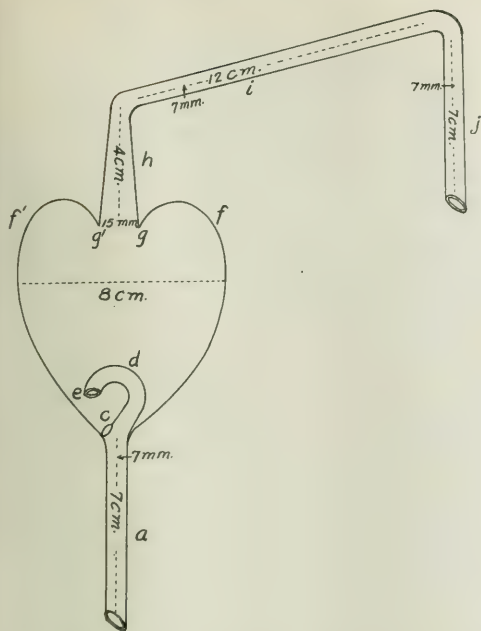
A USEFUL DISTILLING HEAD

By ORLO STEARNS

Received May 28, 1915

The accompanying drawing explains the construction of a useful distilling head. The angle between h and i should be about 110° .

This head was specially designed for and found exceptionally efficient in distilling troublesome fluid extracts. Such liquids often give rise to a good deal of froth which carries some of the liquid along and renders redistillation necessary. Sometimes, however, the liquid is forced up by spurts, or again rises in a body passing into the apparatus connected with the flask. In the first instance the part of the head that does the most service is the lobes f, f' in which the bubbles readily break by expansion and condensation. Bubbles often broke in passing the circular edge g, g' at the lower end of the conical branch of the connecting tube, while the larger opening, across g, g' , is less favorable for the entrance of bubbles than a smaller one. The opening e in the lower part of bulb is directly over the drainage hole c and the re-



action produced when the liquid spurts has a tendency to check or force back the ascending liquid. In case the tube *d* becomes submerged, a small syphonic force is generated which tends to empty the bulb.

It is possible that this head may be adapted on a different scale for other similar purposes.

Eimer and Amend will make this form of distilling head upon application.

4629 CARROLLE ST.
PITTSBURGH, PA.

AN ELECTRICALLY HEATED AND CONTROLLED AIR BATH

By WALTER P. SCHOCK

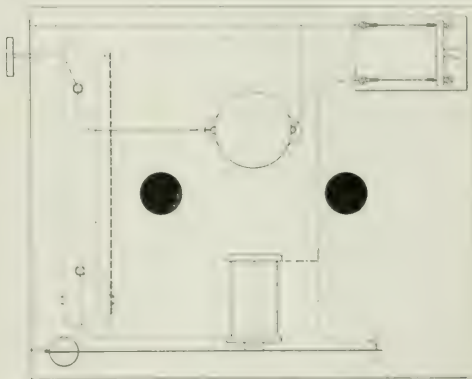
Received August 27, 1914

The writer recently installed electric heating and temperature control devices in a common air bath for use on 120-volt direct current. The details and results may be of interest to others.

The air bath was of the single-walled type 10 in. X 10 in. X 12 in. To conserve heat it was first covered with asbestos on all surfaces by gluing the same on. The heating element consists of three coils of No. 28 "Climax" resistance wire, each coil containing 30 ft. and all connected in parallel. These coils are mounted on a piece of asbestos mill board $\frac{1}{4}$ in. thick that fits into the bottom of the air bath. Each coil is stretched three times across the width of the board so that the terminals are at landing points on opposite sides. At the two other points the coil is laid around short studs of slate pencil set into the board. For the control of temperature a thermostat was made by soldering together a strip of zinc and copper each $\frac{1}{4}$ in. X

in. on their flat surfaces. This is mounted on a piece of oak so that it is securely fastened at one end and free to move at the other. When the temperature to which it is subjected varies, the unequal expansion of the metals causes the free end to move towards or away from an adjustable contact point. If the entire current of the heating coils were passed through this thermostat, the contacts even of platinum would be fused by the arcing of the current. Therefore only as much current as will pass through an incandescent lamp is relayed through the thermostat. This thermostat is bolted to the top of the air bath inside but the screw which adjusts the temperature at which the current is broken projects outside. The location of the thermostat is shown in dotted lines in the diagram. The current passing through the lamp and thermostat actuates a magnet which breaks the heating current.

This magnet and the interrupter which it operates, as well as the lamp and main switch, are mounted on top of the oven on a wooden board cut to the size of the oven and having holes bored in it to accommodate the thermometer and ventilating holes. The magnet used by the writer has 4 oz. of No. 26 double silk-covered copper wire wound on a $\frac{1}{2}$ -in. fiber tube with soft iron wire core. With a 50 watt lamp in the



socket this magnet operates the interrupter quickly and holds it well. If other voltages or different sized lamps were used the ampere turns of the magnet could of course be adjusted to suit. The interrupter is a piece of spring brass about 9 in. long and one-half in. wide which is securely fastened into a post at one end and at such a height that it is opposite the core of the magnet. The armature is soldered on this strip of brass and is of soft iron one-half in. square and $\frac{1}{4}$ in. thick. At the free end of the interrupter is the platinum contact that makes and breaks the heating current. The brass strip is bent so that normally it would keep the interrupter about 1 in. apart, but as this throws the armature too far from the magnet, a peg is set into the board so such position that it keeps the strip from pulling the contacts more than $\frac{1}{2}$ in. apart. It is also necessary to put a piece of cardboard 1 mm. thick between the armature and the

core of the magnet to keep the former from sticking after the exciting current is stopped. The current connections are shown in the diagram as dot and dash lines. The current passes from the switch to one side of the three heating coils. From the other side of the coils it passes through the interrupter back to the switch. All make-and-break contacts are made of platinum and where the wires or current-carrying bolts pass through the walls of the air bath they pass through glass bushings.

In the operation of the air bath the switch is closed and then the contact adjusting screw of the thermostat is turned until contact is made. This will be shown by the lamp lighting and if properly adjusted the magnet will draw the armature up and close the heating circuit. In a short

time the rise of temperature will break the thermostat circuit and the magnet being killed will release the armature so that the spring will pull the heating circuit contacts apart. To bring the air bath to the desired temperature the thermostat contact screw is turned until the make-and-break action occurs at that temperature as shown by a thermometer inserted in the air bath in the usual manner. The air bath constructed by the writer holds its temperature to within 1° . It requires 2.5 amperes of current at the start and drops to 2.35 at 100°C . The cost of the materials required to make the air bath electrically heated and controlled was \$1.50, exclusive of the platinum contact points.

2513 62ND STREET, S. E.
PORTLAND, OREGON

ADDRESSES

STELLITE AS A SUBSTITUTE FOR PLATINUM¹

By ELWOOD HAYNES

Owing to the great scarcity of platinum and its consequent high price, platinum substitutes have been eagerly sought, particularly within the last three or four years. From what has already been accomplished along this line it is evident that no single metal or combination of metals will fully take the place of platinum. There are certain other of the polyxene metals associated with platinum, which possess refractory power superior to those of platinum, but unfortunately these are out of the question, since the metals themselves are more costly than platinum.

The alloy of gold with palladium affords a partial substitute for crucibles and dishes, and perhaps comes more nearly filling the place of platinum in this respect than anything yet offered. The price of this alloy, however, is comparatively high, though bulk for bulk, it is only about half as costly as platinum.

The alloy of nickel with chromium, known as chromyl, discovered by the writer in 1899, though less refractory, affords a partial substitute for platinum for electric resistance coils employed as heating units for combustion tubes, small electric furnaces, etc. The same alloy, used in conjunction with pure nickel or certain nickel-silicon alloys, is also employed for making thermocouples for determining high temperatures.

The silicon-iron alloys are now employed to a considerable extent for evaporations, and even for concentrating the strong mineral acids, but they are rather heavy and somewhat easily broken or cracked.

Pure quartz or silica vessels give excellent results within certain limits, and while they are practically unbreakable under sudden changes of temperature, they are fragile when subjected to sudden shocks or blows, and while they may be used for evaporating solutions to dryness, they are likely to be cracked if the residue sticks to the vessel, particularly if the coefficient of expansion of the residue is higher than that of the vessel.

A short description of the Stellite alloys may be introduced to advantage at this point. First, it may be said that these alloys are not fixed or definite in their composition, and may be divided broadly into two classes: (1) those malleable at a red heat; and (2) those which can be worked into the desired form only by casting.

The MALLEABLE ALLOYS are composed almost entirely of cobalt and chromium only, though the proportion of the constituents may vary from 10 to 50 per cent chromium, with a corresponding variation in the cobalt. These alloys are all hard, and while they may be scratched by the file, none of them is practically workable by this means. They cannot be machined, but some of the softest ones may be drilled by means of a hard-carbon steel drill or a drill composed of hard stellite. They resist nitric acid almost perfectly, even when boiling, particularly if the chromium content is over 15 per cent. They forge with difficulty at temperatures ranging from 750 to 1200°C .

They have been forged into the following forms:

- (a) Tableware, such as spoons, forks, knives, ladles, etc.;
- (b) Surgical instruments, pocket knives, dental instruments, etc.;
- (c) Evaporating dishes, crucible supports, lamp stands, etc.;
- (d) Jewelry, including finger rings, cuff buttons, scarf pins, etc.

These malleable alloys are all slowly attacked by either hydrochloric, sulfuric, or hydrofluoric acid, but are nearly immune to all chemical combinations, as well as the fruit acids. As the evaporating dishes made of this metal take a bright polish, and can be made of comparatively light section, they will prove suitable for evaporating many chemical salts to dryness, and are particularly suitable for boiling the caustic alkalis. Substances may be evaporated to complete dryness in these vessels without any danger whatever of breaking the vessel, since the tensile strength of the alloy exceeds 100,000 lbs. to the sq. in., and it also shows considerable elongation before rupture. When a vessel made of this material is struck by a hammer, it emits a clear, musical tone, and continues to vibrate for a considerable length of time. The vessels retain their luster in the chemical laboratory under practically all conditions, since they are not affected in the slightest degree by sulfuretted hydrogen, ammonium chloride, or other vapors. Furthermore, they are practically immune to acid vapors. They give most excellent results in the form of lamp stands, supporting rings, triangles, etc. When these are heated to full redness, they become covered with a deep blue-black film, which does not change either in weight or appearance by repeated heating, and as no scale ever forms, these articles retain their weight, stability, and smooth surface indefinitely under all sorts of use. They can be subjected to temperatures up to 1200°C ., and still retain a considerable amount of strength. In fact, the Stellite alloys possess the highest "red hardness" of any of the alloys yet discovered.

¹ Presented at the Metallurgical Symposium, 55th Meeting of the American Chemical Society, Boston, September 10 to 13, 1917.

JEWELRY

The chemist is, as a rule, not much interested in jewelry excepting from a scientific standpoint. He is vitally interested, however, in the fact that the demand for platinum in jewelry has rendered the price of this material so high that it is almost unobtainable. Unfortunately, the demand for platinum in this line is largely based upon its high price. Comparatively a small amount was used in jewelry until after the price of platinum exceeded that of gold. It then became a fad, amounting almost to a mania, to substitute platinum for gold, wherever one's means would permit of doing so. All efforts to produce a substitute for platinum, which would give results equal or superior to that metal in many respects, have proved almost futile, since the very evil which these attempts have sought to remedy is held up by the purveyors of platinum jewelry as a virtue; namely, its high price; and notwithstanding "a rose by any other name would smell as sweet," it must in the eyes of fashion also cost as much, or more; in fact, the more the better. Whether this condition is to continue indefinitely or be limited by a legal enactment is a question for our Government to decide. Fashion, like fortune, is fickle, and may change radically at almost any instant.

Stellite would in many cases substitute to great advantage for platinum in jewelry. It is almost the same color, possesses a higher luster, and retains its luster very much better than platinum, since it is so hard that it is not easily scratched or abraded by ordinary use. It is absolutely immune against tarnish or corrosion in the air, and while it is not nearly so pliable as platinum, it can be worked into many of the forms used in jewelry without special difficulty. Finger rings can be made from it either in the plain form, or adapted to the Tiffany setting, so that it may be used in conjunction with any gem desired. If preferable, plain band rings can be made of the cast metal, which are practically life-proof, and at the same time possess a beautiful color and permanent luster.

305 N. WASHINGTON STREET
KOKOMO, INDIANA

THE INFLUENCE OF ADDED SUBSTANCES ON THE END-POINT IN THE IODOMETRIC TITRATION OF HYDROGEN SULFIDE

By ALFRED R. JAYSON AND RALPH E. OESPER¹

INTRODUCTION

Wide use is made of the reaction



in estimating the sulfur content of systems or materials containing this element either as hydrogen sulfide or as other compounds easily converted into hydrogen sulfide. Furthermore, such metals as zinc, cadmium, etc., whose sulfides are readily soluble in acid, may be determined by isolating the sulfide, dissolving it, and titrating the resulting hydrogen sulfide with standard iodine.

The evolution methods of determining the sulfur content of irons and steels are in common use. The sample is dissolved in acid and the evolved hydrogen sulfide absorbed in a reagent whose nature is usually determined by whether the subsequent course of the analysis is to be a gravimetric, colorimetric or volumetric process. Numerous alterations have been proposed.²

¹ The work reported in this article constitutes the basis of a thesis submitted by A. E. Jayson to the Faculty of the Graduate School of New York University in part fulfillment of the requirements for the degree of Master of Science.

² von Berg, *Z. anal. Chem.*, **26** (1885), 51; *Möller, Bull. chim.*, [11] **1** (1902), 14; *Robinson and Atkinson, Analysis of Non-Ferrous Alloys*, **1916**, 168; *Scott, Standard Methods of Chemical Analysis*, **1917**, 8.

³ Compilations and abstracts of the various proposals have been made by *Bradley, Chem. News*, **82** (1900), 306; *Pulcher, Trans. Journal*, **6** (1916), 1119.

but those most generally employed in connection with the iodometric estimation of the hydrogen sulfide liberated are: sodium or potassium hydroxide; ammoniacal zinc solution or ammoniacal cadmium solutions. After absorption, these solutions or suspensions are made strongly acid and titrated with iodine in the presence of starch. The reaction between iodine and hydrogen sulfide takes place in the presence of a considerable quantity of acid and under these conditions the end-point is uncertain, for an excess of iodine is not made manifest by a sudden change from colorless to blue, but even in the early part of the titration the solution turns yellow, and passing through orange, red and purplish red, deepens, and forms a final purple instead of a pure blue. This difficulty may be overcome in part by standardizing the iodine solution by means of a sample of known sulfur content carried through the same procedure, but this is often inconvenient. It is better to add an excess of iodine to the acidified solution and titrate back with thiosulfate, as this gives a sharp end-point.

The appearance of the interfering colors is a matter of common knowledge and is usually ascribed to the presence of erythro-dextrin or similar products of the hydrolysis of starch, though this is still an open question. Indeed, the real nature of the blue color produced by starch itself and iodine is still a matter of dispute.¹ Some have asserted that it is a mere physical phenomenon; others claim the existence of a definite compound, though the actual composition appears to vary with the concentration, temperature, etc., while still others view this as a case of adsorption. Harrison,² in particular, holds this latter view. He claims that the blue material is a colloidal suspension of iodine, starch acting as a protective colloid. He further states that starch, dextrans, starch-celluloses, etc., do not differ chemically but are merely different degrees of dispersion of the same substance. The various colors produced by these materials and iodine may be produced by addition of alcohol to aqueous starch iodide suspensions and *vice versa*; by warming and cooling; by addition of salts; processes which he holds merely change the degree of dispersion and consequently the protective action of the starch. As this decreases, iodine tends more and more to form true solution, and hence the color changes.

The influence of salts and other added substances upon the color produced by iodine and starch has been studied by Fresenius,³ Meineke,⁴ Pinnow,⁵ Lonnes,⁶ Burgstaller,⁷ and others. In general, salts increase the sensibleness of the action and potassium iodide is particularly effective.⁸ However, excessive salt addition decreases the sensibility and often leads to changes in the starch so that yellows and reds appear when iodine is added. Meineke claims that large quantities of salts bring about a partial change of starch into materials less sensitive to iodine or into dextrans coloring red or yellow, i. e., shades less noticeable than blue. Harrison ascribes this action of salts to changes in the degree of dispersion of starch. Hild⁹ found that ordinary starch contains as impurities, erythro-dextrin, coloring red with iodine, and amylum, coloring blue. The change of amylose to erythro-dextrin is caused by potassium bisulfate in the presence of an oxidizing agent and he thus explained the red

¹ Comments and references to the original papers may be found in *Dammer, Handbuch der analytischen Chemie*, **1** (1906), 11; **4** (1907), 229; *Brakeman, J. I.*, **1** (1901), 100; *Brakeman, J. I.*, **2** (1902), 14; *Journal of Applied Chemistry*, **5** (1903), 31; *Transactions of the American Chemical Society*, **56** (1904), 260.

² *J. Res. Chem.*, **9** (1906), 1; *Chem. News*, **56** (1907), 100.

³ *Ann.*, **102** (1858), 183.

⁴ *Monat. Ber.*, **18** (1885), 13.

⁵ *J. anal. Chem.*, **41** (1906), 98.

⁶ *Ber.*, **33** (1887), 100.

⁷ *Monat. Ber.*, **36** (1903), 100.

⁸ *Wiedemann, Z. anal. Chem.*, **30** (1901), 100; *Journal of Applied Chemistry*, **2** (1900), 100.

⁹ *Ann. Chem. Phys.*, **13** (1906), 100.

color appearing during the titration of arsenious acid with iodine in the presence of this compound.

We have assumed that the red color appearing during the titration of hydrogen sulfide is due to the presence of erythro-dextrin. The acid brings about the hydrolysis of starch but it ordinarily acts very slowly in the cold. The depth of color appearing during the titration carried out under the conditions being discussed indicates that the hydrolysis is catalyzed and we believe that hydrogen sulfide is the principal accelerator, functioning in acid solution somewhat as Hale found potassium bicarbonate to act in an alkaline medium. Our work was directed toward the discovery of a preventative of this hydrolysis and titrations were carried out in solutions of varying acid concentration and in the presence of numerous salts. None of these altered conditions brought about sufficient improvement in the end-point coloration to warrant adoption in technical practice, but the results were of enough interest to justify their appearance at this time.

EXPERIMENTAL

The solutions of iodine and thiosulfate used were *N*/100. Five cc. of a fresh solution containing 5 g. soluble starch (Lintner) per liter were used in each case. Preliminary tests showed that ordinary wheat and potato starch gave the same result. A fresh aqueous solution of hydrogen sulfide was used.

The conditions under which the interfering colors would form were first determined. Starch and iodine gave a pure blue; 25 cc. hydrogen sulfide solution diluted with 500 cc. water and titrated with iodine gave a blue end color and no preliminary reds. When, however, the hydrogen sulfide was diluted with 500 cc. water, 75 cc. hydrochloric acid (1 : 1) added and then titrated, a red color appeared almost immediately, growing deeper as the titration proceeded and finally changing to purple. The acid is necessary for the appearance of the red color, and, accordingly, tests were made using decreasing volumes of acid, the total volume of solution being kept constant by the addition of water. The results are given in Table I.

Hydrogen sulfide solution	25 cc.	Starch paste	5 cc.
No.	HCl (1 : 1) Cc.	H ₂ O Cc.	Color of solution during titration
1	0	575	Pure blue
2	5	570	Colorless
3	10	565	Pinkish
4	15	560	Pink
5	25	550	Red
6	50	525	Deeper red
7	75	500	Deeper red

The intensity of the red color increases with the acidity of the solution, and the interference of the pink with the blue is not very noticeable when less than 15 cc. acid is present; 0.02 g. cadmium sulfide was suspended in 500 cc. water, 15 cc. acid added, and the resulting hydrogen sulfide titrated with iodine. Although the red color was not very pronounced, the sulfide dissolved so slowly that the results were far from accurate. It is possible to add an excess of iodine to the suspension containing no acid, allow to stand for half an hour or so and then titrate the excess. This method has been recommended for the estimation of zinc.¹ However, if immediate results are desired, or if the use of a second standard solution is not convenient, it appears impracticable to reduce the acid to the point where the interference of the red is negligible.

Titrations were carried out in the presence of other acids. Sulfuric acid in quantities equivalent to the hydrochloric acid used above produced the corresponding red color, but the slightly dissociated acids, acetic and boric, gave no red during the titration and a pure blue end-point: 75 cc. of 15 per cent phosphoric acid in a total volume of 575 cc. gave a light pink, changing to a

purple end color, thus showing an intermediate behavior.¹ However, cadmium sulfide dissolves in acetic acid so slowly, even in the presence of iodine, that its use does not seem feasible. The effect of adding rather high concentrations of chlorides to the hydrochloric acid solution was studied in the hope that they would sufficiently depress the ionization of the acid to overcome the color formation. The results of adding saturated sodium chloride solution are shown in Table II.

Hydrogen sulfide solution	Hydrochloric acid (1 : 1)	Starch paste
25 cc.	75 cc.	5 cc.
No.	NaCl (sat. sol.) Cc.	H ₂ O Cc.
1	0	500
2	50	450
3	100	400
4	200	300

No improvement was noted: 500 cc. saturated sodium chloride solution containing 75 cc. acetic acid (20 per cent) gave a light red, changing to purple; 500 cc. saturated sodium acetate solution containing 75 cc. hydrochloric acid (1 : 1) gave a yellow, passing through reddish yellow to purple; 500 cc. saturated solution disodium hydrogen phosphate containing 75 cc. hydrochloric acid (1 : 1) gave a pink, changing to purple. These attempts to decrease the hydrogen ion content by addition of salts derived from weak acids had no favorable effects, and the hydrochloric acid present in these equilibria was sufficient to hydrolyze the starch. The results with 15 per cent calcium chloride solution are shown in Table III.

Hydrogen sulfide solution	25 cc.	Starch paste	5 cc.
No.	15% CaCl ₂ Cc.	HCl (1 : 1) Cc.	H ₂ O Cc.
1	0	0	575
2	0	75	500
3	20	75	480
4	40	75	460
5	60	75	440
6	80	75	420
7	100	75	400
8	150	75	350
9	200	75	300

A repetition of these experiments, using 10 per cent, 20 per cent and saturated solutions of calcium chloride, showed no improvements. Meineke² noted that calcium chloride produced a red end color even when no acid was present; he found bismuthates to show the same tendency and even large concentrations of potassium iodide have the same effect. Titrations in the presence of varying concentrations of potassium chloride, sodium sulfate, magnesium sulfate, barium chloride and aluminum sulfate showed no reduction of the red color. Goppels-roeder³ found that magnesium sulfate, even in the absence of acid, tended to give red tints to the starch iodide coloration, while large amounts of potassium alum gave red colors exclusively.

Cadmium sulfide	0.02 gram	Starch paste	5 cc.
No.	NaCl (sat. sol.) Cc.	HCl (1 : 1) Cc.	H ₂ O Cc.
1	0	75	500
2	100	25	450
3	150	25	400
4	200	25	350
5	300	25	250

Cushman⁴ has shown that cadmium sulfide will dissolve in strong sodium chloride solutions containing low concentrations of hydrochloric acid. This seemed to offer a method of avoiding the undesirable effects of excess acid while permitting solution of the sulfide. The results are given in Table IV.

¹ Pinnow (*loc. cit.*) found acids to increase the sensitiveness of the iodostarch reaction in the order of their electrical dissociation, but he points out that the H ion concentration is not the only factor involved since salts are often more effective than the corresponding acids.

² Loomis.

³ *J. Eng. Chem.* **1863**, 670, *Ann. Phys.* **209**, 57.

⁴ *Am. Chem. J.*, **17** (1895), 379.

Although solution of the sulfide still occurred when the volume of acid was reduced to 15 cc., one hour was required to complete the solution and titration. Less than this quantity of acid produced no appreciable solution of sulfide no matter how much sodium chloride was present. In no case was the red color reduced.

The failure of the coagulating electrolytes to bring about improvement indicates that the colloidal sulfur produced during the reaction is not responsible for the red coloration. Likewise, acidified, solutions of thiosulfate containing sulfur in varying stages of aggregation gave pure blue end colors with no preliminary reds when treated with iodine. If a small quantity of hydrogen sulfide was added before beginning the titration, reds and purples appeared as soon as any thiosulfate still present had reacted. The starch and acid could be left in contact for a considerable period without influencing the end color. Titrations were made as usual except that the acid was not added until the end-point was almost reached, and when the few drops of iodine necessary to complete the reaction were added carefully no red appeared and the end color was pure blue. If the addition of the starch was deferred until just before the end-point was reached, the acid being present from the beginning, no interfering colors formed. If, in either of these cases, the solution was allowed to stand for some time before completing the titration, the end color was pure blue, if the last iodine was added slowly. If added rapidly, a faint pink appeared which deepened and gave way to a purple end color, and the faster the iodine was added, the deeper the red. The significance of this will be discussed later.

Although a deepening of the red color as the titration progresses is accompanied by an increase of both hydrogen iodide and sulfur, these materials probably exert no catalytic action, since titration of acidified suspensions of cadmium sulfide which slowly liberate the same total quantity of hydrogen sulfide as was present in 25 cc. of the aqueous solution, show a much deeper color even from the beginning than was observed with the aqueous solutions. It seems improbable that equal quantities of sulfur and hydrogen iodide should exert increased catalytic action, and as will be pointed out later, depth of color appears rather to be dependent on the local concentration of hydrogen sulfide. If hydrogen sulfide is the catalytic agent, why should the red color increase as it is progressively removed? When titrating aqueous solutions there is so much hydrogen sulfide present at the beginning that it reacts rapidly with the iodine and so prevents, to a great extent, the formation of the red erythro-dextrin iodide. As it is used up the erythro-dextrin has more opportunity to combine with the iodine and the red color deepens. No red at all appears when a concentrated solution of hydrogen sulfide is titrated, until its concentration is reduced to about that prevailing in our solutions. Furthermore, if the iodine is added slowly and the solutions thoroughly stirred after each addition, little if any permanent red appears as long as the concentration of the hydrogen sulfide is comparatively high. As the reaction progresses, it becomes increasingly difficult to remove the color by stirring, for now the erythro-dextrin has a chance to combine with the iodine. If the iodine is added rapidly, the red appears immediately and quickly deepens. Under these conditions the local concentration of hydrogen sulfide is not sufficient to react with all the iodine and erythro-dextrin iodide forms. The increased red observed when titrating a slowly dissolving sulfide may be due to the low local concentration of the hydrogen sulfide.

If the titration is carried past the end point and then back-titrated with hydrogen sulfide, the solution becomes colorless. If more iodine is then added the red reappears and gives a purple end color. If the first color is discharged with thiosulfate, the subsequent addition of iodine produces no red or purple but a pure blue. This difference is significant. Addition of

excess iodine and back-titration with thiosulfate leads to a sharp end-point and so this procedure has been recommended and we find this the only method giving constant agreement when titrating hydrogen sulfide solutions. Hale points out the following facts in explanation of this feature: Although starch will remove iodine from erythro-dextrin iodide, and form starch iodide, toward the end of the titration, an excess of iodine is present for a short time and both iodides are formed together. Although in alkaline solution, a reducing agent (sulfurous acid) fades the blue first, leaving the red to fade more slowly; in acid solution the red fades first and the blue last, even in the presence of an abundance of materials coloring red with iodine. This may explain why in the back-titrations with thiosulfate one is not bothered by the appearance of red hues.

We believe that the erythro-dextrin is formed at the point of reaction of the iodine and hydrogen sulfide and the resulting relatively high local concentration of erythro-dextrin permits the formation of the red material, if the concentration of hydrogen sulfide at this point is not too great. This conclusion is analogous to that arrived at by Hale who found that potassium bicarbonate catalyzes the change of amidulin to erythro-dextrin only in the presence of an oxidizing agent. In the same way we believe the hydrogen sulfide accelerates the hydrolytic action of the acid in the presence of iodine. Hale found that starch prepared according to Zulkowsky¹ gave no interfering colors. We prepared a sample of this "amorphous amylo-dextrin," which, when tested in the iodometric titration of an arsenite in the presence of potassium bicarbonate gave a pure blue end color. When used as indicator during the titration of hydrogen sulfide in acid solutions, this pure starch showed slightly less red, but the end color was purple and the exact end-point as uncertain as when ordinary starch was used.

CONCLUSIONS

The following hypothesis is advanced to account for the red color appearing during the iodometric titrations of hydrogen sulfide in acid solution: the acid hydrolysis of starch to erythro-dextrin is accelerated by hydrogen sulfide in the presence of iodine. This hydrolysis occurs at the point at which iodine and hydrogen sulfide react, and though, at ordinary concentrations, iodine reacts with hydrogen sulfide and combines with starch in preference to erythro-dextrin, under conditions of high local concentration erythro-dextrin iodide may also be formed. At the end of the titration the formation of erythro-dextrin no longer occurs, blue starch iodide forms, and a mixture of the latter and the red erythro-dextrin iodide already present gives a purple end color. On standing, the erythro-dextrin iodide gives up its iodine to the starch, and the purple changes to a pure blue, but this final color change proceeds too slowly to be of practical significance.

LITERATURE

I.—The conditions leading to the production of erythro-dextrin, the titration of hydrogen sulfide with iodine in acid solution, has been studied and an hypothesis advanced to account for the phenomenon.

II.—The quantity of erythro-dextrin formed (measured by the red color) is dependent on the nature of the acid present and the formation of erythro-dextrin is greatly accelerated by the addition of the concentrated hydrochloric and sulfuric acids to the starch solution which contains hydrogen sulfide.

III.—The addition of concentrated acid to a starch solution more dilute than that used in the above experiments produces a purple end color.

RECEIVED SEPTEMBER 11, 1917
REVISED JANUARY 10, 1918

THE HANDLING AND TRANSPORTATION OF LIQUIDS ON AN INDUSTRIAL SCALE

LECTURE GIVEN BY THE ROCHESTER SECTION OF THE AMERICAN CHEMICAL SOCIETY at the University of Rochester, Rochester, N. Y. May 21, 1917

THE STORAGE AND TRANSPORTATION OF LIQUIDS

BY FREDERICK R. BENTLEY, of the Vacuum Oil Company

The transportation of liquids in large quantities was started in this country shortly after the beginning of the era of the production of crude oil in commercial quantities, and due to that fact.

As far back as 1781 Lord Dundonald secured an English patent for "A Process of Obtaining Naphtha, Brown or Heavy Oil from Coal by Distillation." In 1830, Laurent in England made paraffine by the distillation of bituminous shale. The following fifteen years witnessed considerable progress in distilling shales, and a patent taken out in England in 1845 describes the purification of the distillates with sulfuric acid and with alkali, the method still used for deodorizing and decolorizing the burning oils.

From 1840 to 1850 many experiments were made both in England and in the United States for the production of a fluid that could be burned for illuminating purposes to take the place of candles. In 1847 Dr. James Young, of Renfrewshire, succeeded in extracting, on a commercial scale, wax and light-burning oil as well as a heavy lubricating oil from a crude oil that flowed from the top of a coal working at Alfreton in Derbyshire. In 1850 he took out his celebrated patent for "Obtaining Paraffine Oil, or an Oil Containing Paraffine and Paraffine from Bituminous Coal." Incidentally this paraffine of the English people is the product we know as "kerosene."

During the next ten years some fifty or sixty coal oil refineries in the United States alone were licensed by Dr. Young to distill both bituminous coal and bituminous shale, and their manufactured products were equal in every way to the foreign articles. The most important of these refineries was the Downer Kerosene Works located at Boston. The word "kerosene" was their trademark, but it persists and is used to-day to designate the ordinary grades of burning oil.

TRANSPORTATION BY BOAT

Experiments had been made in a small way with the crude oil obtained in the Oil Creek region and had established the fact that the kerosene made from the distillation of coal and shale could also be made from the crude petroleum and at a considerable saving in price. The supplying of crude oil therefore to the several refineries (many at a considerable distance from the oil fields) necessitated an increased production and inaugurated transportation in the large way. At first oak barrels holding 40 to 42 gallons were either hauled out by teams to the nearest railroad station where they were placed on platform cars for shipment to the distant refineries, or they were floated on boats down Oil Creek. The boats loaded with empty barrels were towed up the Creek by horses or mules, wading in the stream, there being no tow-path. After filling, the barrels were again loaded on the boats which were released at the next freshet. As a matter of economy, two upright wooden tanks or cisterns holding 2000 gallons each, replaced the barrels on barges and platform cars, and boats having a number of water-tight compartments took the place of the barrel barges.

In 1871 the wooden tanks began to disappear, their place being supplied by the horizontal, cylindrical boiler iron tanks now in general use. Those made in 1880 held from 3000 to 5000 gallons. To-day two- or three-compartment tanks afford capacity as low as 2000 gallons while the largest tanks hold 12,000 gallons. If this latter quantity were filled into 50-gallon barrels,

the average size, three large box cars would be required for its transportation.

The first vessel fitted with iron tanks for the marine transport of petroleum was the wooden ship "*Charles*," which was employed between the years 1869 and 1872 in the trade between the United States and Europe for the transport of crude oil. Her capacity was 794 tons and this was carried in a double row of tanks, 59 in all. Apparently this was either a barge or a sailing vessel, for the statement is made that the first steamer built especially for this trade was completed in 1872. Numerous improvements were made in ocean-going ships, the number of tanks being gradually diminished until eight appears to have been settled on as the proper number of divisions. In 1903 the "*Narragansett*" was completed for the Anglo-American Oil Company. Boverton Redwood says of her: "The '*Narragansett*' is in several respects a notable vessel; she is built of steel, 531 feet long, 63 feet 6 inches broad, 42 feet deep and is fitted with engines amidships. She has a gross tonnage of 9196 tons, a deadweight carrying capacity of 12,000 tons of which 10,500 to 11,000 tons may be held in bulk, and the remainder coal or fuel oil, and her displacement at low draught is over 20,000 tons.

"At that time she was one of the largest bulk oil carriers afloat and one of the heaviest ships ever launched on the Clyde. More notably still is the fact that she can be quickly turned into an ordinary cargo steamer.

"The oil tanks proper, of which there are eight, are situated four forward and four aft of the machinery space and are divided by a longitudinal bulkhead running fore and aft through all the tanks.

"There are four cofferdams situated one at each end of the forward oil tanks and one at each end of the after oil tanks.

"The pumps are of the duplex type, latest available plate pattern and have a combined maximum output of 900 tons per hour. A cargo of 10,800 tons may thus be discharged in 12 hours.

"The engines, which are of the triple expansion type, are of very massive design and develop 5200 I. H. P., giving a speed of 13 knots."

As a matter of information a ton of refined oil (kerosene) is equivalent to approximately 7 barrels of 50 gallons each, so we may figure that the actual number of barrels that may be filled from one cargo of this ship is 75,600.

You will be interested to know that while the Vacuum Oil Company does not own as large a ship as this, it has two tankers in service, one of which compares favorably with it. The "*Bramell Point*" named for the point on the Delaware River at which is located its new refinery, was launched last year and on its second trial trip it was my pleasure to be a passenger. It is a tanker of modern type and is the first commercial motor vessel to be built in the United States. She is a triple screw vessel, driven by three Bolinder oil motors developing 1650 H. P. Her dimensions are: Length, 293 ft.; beam, 47 ft.; depth, 28 ft. When fully loaded she will carry approximately 34,500 barrels of refined oil, her deadweight capacity being 4950 tons.

The other tanker is the "*Paulsboro*," named for the new works just referred to, and is over twice the size of the motor vessel "*Bramell Point*," having a capacity of 11,700 tons. Loaded she will carry approximately 80,500 barrels of refined oil. The "*Paulsboro*" is 435 ft. long, 56 ft. beam and

has a depth of 33½ ft. She is propelled with triple expansion stem engines, single screw and has a speed of 11 knots per hour.

TRANSPORTATION BY PIPE LINE

The first pipe line was 3 miles long and was laid in 1862. It was a gas pipe 4 in. in diameter and with caulked joints. The leakage was so great that little oil was delivered at destination and the line was soon abandoned. In 1865 the first successful line was constructed and was the forerunner of this most useful method of transportation. It connected the Shaffer Farm with Benninghof Run, was of 4 in. pipe and was 4 miles long. All the great oil-producing territories are now connected with the seaboard refineries.

In Russia kerosene is pumped through lines connecting refineries on the Caspian Sea with the open Black Sea. Just one concrete example will be given to show the magnitude of this method of transportation. Crude oil is pumped from the Kansas fields to New York—by relays of course.

I have not obtained definite figures as to the lines between Whiting (Chicago) and Kansas City, but from data feel safe in assuming there are at least an equivalent of two 8-in. lines all the way. A map issued by the Department of the Interior shows two lines all the distance of 450 miles, but not their size, many sections of three lines, a less number with four lines and one considerable distance having five lines. From Whiting to New York the following data on lengths of lines are taken from Redwood's "Treatise on Petroleum." The trunk lines are of various diameters and contain the following number of barrels of 42 gallons each per mile in length:

4 in.	5 in.	6 in.	8 in.
82.07 bbls.	128.23 bbls.	184.67 bbls.	328.24 bbls.

From Whiting to New York the trunks are in pairs nearly all the distance and include:

129.20 miles of 5 in. pipe holding	16,567 bbls.
1316.93 miles of 6 in. pipe holding	243,192 bbls.
624.48 miles of 8 in. pipe holding	204,979 bbls.
900.00 miles of 8 in. pipe from Whiting to Kansas City ..	295,416 bbls.
Total	760,159 bbls.

The average price for the crude oil that is pumped through this line was quoted in May, 1917, as \$1.00. The value of the oil in the line therefore is \$1,444,302. This line must be full of oil before a single barrel can be delivered at the other end; in other words, it represents actual dead capital.

The pipe itself is of special construction, wrought iron, lap welded, tested to 1200 lbs. pressure. The ends are threaded with greater taper than for ordinary work and the unions are correspondingly better made. At distances of approximately 25 miles, pumping stations are located. The oil is usually discharged into tanks from which the pumps draw it and force it along to the tanks at the next station.

As an indication of the capacities of these lines we find the following definite statements:

"The Gulf Pipe Line Company has an 8-in. trunk line from Watkins Station Glen Pool to Sour Lake, a distance of 310 miles. It has a capacity of 1,000 barrels per day.

"The Texas Company has an 8-in. trunk line from Leche Station, Tulsa, to Humble, Texas, the length of which is 170 miles. The capacity of the line is 12,000 barrels daily.

STORAGE

Storage of crude oil, at the wells, is usually in wooden tanks having capacities of 2 to 5 barrels and upward. They are connected with the trunk line through 2-in. pipes and are practically measuring tanks.

As soon as the tanks are pumped the oil is taken away through the trunk line and delivered either into tank cars or into storage. The standard size for the tanks for storage of crude by the National Transit Company is 30 ft. high by 9 ft. in diameter; these hold 15,000 gallons.

Iron tanks are quite generally used for storage in the oil-producing countries, though earthen reservoirs, either clay or timber lined, are not unusual in Russia. In some of the newer fields in this country where it has not been possible to erect wrought iron tanks, before some of the first wells were brought in, earthen tanks are now being utilized. A large concrete lined reservoir has recently been constructed in the Southwest section of our own country for experimental purposes.

The most unique reservoirs, however, will be the ones eventually to be owned by our own government. Secretary Daniels states that when the three years' program of oil-burning naval vessels, authorized by Congress, is completed, the navy alone will require 6,721,000 barrels of fuel oil annually and by 1927 this will amount to 10,000,000 barrels. The present oil reserves Nos. 1 and 2 are located in California and No. 3 in Wyoming. Reserve No. 2 is in proven fields and probably contains above 400,000,000 barrels of oil. The scheme is to hold the oil in nature's great reservoirs safe from fire and wastage until needed. When this time arrives the drills will be started. The one great precaution is to keep "poachers" at a safe distance away from these preserves, because it has been pretty well established that the crude in one lease can be drawn away by an adjoining one.

With a careful selection of such great bodies of crudes and with proper safeguarding, our country can be made reasonably sure of an ample supply of fuel oil for many years to come, and let us hope until the time arrives when it will no longer be necessary to have a fleet of battleships afloat.

TRANSPORTATION AND STORAGE OF LIQUIDS IN SMALL PACKAGES

By I. R. ADKINS of the Vacuum Oil Company

The container next smaller than the tank and pipe line used in storing and transporting liquids is the barrel. The barrel as a unit of quantity is a rather variable standard. According to the old arithmetics it contains 31.5 gallons and this figure is still used in wine statistics. Crude petroleum in bulk is bought and sold and also calculated by the refiner as of 42 gallons. The container in which the finished products are shipped out holds approximately 50 gallons. This discrepancy sometimes causes errors in calculating and is taken advantage of by the unscrupulous Oil Company promoter, who figures a very nice profit on that eight gallons in the size of his barrels from crude oil purchased to gasoline sold.

THE WOOD BARREL

The wood barrel used in the petroleum industry in the Eastern United States is made of red and white oak. Some light pine wood barrels are used for soft storage such as the burning liquid oil goes into oak. These products are made at the works or by independent cooper in the oil regions, Kentucky and Texas, manufactured in the oak forests of Arkansas. The best material goes to the wine barrel people. They barrel some light liquid without so much concern as the softness would be hurt right. The oil men want more barrel capacity to make the barrel make so that small barrels have no one else but no great consequence.

The staves are tapered at the ends to 24 in. diameter, 1 in. thick and from 1 to 1 1/2 in. wide. The heads are of the same size by 18 in. diameter. The staves are put in by hand in a wooden barrel hoop that is driven into the wood by using the barrel to crack and are generally very good. The staves are put on by the cooper's power, driving the hoops. The hoops are formed and riveted carefully.

A good cooper will select barrel staves of the best quality, must take care of the grain of the wood. They will select the best wood, usually from the bottom of the tree, and will select the best wood, usually from the bottom of the tree, and will select the best wood, usually from the bottom of the tree.

make a fair first coating; they fill the pores and prepare the wood for the second coating, which is a heavy one. High-grade hide glue has proved to be the only practical second coat material. It has resilience and elasticity, is unattacked by oil and forms a smooth, impervious coat.

The wood barrel has many good points. On account of its "barrel" shape it can be easily rolled on a fairly smooth surface and will roll by gravity on tracks. Transportation of packages into the warehouses, cars or steamers is thus an easy problem. This barrel can be easily repaired without machinery, with a few special tools by an expert cooper; broken heads, staves and hoops can be easily replaced; the interior can be readily cleaned and reglued. When full, it is a remarkable fire-resistant. It is cheap. It has one great disadvantage, the seeming impossibility of making it do what it is made for—hold liquids without leaking. Aqueous liquids of course swell the wood enough to keep the barrel tight, but oil barrels left out in the hot sun or stored in cool warehouses must periodically have their staves redriven to make them reasonably oil-tight.

THE IRON BARREL

In recent years the iron barrel has been coming more and more into use. These packages are made entirely in large establishments through the outgrowth of smaller stamping operations or recently by companies organized for their exclusive manufacture. They are made in several sizes from 5 to 110 gallons capacity. The 15-, 30- and 55-gallon drums are the sizes used in the petroleum industry. Several patented and unpatented features, such as the form of the chime, the arrangement and kind of faucets and bungs, the use and method of application of hoops, make talking points for the various varieties. These barrels, or drums, as they are ordinarily called, are made from 16- to 19-gauge iron, according to the use to which they are to be put. The lighter drum is usually designed to sell outright to the customer, while the heavier ones are sold on some sort of return basis. Thirty round trips is not too much to expect of a good drum used with care and systematically repaired. In their manufacture the sheet iron is rolled out in heavy shaping machines, the heads are pressed by heavy presses and they are put together in much the same way as all sheet metal containers from pill boxes to dish pans. Gas or electric welding has replaced in recent years riveted seams and tightly pressed chimes, making a tighter, stronger and neater package.

The ordinary "barrel" or bilge form is used in a few iron drums but the greater number of them are cylindrical. The bilge form can be easier rolled on runways and headed up. The cylindrical form, if the hoops are well made, dents less easily and generally stands abuse much better than the other form. The one great advantage the iron barrel has over the wood barrel is that it can be made oil- and naphtha-tight. If not too badly damaged it can be made tight again after puncturing. Its chief disadvantages are that oxide will flake and fall off on the inside, thus contaminating the liquid, particularly if the empty barrel is allowed to become rusty. This barrel is difficult to handle and it is very expensive. The difference in price between the two kinds of packages is of course much greater now than in peace times.

THE TIN CAN

No one has yet invented a satisfactory small container for non-corrosive products to replace the common tin can. It is made in countless shapes and sizes to contain talcum powder, French peas, paint, axle grease and gasoline. The small tin or sheet iron package has driven the small wooden one entirely off the market. Many designs of wood paint kegs which were formerly made have been replaced by metal ones.

Cans for the petroleum trade are made of metal from 26 to 28 gauge, either tin or terne plate. They are made by semi-automatic and automatic machines which cut, shape and solder

with amazing rapidity. The standard 5-gallon can is made in enormous quantities, one of the seaboard refineries having a daily capacity of 120,000 cans. In such cans burning oils and naphthas are shipped to all parts of the world, particularly to South Africa, South America and the Orient. They are packed two cans in a wooden case. These cases can be carried on the backs of animals over mountains and on the backs of men through the jungle where barrel goods cannot be transported. The empty cans are made use of in innumerable ways. A great many of them come back to us from the Orient filled with Soja bean and tung oil. They cover roofs, patch leaky boats, and serve as containers for many substances.

A large business has grown up in recent years in automobile oils. As this is a highly advertised business it is largely a package one. Every cross-road grocery store now carries a few fancy, lithographed cans of oil, grease and soft soap. These cans are usually made more carefully than the unlabeled packages; they have special pour-out spouts and sealing devices for prevention of fraud.

The transportation of cased goods in the refinery and warehouses has been developed very highly. Special elevators, belt and roller conveyors carry empty cans and full cases from floor to floor, building to building, into box cars and into the holds of ships with very little handling.

Before the advent of the automobile, "oil" to the average layman meant kerosene, linseed, or the small bottle on the pantry shelf labeled "Sewing Machine Oil, will not gum," which was used also on the lawn mower, door hinges, razor strop and bicycle. Many thousands of these small bottles are sold for domestic lubricating purposes each year. The total volume of oil in them is small, however, as a 2-doz. case of 4-oz. bottles contains less than one gallon. Their sale is more of a grocery and drug-store business, discussion of which would carry us far beyond any reasonable limits of the transportation and storage of liquids.

THE HANDLING AND TRANSPORTATION OF LIQUIDS

By M. H. EISENHART, of the Eastman Kodak Company

This question of the handling and transportation of liquids on an industrial scale is one which necessarily must absorb considerable attention and thought in normal times, and especially is this so now, when the chemical industry generally is being so greatly expanded in this country. The developments along this line are taking place so rapidly that many materials, which only yesterday perhaps we were concerned with in the smaller laboratory way, to-day we may be handling in lots of many tons. This question then of the handling on a large scale of some new chemical or even one with which we are very familiar, necessarily means the investigation and use of many new processes, which in turn means a study of the many problems of how best large quantities of liquids can be handled for the particular end desired. This problem pertains to many different kinds of chemicals, such for example as very light liquids or oily materials, the heavier viscous oils, liquids carrying solids in suspension, acids or corrosive liquids, etc., and it is the last of these, namely acids and more particularly nitric and sulfuric acids with which this paper is concerned.

For the sake of convenience, I have chosen to look at the subject from two separate angles:

I. TRANSPORTATION BETWEEN PLANTS—If, for example, you are operating a plant here in Rochester and find it to advantage to purchase large quantities of sulfuric acid in Buffalo, Cleveland, or even farther away, then, of course, somebody must concern himself with how that acid is to be gotten here.

II. LOCAL TRANSPORTATION—For example, you have a stock of sulfuric acid on hand at the plant, how are you storing it, how do you inventory it, how do you get certain quantities when you want them, how do you weigh it for use, how do you get

it from one building to another, etc.? These, of course, all sound simple, but at times the simplest chemical to handle, at least as you would suppose, may puzzle one the most before just such questions can be answered.

TRANSPORTATION BETWEEN PLANTS

For all the smaller quantities of liquids there is, of course, available the carboy or drum. For C. P. acids, carboys must necessarily be used for obvious reasons; and in fact where C. P. nitric or sulfuric acids are used in large quantities, the carboy is always used. If, however, purity is not a prime factor, then drums, and in even larger shipments, tank cars are used. While the initial expense in the use of cars is quite heavy, yet it is quite easy to realize that the saving in the loading and unloading of a carload of say 40 to 50 drums is beyond comparison.

The drums are either pumped out direct or dropped into a tank from which the liquid is then pumped. A tank car can be either pumped out direct or can be piped up and the compressed air turned on. This is quite a common method for unloading cars and by the application of 20 to 25 lbs. a car can soon be emptied. Since these tank cars are the property of the concern making and selling the acid, the man buying the acid is only interested in the simplest and most satisfactory and economical way of getting it out of the car, and distributing it for storage or use. Other acids, such as acetic, hydrochloric, etc., are generally handled in the small containers, the former for example often being shipped in wooden barrels.

LOCAL TRANSPORTATION

In considering this phase of the question several very evident subdivisions suggest themselves:

- (1) Types of liquid to be handled.
- (2) Kind of metals or other materials to be used.
- (3) Means of power to be used.
- (4) Type of valve to be used.
- (5) The question of measuring or weighing.

The headings show at once how much more there is to this part of the study than to the first part, because of the larger number of individual problems which must be solved. And now let us look these over in order:

(1) TYPE OF LIQUID TO BE HANDLED.—If we are concerned with acids only, then we must consider the handling of a corrosive and probably thick liquid. Besides this, however, we may be asked to handle a thin solvent such as alcohol, or a thick, heavy, pasty solution such as a nitrocellulose solution, or a liquid carrying some heavy salt in suspension. These conditions are all of the utmost importance, not only to aid in coming to the decision as to what kind of power can be used, but also to the other more important question as to what kind of containers, pipes, pumps, etc., will stand up in the particular case. This question of the type of liquid to be handled is really the basis of this whole subject, for as you think over the matter you will soon see that it is the determining factor, in not only this consideration of metal or material to be used, and the kind of power as just stated, but also in the selection of valves to be used as well as in the question as to what method of measuring or weighing can be employed.

CHOICE OF METAL OR OTHER MATERIAL TO BE USED FOR THE CONTAINERS, PIPES, VALVES, AND IN FACT ALL APPARATUS WHICH COMES IN CONTACT WITH THE LIQUID UNDER CONSIDERATION.—I might say that anyone having to do with a chemical plant in which new problems are continually coming up for solution, can follow no better practice than to start first with small samples of various metals or other materials, when working with liquids, which may eventually be handled on a commercial scale. It is advisable to do this so that these questions can be answered by the time the laboratory investigations have reached such a point that the chemical engineer is prepared to adapt the whole process to a commercial scale. Quite frequently you may find that unless you have such information available, and it can very seldom

be gotten as you need it from any books, you may make heavy investments for apparatus which must only too soon be torn out and entirely replaced with something of a different nature. We are accustomed, from time to time, as a new problem arises which involves some new chemical or even chemical combination, to cut small strips of various irons, copper, nickel, tin, aluminum, etc., of say $1\frac{1}{2} \times 4$ or 5 in. and to suspend these half immersed in a small bottle of the material under consideration. A record is then made periodically of the different effects both by the liquid itself and by the fumes.

Iron and Steel—All things considered, undoubtedly iron in one of its various forms, such for example, as cast or malleable iron, steel, or the more recent alloys of iron with silica, is the most common of the metals employed in the chemical industry; and rightly so, for there are now comparatively few processes in which it cannot be used. For the great quantities of sulfuric and mixed acids now being used in nitrocellulose manufacture, steel is almost exclusively employed. Of course for nitric alone, it is not suitable, but as this is always handled for this work in a mixture with sulfuric, steel can well be used. And now the introduction of the alloys of iron and silica which have come on the market under the trade names of Duriron, Tantiron, Buflokast, etc., has made it possible to handle much weaker grades of sulfuric acid as well as nitric alone. I might say that the discovery of these irons and the willingness of some of the firms making them to cooperate with those running chemical plants have made many of the most troublesome problems very easy. In places, where up until recently it has been necessary to use stoneware, with its high breakage and other attendant difficulties, we can now use these special cast irons and apparently can see no reason for any further anxiety. A very good example of this is the condensation of vapors during the manufacture of nitric acid. Of course, besides for all these large quantities of acids, iron and steel are the most used metals in the alkali industry.

Stoneware, Glass and Silica Ware—The stoneware industry plays even yet a big part in the chemical manufacturing line, but it is not what it was a few years ago. As stated above, the high silica irons have displaced many of the old stoneware installations. I feel pretty well convinced that the time will come when there will be very little of it used. We find for instance where we have occasion to handle very hot weak nitric acid that we can now almost completely displace the stoneware. This means a big saving financially, not only because of the breakage of the stoneware itself, but also when you consider that to replace any piece of apparatus means necessarily an interruption in the output of the plant, which may be even much more costly and inconvenient. As for glass, it still remains a very important and necessary factor in the production of C. P. chemicals. Closely related to it is the silica ware, which is now extensively advertised. This is just as fragile as glass, but has the additional advantage of being able to stand up to extreme thermal changes without breaking. These materials, naturally, are used only where absolutely necessary for any reason.

Wood—For the handling of weak acid solutions wood is very well adapted. For heavy handling in more corrosive solutions also be used very well. Thus there are the common staves, lined by half and full valve wooden pumps, and so on, well adapted for certain types.

Aluminum—While it is not possible to handle very strong sulfuric acid, aluminum will stand up to most acids, and especially to alkalis. As an example, the nitrocellulose process, where the aluminum can be used with the very hot acid, is a very suitable one for the handling of such strong acids in a commercial plant. The great advantage of aluminum is that it is not attacked by the fumes of the acids.

It is not possible to handle very strong acids in steel, and

done, for example, by the Pfaudler Company here in this city, has wrought a complete transformation in many industries, such, for example, as the breweries. All sorts of big tanks which were previously made of wood have now been replaced with this enameled iron. Besides all kinds of big tanks enameled-lined, this ware is more and more being applied in kettles, piping and all manner of special apparatus. It is particularly adapted for use in the hauling of edibles and drinks, and it is found to give very satisfactory results, where its use is possible.

Copper—I merely mention this, as it is not applicable at all for practically any acid work, except acetic.

Lined Pipes—Because of the rapid strides which have only recently been made in the lining of pipe with tin, copper, lead, etc., and the satisfactory resulting product, I must mention it here. For example, in nitric acid work, where ordinary lead pipe is used, it is very possible that this lead-lined iron pipe would be more satisfactory.

(3) **MEANS OF POWER TO BE USED**—After solving the problem as to what kind of container shall be used for handling any liquid, of course the next question is, what means shall be used to move it from one point to another?

Gravity—Wherever possible it is naturally advisable to arrange the layout of any plant so that liquids as well as solids can be moved through each successive step of the process by gravity, which, of course, leaves nothing to get out of order and no cost for power. It is only in comparatively few plants, however, that this is possible, and it is with the others, which we will now concern ourselves. Of these, we have *Syphon*. This can be used and is quite frequently, even when air pressure is used. It can be used very nicely where liquids are lowered from an elevated tank to one below or even to one about on its own level. Alone, however, the syphon is not entirely dependable for large work.

Air Pressure is probably as simple a method of moving liquids in general, and nitric and sulfuric acids in particular, as can possibly be found. It is true that a compressor is needed, which means the operation of blowing acids, and is probably not as economical as to pump them; but the blowing operation is much more simple and considerably less trouble. For this work, where large quantities of acids are handled, it is customary to have what is known as a blow-egg or tank of steel or cast iron below the level of all the other tanks and lines in the installation.

Then by gravity the liquid to be drawn can be dropped into the egg, and, under pressure, depending on the distance and height to be delivered, it can be blown any reasonable distance. For delivery to any distance, it is more advisable to elevate almost vertically and then flow by gravity. With this system, of course, the tank must be equipped with the necessary air inlet, and liquid inlet and outlet as well as a vent.

Pump—In a good many cases gravity or air pressure may be impracticable or even impossible, and hence you must use a pump of some kind. Here again, as I stated above, the discovery and use of high silica irons has helped to solve many knotty problems. Special pumps, for example, are now pumping materials for which it has always been necessary to use stoneware. Taken for granted that it is necessary to pump the liquid, you must then decide, shall it be a centrifugal or a regular steam pump? The answer to this depends entirely on the local conditions. We find in our work that the centrifugal has advantages in one place, while the steam cylinder pump has them in another, and as a result we have both types well represented.

Injector and Air Lift are merely mentioned at this time.

(4) **TYPE OF VALVE TO BE USED**—The question of valves in any commercial installation sounds very simple and as a matter of fact is so in most cases; however, in acid work, it is a source of considerable anxiety and worry if you are concerned with exact weights and inventories. We have found that in certain cases where a certain make of valve might stand up very well against the liquid itself, on the other hand, if it were in contact with the fumes it would soon lose its effectiveness. Here once again high silica iron has shown fine results. Plug-cocks of this material we have had in use in certain very bad positions for 3 or 4 years, with no apparent wear, while previously we would replace the ordinary valve every 3 or 4 weeks.

(5) **MEASURING OR WEIGHING**—In any well managed plant it is, of course, of the utmost importance that all liquids used in the various processes shall be accurately weighed and accounted for. As stated above, an effective valve is absolutely essential for this. We weigh practically all our acids as used, and for this purpose have a tank located right on the scale platform. For some work, we rely entirely on measurement in the tank and for this have the tanks fitted up with sight glasses. For this, of course, the temperature should not vary greatly or there will be a large error introduced.

CURRENT INDUSTRIAL NEWS

HARDENING OF WATER-GLASS PAINTS

The quickened hardening of water glass paints into an impervious layer is the subject of a lately reported German patent. The paints are mixed with an alkali bicarbonate or other material yielding carbon dioxide on heating and are heated just before use. The finely divided silicic acid uniformly separated out gives increased viscosity to the mixture. The covering properties are not affected and, within twelve hours after application the paint forms a firm waterproof and weatherproof coating.—A. MACMILLAN.

JAPANESE COPPER ORE

The output of copper ore in Japan in 1916 amounted to 111,562 tons as compared with 83,017 tons in 1915 and 78,700 tons in 1914, while exports amounted to 57,462 tons in 1916 as against 56,528 tons in 1915, and 43,305 tons in 1914. Russia now buys most of Japan's copper ore, her purchases amounting to 60 per cent of the total exports. The United Kingdom takes 20 per cent, while France, the United States and India share the balance, but their dealings are not large.—M.

SPITZBERGEN COALFIELDS

Hopes had been expressed in these times of international coal famine, says *Engineering*, 103 (1917), 590, that the Spitzbergen coal deposits might help at least the Scandinavian countries, but matters do not seem to progress very favorably. The contemplated Norwegian company for the exploitation of the so-called Svalbard coal fields at Advent Bay and Green Harbour with a capital of \$850,000 has not materialized, the funds not being fully subscribed and money not being found by other methods.

The scheme, principally started by Norwegian shipowners, has been abandoned in the original shape, but a company will be formed to protect the rights in question. It remains to be seen whether the Swedes will be more successful. The Swedish expedition for coal mining is about to start and comprises about 150 men, of whom 100 are to winter there. For the present year only a few thousand tons of coal are expected to be worked, but a great deal of preparatory work has to be done before rational coal mining on a large scale can commence.

M.

JAPANESE WHALING INDUSTRY

The British Commissioner at Yokohama reports that whaling in Japan waters is carried on under license from the Government, the number of whalers being restricted to 30, of which one company owns 24. There seems little prospect of the number of vessels being increased at present.

The whalers are steam vessels of about 100 to 150 tons and are built after the Norwegian whaling type. The boats seldom venture out more than 50 or 60 miles from land and remain out a day or so at a time. The varieties of whale mostly caught are the sperm and sulfur bottom.

According to the report, the estimated number of whales caught in 1916 was 1,400, valued at \$1,150,000, compared with 1,710, valued at \$1,064,809, in 1915, and 1,700 worth \$1,412,465 in 1914. The approximate yield of whale oil in Japan is stated to have been 2,500 tons in 1913, 4,500 tons in 1914 and 5,500 tons in 1915.—M.

ASBESTOS-CEMENT ROOFING

In the course of the last 12 months, says the *Times Engineering Supplement*, No. 512, a factory has been built and equipped by the British Everite and Asbestilite Works, Lancashire, for the manufacture of asbestos-cement products, especially corrugated sheets for roofing, which in the past have been largely imported from abroad.

After being finely ground and freed from extraneous matter the asbestos, which acts as a reinforcing agent, is mixed with Portland cement in the proportion of about 1 to 6, and made into a kind of paste with water. This paste is then taken to a machine of the paper-making type, where, on a large revolving drum, it is formed into sheets or felts. After being trimmed to size, these sheets, if they are to be made into corrugated roofing, next have the corrugations impressed on them, the important condition of this operation being to ensure that the tops of the corrugations are as strong as other parts of the sheets. Finally, the sheets are subjected to a seasoning process.

The corrugations are made to the 3-in. pitch, which is usual with corrugated iron sheeting, not to the $2\frac{1}{2}$ -in. foreign pitch, and they can therefore be used to repair roofs composed of corrugated iron sheets. One of the chief advantages claimed for them is durability and resistance to climatic conditions, especially to an acid-laden atmosphere which rapidly destroys corrugated iron; they are also fire-proof and poor conductors of heat.

The factory is well situated as regards supply of water, of which large quantities are required. The machinery is driven by electricity, current being obtained by means of a 250 H. P. National gas engine, and the power house is designed so that additional sets can be installed as the manufacture develops.—M.

JAPANESE GELATINE AND GLUE

The importation of gelatin and glue, says the *Chemical Technology of Tokyo*, had increased in amount to 5,000,000, and the quick development of the paper-making, cloth-making, sweets-making and match industries has demanded more and more importation, but the manufacture of the gelatine and glue at home has also quickly developed. Research work has been begun at Tokyo, Osaka, Wakayama, Nara and Tokushima. Among the new establishments, the Tokucho Kogyo Kaisha, Ltd., at Kawanishi, the largest, is going to produce 1,000 lbs. of gelatine and 1,000 lbs. of glue monthly. This amount will well build the home demand. Furthermore, the Osaka Akiba Company is going to start the manufacture of gelatine, while the Mitsubishi Company is planning a big firm at Takasago. The big firms will certainly bring a big surplus against the home trade, and so it is anticipated that there will be certain gains in the near future, unless a proper market is found.—M.

NEW PLASTIC MATERIAL

India Rubber Journal, 53 (1917), 2, describes a French invention for a new plastic material which is non-inflammable and odorless. The material is obtained by transforming gelatines, glues and such substances of animal origin by suitable chemical reagents, giving them plastic and malleable properties which allow them to be used industrially in a manner similar to natural products. The gelatines or glues are first melted in a water bath at a temperature of 90° C. A decoction of hop flowers is then prepared and mixed with dilute oxalic or any dibasic acid of that series and the solution is added to the melted gelatines or glues in varying proportions according to the quality of the materials employed. The addition of this solution has the effect of rendering the gelatine more supple and of causing the impurities they contain to deposit at the bottom of the vessel. When the gelatines are liquefied they are poured out in the form of sheets or sticks of the desired thickness and left to dry in the cold air.

The coloring of the material is then proceeded with, natural or artificial dyes being employed. The sheets, when colored, are plunged into a bath of approximately the following composition: 25 to 35 per cent formaldehyde, 25 to 35 per cent water, 25 to 35 per cent alcohol and the rest composed of a mixture of oxalic acid, tannin and glycerine. The oxalic acid may be replaced by any other acid of that series. The plates should be left in this solution until the liquid has penetrated into the entire plastic mass. In the case of rich gelatines, the proportion of alcohol must be increased. The sheets when taken out of the bath are dried, preferably in hot air. The substance when suitably worked may serve for the manufacture of combs, buttons, brushes, etc., as an imitation of tortoise shell, horn, amber or ivory, and is unlike other cellulose products used in industry, in being absolutely non-inflammable and odorless.—M.

TUNGSTEN ORES IN RHODESIA

According to an article in *Mining Journal*, 117 (1917), 416, occurrences of tungsten ore have been known for a considerable time in Rhodesia, though they have never been worked save in a desultory fashion. Prospecting was begun as far back as 1906, but in 1909 all work was abandoned. Another attempt was made in 1912-13 and, during last year again, the demand for the material caused attention to be devoted to this locality. The occurrences, which are known, have been found close to the Essex Vale siding and 16 reefs have been located, 11 of which have been at one time or another worked and concentrates to the amount of 88 tons obtained. In addition to the rocks, there are also alluvial patches, but it does not appear that any extensive development has been done.

A report has recently been issued by the Rhodesian Geological Survey in which the geology and mineralization is discussed.

The mineral appears to be found entirely in quartz, similar to the ordinary vein quartz of the gold deposits. In one instance, at Tumbon Koppe, a small work was begun but soon abandoned, but, for the most part, the quartz is lenticular. Large bunches of wolfram ore (100 lbs. weight) of these dimensions (14 in. and 17 in.) have been found in the same rock when weighing up to 8 lbs. are not uncommon. Both wolfram and scheelite occur, the crystals being frequently irregular. The scheelite seems to be in the form of a druse, and the rock and its associated veins have served as a nucleus for the collecting of quartz. In some of the alluvial patches, also, there is a little of the quartz, excluding the large bunches of scheelite. Considerable work had been done when the war broke out, and a great amount being described in the report of the survey. These specimens, both of scheelite and wolfram, are in the form of small, thin, flat, rhombic crystals, some of which are possibly the result of secondary alteration of the primary material. The report is published in a pamphlet, for further information.—M.

AN ADVANTAGE FOR THE GAS-ANNEALING FURNACE

In these days of scarce and dear sulfuric acid, says *Gas World*, 66 (1917), 522, when endeavors are being made to substitute nitre cake in many processes, it would appear that an additional merit has been found in the gas-annealing furnace. In a paper before the Birmingham Society of Chemical Industry, Dr. H. W. Brownson, giving his experience with nitre cake in the pickling of annealed brass, says that, according to the conditions of annealing, the brass may be clean, practically free from superficial oxides and of a brassy lustre, or it may be dirty, black in color and badly stained through oxidation and contact with injurious furnace gases. Given clean work, nitre cake replaces dilute sulfuric acid quite efficiently, the nitre cake being, of course, applied as a solution. With dirty work, the difference is much more marked and nitre cake solution, even under the most favorable conditions, may fail to pickle the work satisfactorily. In the latter case, the use of nitre cake in place of sulfuric acid becomes a serious handicap and deterrent to rapid production, especially when manufacture consists of a sequence of mechanical operations between each of which the product has to be annealed, pickled and cleaned.

From the point of view of economy in future developments, with ruling prices in England, at present, of \$20 per ton for sulfuric acid and with nitre cake at \$5 per ton, there is not much to choose but the economy of metal which would result from the more general use of muffles annealing bright and clean would be considerable and, if the use of nitre cake forces us to pay more attention to economical annealing conditions, it will have achieved indirectly some good purpose. The cleanliness and easy regulation of the gas-heated annealing furnace should make themselves felt here. —M

SYNTHETIC RUBBER FROM CARBIDE

The manufacture of acetone with a view to the production of synthetic rubber is of considerable importance in Germany at present. The importance of this industry, says *Chemical Trade Journal*, 61 (1917), 26, is indicated by the fact that some of the largest firms in Germany, such as the Konsortium für Elektrochemische Industrie of Nürnberg, the Elektrotech. Werke of Bitterfeld, the Farbenfab. of Bayer & Co., Griesheim, and others, have been occupied with this problem for some years. There are firms in Germany producing 10 to 50 tons of carbide per day in order to convert the acetylene into acetic acid and acetone, the latter being intended chiefly for the production of synthetic rubber.

This new industry should be of special interest to Switzerland, since the necessary carbide will in the future be available in large quantities in that country. After the war, the export of carbide will be considerably reduced and this product will, therefore, become much cheaper. On the other hand, the price of rubber will remain high for several years.

In order to protect this young industry, it is suggested that Switzerland should impose a duty on imported rubber, since the countries which export crude rubber will doubtless put an export tax thereon. —M

ESTIMATION OF BENZOL IN GAS

Dr. Ott, of the Zurich gasworks' laboratory, has been trying Neubek's method of freezing out benzol from gas with solid carbonic oxide and has found it to work very well. It gives a condensate unmixing with oily matter but, as it has a specific gravity of only 0.852 at 17° C., it probably contains lighter components dissolved out of the gas. The method enables a uniform temperature of 0° C. to be repeated and maintained in successive experiments. —M

BROWN PAPER FOR LEATHER

Under the provisions of the long-delayed Footwear Regulation Act, says the *Melbourne Age*, the people of Australia will be entitled the protection against the audacious swindling which has led to the substitution of brown paper for leather in certain classes of boots. The Law provides that they may ascertain whether the boots offered them by the mender are made of genuine leather or of mere shoddy. The sole of a boot or shoe must be stamped with particulars of the material of which it is made. The Act, unfortunately, is not to operate at once. Parliament decided to allow the trade six months within which to get rid of old stocks of shoddy material before the coming into force of the measure. The Chief Secretary said recently that the act would operate from July 1st and there would be no postponement. —M

PROJECTION OF BOMBS

When a bomb is dropped from a moving aeroplane the point at which it strikes the earth depends primarily on its altitude above and speed with respect to the earth's surface, and to a smaller extent on the speed of the wind and the mass and surface of the bomb. In order to allow the aviator to drop his bomb on a given object, the most recent German aeroplanes are provided with an instrument made by Goerz, which consists of a telescope kept vertical by means of a bubble of air in the eyepiece.

By means of a movable prism below the objective, the observer can adjust his instrument, so that he sees objects through it at a given angle ahead or in the rear. The instrument is generally used when the aeroplane is moving against the wind. From the aneroid reading of the height of the aeroplane and the time taken to get vertically over an object seen previously 22.5° ahead, the speed of the aeroplane is known. The speed of the engine gives the speed of the aeroplane through the air so that the speed of the air is known and for a given bomb the angle at which the line of sight of the instrument must be ahead in order that a bomb released when the object is seen in the telescope may strike that object is also known.

Variations of direction of flight of the aeroplane and of strength and direction of the wind cause errors which are to some extent eliminated by further devices which are described in *La Nature* for June 19.—M

BRITISH BOARD OF TRADE

During the month of July inquiries have been made by firms in the United Kingdom and abroad concerning the following articles. Firms able to give information regarding sources of supply of these articles are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.

Bangles and bracelets, imitation silver	Machinery for making leather
Beads, imitation	Machinery for making glass beads
Brace wire brushes for goldsmiths	Machinery for plaiting cane
Carbon electrodes	Machinery for making basket chairs, etc.
Circular saws, 3 in. diameter and 3/4 W. G.	Made of soda
Coffetti	Nitrate of soda
Citrate of iron and ammonium (500 kil. for export)	Pendants, for African trade
Clock escapements for ships' lever movements	Persulfate of soda
Diamond dies for wire drawing	Piercing saws for metal
Drawing pens	Pony hair, fine brown, Japanese or other, for camel hair
Enamelled kettles	Pencils for medical trade
Fine silver chain, machine made	Rubber tabs for sock suspenders
Glove stretchers, boxwood	Stamped brass coats of arms, size about 8 1/2 in. X 6 1/2 in.
Gramophone motors	Silver, bags, ladies
Gilt guard chains	Steel and brass pins, fine
Granular-ink charcoal	Schools chalks
Machinery, s.s. 10 x 1/2	Tin, brass and copper linings and angle plates for ammunition boxes
Boilers designed for using peat as fuel	Thimbles
Gas generators designed for peat	Wood tar
Machinery for excavating and handling peat	Yellow ochres suitable for grinding zinc sheets 14 gauge for war work
Paints for tanning machinery, for treating leather waste	

—M

SCIENTIFIC SOCIETIES

CALENDAR OF MEETINGS

- National Wholesale Druggists Association**—Annual Convention, Chicago, October 1 to 4, 1917.
- American Electrochemical Society**—Autumn Meeting, Pittsburgh, October 3 to 6, 1917.
- National Paint, Oil and Varnish Association**—Annual Convention, Chicago, October 8 to 10, 1917.
- American Institute of Mining Engineers**—Annual Meeting, St. Louis, October 8 to 13, 1917.
- American Gas Institute**—Washington, D. C., October 16 to 19, 1917.
- American Society of Mechanical Engineers**—New York City, December 26 to 29, 1917.

FIFTY-FIFTH MEETING AMERICAN CHEMICAL SOCIETY BOSTON, SEPTEMBER 10 TO 13, 1917

PROGRAM OF PAPERS

GENERAL SESSION

- Address of Welcome.** DR. R. C. MACLAURIN, President of Massachusetts Institute of Technology.
- Response.** JULIUS STIEGLITZ, President of American Chemical Society.
- American-Made Optical Glass.** ARTHUR L. DAY, Director Geophysical Laboratory, Washington, D. C.
- The Isolation and Identification of the Iodine-Containing Compound which Occurs in the Thyroid.** E. C. KENDALL, Mayo Clinic, Rochester, Minn.
- General Conference on Chemists and Chemistry in Warfare**, opened by WILLIAM H. NICHOLS, Chairman of Committee on Chemicals, Council of National Defense, and MARSTON T. BOSSERT, Chairman of Chemistry Committee, National Research Council.
- President's Address.** The Outlook for Chemistry in the United States. JULIUS STIEGLITZ.

AGRICULTURAL AND FOOD CHEMISTRY DIVISION

- T. J. BRYAN, *Chairman* G. F. MASON, *Secretary*
- The Effect of Granulation of Flour on the Baking Quality. J. A. LECLERC, H. L. WESSLING and L. H. BAILEY.
 - The Composition of Japan Rices (Natural Brown and Polished) from the Standpoint of Food Conservation. J. A. LECLERC and R. M. BOHN.
 - Pearl Barley, from the Standpoint of Food Conservation. J. A. LECLERC and C. D. GARBY.
 - The Use of Substances as Part-Substitutes for Flour in Bread-Making. J. A. LECLERC and H. L. WESSLING.
 - The Composition and Baking Quality of Flour Made from Einkorn, Emmer, Spelt, and Polish Wheat. J. A. LECLERC and L. H. BAILEY.
 - Influence of Season upon the Deterioration of Food Samples. C. A. BROWNE.
 - Bureau of Markets in Relation to the Conservation of Foods. C. BRAND.
 - Investigations of Shoe Soling Materials. (By title) F. P. VITCHEL, J. S. ROBERTS and R. W. FRYE.
 - Blue and Brown Print Paper; Characteristics, Tests, and Specifications. (By title) F. P. VITCHEL, C. FRANK SUMMITT and E. G. RHOE.
 - Studies on Mustards and Mustard Substitutes. A. VIMHOFER, C. O. EWING and J. E. CHANDLER.
 - The Conservation of Poultry and Eggs. MARY E. PENNINGTON.
 - Practical Food Conservation. A. M. G. SOULE.

BIOLOGICAL CHEMISTRY DIVISION

- C. L. ALBRIGHT, *Chairman* I. K. PHILLIPS, *Secretary*
- I. Special Program on Enzymes and Their Behavior
- Oxidase Action on the Nucleus. W. J. V. OSTERHOUT.
 - The Adsorption of Flour Enzymes by Gluten Colloids. R. W. THATCHER and CORNELIA KENNEDY.
 - Catalytic Poisons. W. D. HANCOCK.
 - False Equilibrium. W. D. HANCOCK.
 - Surface Relations of Enzymes. G. H. A. CLOWES.
 - Notes on the Determination of Urea by Urease. I. F. HARRIS.
 - Studies on Peptic Digestion. H. T. GRADNER and I. W. M. HUNTER.
 - Some Enzyme Reactions as Influenced by Hydrogen-Ion Concentration. J. H. LOSE.
 - A Chemical Study of Enzyme Action. K. G. FAIR.

II—Papers

- The Origin of the Humin Formed by the Acid Hydrolysis of Proteins: III. Hydrolysis in the Presence of Aldehydes; II. Hydrolysis in the Presence of Formaldehyde. R. A. GORTNER and G. E. HOLM.
- The Effect of Prolonged Acid Hydrolysis upon the Nitrogen Distribution of Fibrin. R. A. GORTNER and C. E. HOLM.
- Comparative Analyses of Fibrins from Different Animals. R. A. GORTNER and A. J. WURTE.
- The Nitrogen Distribution in Protalnic and Lysalbinic Acids. CORNELIA KENNEDY and R. A. GORTNER.
- On the Relative Imbibition of Glutens from Strong and Weak Flours. R. A. GORTNER and E. H. DUFFERTY.
- The Nitrogen Distribution in Fibrin Hydrolyzed in the Presence of Ferric Chloride. C. A. MORROW.
- Copper Phosphate Mixtures as Sugar Reagents. O. FEJEN and W. S. McELROY.
- Dynamics of Photosynthesis. W. J. V. OSTERHOUT and A. R. C. HAAS.
- The Dynamics of the Process of Death. W. J. V. OSTERHOUT.
- Note on the Physiological Action of Cordyrops Sinensis. C. L. ALBRIGHT and J. F. BREWSTER.
- Biological Effects of Ultraviolet Rays of Extremely Short Wave Lengths. W. T. BOYDE and D. N. HUGHES.
- Action of Ultraviolet Rays on Complement. W. T. BOYDE and C. WILLIAMS.
- Contributions to our Knowledge of the Abiotic Action of Rays from Radio Active Substances. W. T. BOYDE.
- An Improved Direct Reading Potentiometer for Measuring and Recording both the Actual and the Total Reaction of Solutions. W. T. BOYDE.
- A New Logarithmic Paper for Plotting Ion Concentrations. W. T. BOYDE.
- The Necessity for Revision and Standardization of the Terminology of Colloid Chemistry. A. W. THOMAS.
- Premedical Training in Chemistry. F. S. HAMMETT.
- The Influence of Phosphates on the Action of Alpha Crotonic Acid on Plants. I. I. SKINNER and F. R. REID.
- The Oxidation of Vanillin to Vanillic Acid by Certain Soil Bacteria. W. J. ROBINSON and E. C. LESTER.
- The Symptoms of Potash Starvation in Field Crops. O. SCHREINER.
- The Hydrolysis of Kaffrin. D. B. JONES and C. O. JOHNS.
- The Proteins of Buckwheat. C. O. JOHNS and L. H. CHERNOFF.
- Relationship between Cholesterol and Cholesterol Esters in the Blood during Fat Absorption. ARTHUR KNUDSON.
- Further Experiments on the Isolation of "Vitamine" from Yeast. ARTHUR SEIDEL and R. R. WILLIAMS.
- An Alkaloid from *Impatiens* *capensis*. O. F. BEAVER.
- Is Polished Rice Plus Yeast Vitamin "Sured" a Complete Food? A. D. EMMETT and L. H. McKIM.
- The Growth Promoting Value of the Lactalbumins Obtained after Separating Casein by (a) Hydrochloric Acid and (b) Lactic Acid Culture. A. D. EMMETT and M. E. SEIDEL.
- The Influence of Accessory Substances on Growth with a Low Protein Ration Containing Lactalbumin from Lactic Acid Whey. A. D. EMMETT and M. E. SEIDEL.
- On the Histology and Chemistry of Secretory and Nectary Glands of the Cotton Plant. A. VANDERHOEF and E. E. HENNING.
- Studies on Edible and Poisonous Beans of the Lima Type. A. VANDERHOEF, C. O. EWING and M. G. MAGLIS.
- Oxalic Acid in Foods and Spices. A. VANDERHOEF, A. F. KILPATRICK and M. G. MAGLIS.
- A New Form of Ultra-Filtrate. Its Uses in Biological and Synthetic Organic Chemistry. P. A. KILPATRICK and W. C. HARRISON.

INDUSTRIAL CHEMISTS AND CHEMICAL ENGINEERS DIVISION

- H. E. HIGGINS, *Chairman* H. J. HARRISON, *Secretary*

I—Papers

- The Cracking of Solvent Naphtha in the Presence of Blau Oxide. C. E. HARRISON.
- The Effect of Pressure upon the Formation of Benzene and Toluene from Gas Oil. C. E. HARRISON.
- An Experiment in Scrubbing Carbonated Water Gases for Removing Aromatics. J. HARRISON, J. M. HARRISON and J. HARRISON.
- The Deposition of Silver Films on Glass. A. HARRISON, HARRISON and R. M. HARRISON.
- Some Notes on Chars and Other Solid Destructing Agents. C. E. HARRISON.
- Comparative Tests of Porcelain Laboratory Ware. C. E. HARRISON.

7. Comparative Tests of Chemical Glass Ware. PERCY H. WALKER AND F. W. BAKER.
8. Potash Recovery from Greensand and Feldspar and By-Products Therefrom. H. W. CHARLTON.

II—Metallurgical Symposium

1. Some Problems in the Metallography of Steel. H. M. BOYLSTON.
2. Stellite as a Substitute for Platinum. ELWOOD HAYNES. (See page 974.)
3. The Effect of Annealing on the Electrical Resistance of Hardened Carbon Steels. J. P. PARKHURST.
4. Physico-Chemical Data Needed by Metallurgists. J. W. RICHARDS.
5. Recent Developments in Connection with the Use of Sulfur Dioxide in Hydrometallurgy. EDWARD R. WEIDLIN.
6. The Importance of the Flotation Process in the Metallurgy of Copper. E. P. MATHEWSON.
7. The Theory of Froth. WILDER D. BANCROFT.
8. Chemicals Used in Ore Flotation. OLIVER C. RALSTON AND L. D. YUNDT.
9. The Selective Action of Cadmium Salts on Lead and Zinc Sulfides in Flotation. M. H. THORNBERRY.
10. Flotation Experiments on Zinc Sulfide Tailings. W. A. WHITAKER, S. F. FALEY AND H. P. EVANS.
11. The Development of the Iron-Carbon Diagram in Its Relation to Microscopic Analysis and the Heat Treatment of Steel. JOHN W. ALDEN.

III—Conference. The Industrial Chemist in War Time. (See page 987.)

ORGANIC CHEMISTRY DIVISION

J. R. BAILEY, *Chairman*

H. L. FISHER, *Secretary*

I—Joint Session with Physical and Inorganic Division

II—Papers

1. The Constitution of Dicyandiamide. WILLIAM J. HALE.
2. The Composition of Oil of Cassia. (By title.) FRANCIS D. DODGE.
3. The Decomposition Products of the Methyl Ester of Iso-amino-camphomamic Acid. GLENN S. SKINNER AND W. A. NOYES.
4. Alkali Insoluble Phenols. ROGER ADAMS.
5. Oxalyl Chloride as a Reagent in Organic Chemistry. ROGER ADAMS.
6. The Synthesis of Certain Terpene Homologs from 1,4-Di-isopropyl Cyclohexane. M. T. BOGERT AND C. P. HARRIS.
7. Further Studies of α -Uraminobenzoic Acid, Benzoylene Urea and Related Compounds. M. T. BOGERT AND G. SCATCHARD.
8. The Synthesis of Certain Substituted Pyrogallol Ethers Derived from Syringic Acid. M. T. BOGERT AND J. EHRLICH.
9. The Identity of Cyanuric Acid with so-called "Tetracarvonimid." (Presented by Oswald Schreiner.) E. H. WALTERS AND LOUIS E. WISE.
10. 1,4,6-Trihydroxyanthraquinone. M. L. CROSSLEY.
11. Relation of Constitution to Color in Anthraquinone Derivatives. M. L. CROSSLEY.
12. The Use of Prussic Acid in Glacial Acetic Acid. J. R. BAILEY AND R. H. PRITCHETT.
13. A Special Stop-cock for Dropping Liquids Arranged for Equalizing the Pressures above and below the Outlet. HARRY L. FISHER.
14. The Oxidation of Uric Acid with Hydrogen Peroxide. F. J. MOORE AND C. S. VENABLE.
15. Testing of Nitrocellulose Materials. H. C. P. WEBER.
16. Reactions of Quinones. OLIVER KAMM.
17. The Preparations of Anisidine, Phenetidine, and Related Compounds. OLIVER KAMM AND I. N. HULTMAN.

III—Organic Conference

The Supply of Organic Chemicals for Research during the War. Discussion led by PROFESSOR ROGER ADAMS, who will describe the work being done at the University of Illinois.

PHARMACEUTICAL CHEMISTRY DIVISION

L. F. KEBLER, *Chairman*

G. D. BEAL, *Secretary*

I—Papers

1. The Need and Necessity of Pharmaceutical Chemists. OTTO RAUBEN-HEIMER.
2. Woodchuck Oil. GEO. D. BEAL AND J. B. BROWN.
3. Gopher Oil. GEO. D. BEAL AND J. B. BROWN.
4. Studies on the Relative Adsorptive Power of Various Fuller's Earths. ARTHURTON SEIDELL.
5. Some Notes on Court Work. L. F. KEBLER.
6. A Deceptive Practice Occasionally Met, a Case. CHARLES H. LAWELL.
7. Studies on *Piper bredemeyeri*, an Adulterant of Matico. A. VIEHMEIER AND M. C. ALSTON.

II Pharmaceutical Conference

Pharmaceutical Chemistry and the Future, opened by L. F. KEBLER.

PHYSICAL AND INORGANIC CHEMISTRY DIVISION

H. P. TALBOT, *Chairman*

E. B. MOLLARD, *Secretary*

I—Joint Session with Organic Chemistry Division

1. The Factors that Influence the Activity of Chlorine in Organic Compounds. J. F. NORRIS.
2. The Purification and Physical Properties of Some Aliphatic Alcohols. R. F. BREINEL.
3. The Measurement of the Electrical Conductivities of Solutions at Different Frequencies, VII. Sources of Error in the Kohlrausch Circular Slidewire Bridge and in the Anderson Bridge. EDWARD BENNETT AND S. F. ACKEE.
4. The Possibility of Optical Isomerism in the Diphenyl Series. OLIVER KAMM AND C. S. PALMER.
5. The Mechanism of Sugar Hydrolysis. M. A. ROSANOFF AND LILLIAN ROSANOFF.
6. A Substance which in the Liquid Phase Exhibits a Minimum of Solubility in an Unstable Region. (By title.) M. T. BOGERT AND J. EHRLICH.

II—Papers

1. Two New Laboratory Instruments (a) a Burette-Micrometer (b) a Balance for First Year Students. ARTHUR JOHN HOPKINS.
2. Water Lag in a Burette. ARTHUR JOHN HOPKINS.
3. Conductivity of Solutions of Potassium Chloride below One Tenthousandth Normal. E. W. WASHBURN AND H. J. WEILAND.
4. The Limits of Individuality in Chemistry. N. T. BACON.
5. A New Hydrate of Lime. H. W. CHARLTON.
6. Reaction between Antimony and Solutions of Sodium in Liquid Ammonia. EDWARD B. PECK.
7. Standardization of Volumetric Sodium Hydroxide Solution. M. L. HAMLIN.
8. The Fallacy of Determining Electric Charge of Colloids by Capillarity. ARTHUR W. THOMAS.
9. Effect of Acid Concentration on the Photochemical Oxidation of Quinine. G. S. FORBES AND R. S. DEAN.
10. Temperature Coefficient of the Distribution Ratio. G. S. FORBES AND A. S. COOLIDGE.
11. Addition-Compound Formation in Aqueous Solution. (By title.) JAMES KENDALL, JAMES ELIOT BOOGE AND JAMES C. ANDREWS.
12. The Mechanism of the Ionization Process. (By title.) JAMES KENDALL AND J. E. BOOGE.
13. Mechanism of the Potassium Chlorate-Manganese Dioxide Reaction. R. F. BACON AND R. W. MILLER.
14. Measurement of the Compressibilities of Solids under Hydrostatic Pressure up to 12,000 Megabars. ERSKINE D. WILLIAMSON AND L. H. ADAMS.
15. Application of Palladium as an Indicator for Silver Titrations. LOUIS SCHNEIDER.
16. Some Data on the Question of the Existence of Intermediate Ions in Salt Solutions. E. P. SCHUCH.
17. Application of the Thermodynamic Methods of Gibbs to Equilibria in the Ternary System: $H_2O-K_2SiO_3-SiO_2$. GEORGE W. MOREY.
18. Compounds Formed by the Alkali Oxides K_2O and Na_2O with the Trioxides of Aluminum and Iron. GEORGE W. MOREY.
19. The Equilibrium between Sulfur, Water and their Reaction Products. GILBERT N. LEWIS, MERLE RANDALL AND F. RUSSELL V. BICHOWSEY.
20. The Fixation of Nitrogen in Cyanide Manufacture. GILBERT N. LEWIS.
21. The Production of Ozone in the Corona. F. O. ANDEREGG.
22. The Spectrum of the Isotopes of Lead. W. D. HARKINS, LESTER ARONBERG AND H. G. GALE.
23. Secondary Valence and Werner's Coordination Number from the Standpoint of the Existence of Some New Cobaltamines. WILLIAM D. HARKINS AND GEORGE L. CLARK.
24. The Crystal Structure of Chalcocopyrite Determined by X-Rays. CHARLES L. BURDICK.
25. The Activity and Ionization of Hydrochloric Acid. ARTHUR A. NOYES AND JAMES H. ELLIS.
26. A Gas Dilatometer for Ascertaining Decomposition Points; with Determinations of Decomposition Points of Cane Sugar, Dextrose and Soluble Starch. (Lantern.) WILLIAM C. MOORE AND J. B. DAVIES.
27. Some Properties of the Oxides of Lead. L. H. ADAMS AND H. E. MERRITT.
28. The Behavior of Mixtures of Uni-Univalent Formates in Anhydrous Formic Acid. H. I. SCHLESINGER AND F. H. REDD.
29. Hydrogen Overvoltage. D. A. MACINNIS AND L. ADLER.
30. Heats of Dilution of Ethyl Alcohol Solutions. D. A. MACINNIS AND J. M. BENDIXEN.
31. A New Illuminator for Microscopes. ALEXANDER SILVERMAN.
32. Qualitative Separation and Detection of Gallium. (By title.) PHILIP F. BROWNING AND LYMAN E. PORTER.
33. Qualitative Detection of Germanium and Its Separation from Arsenic. (By title.) PHILIP F. BROWNING AND SEWELL E. SCOTT.

34. A Rapid Method for the Volumetric Determination of Zinc. E. K. STRACHAN.
35. Silver Anion. H. C. P. WEBER.
36. Analytical Control of the Ammonia Oxidation Process. GUY B. TAYLOR, JOS. D. DAVIS, JULIAN H. CAPPS AND LEWIS R. LENHART.
37. The Fixation of Nitrogen with the Silent Electric Discharge. FARRINGTON DANIELS AND OLIVER R. WULF.
38. The Displacement of Nitric by Carbonic Acid in Silver Nitrate Solutions and the Relation of this Reaction to the Inclusion Error in the Silver Voltmeter. A. S. MCDANIEL AND H. D. HINELINE.

FERTILIZER CHEMISTRY DIVISION

J. E. BRACKENRIDGE, *Chairman* F. B. CARPENTER, *Secretary*

1. Chairman's Address. J. E. BRACKENRIDGE.
2. A New Fertilizer. (Lantern.) ALFRED H. COWLES.
3. A Comparison of Calcium Silicate, Carbonate, and Hydrate as Fertilizer Materials with Experimental Data. ALFRED W. SCHEIDT.
4. Potash Production in United States. (Lantern.) H. A. HUSTON.
5. The Synthesis of Ammonia by the Haber Process. R. O. E. DAVIS AND HARRY BRYAN.
6. The Availability of Organic Nitrogen in Leather, Hair and Peat. R. E. ROSE.
7. Effect of Fertilizers on Composition of Strawberries. (Lantern.) H. A. HUSTON.
8. Determination of Moisture in Fertilizing Material and Starch. R. N. BRACKETT.
9. The Recovery of Potash as a By-Product in the Cement Industry. W. H. ROSS AND ALBERT R. MERZ.
10. Fertilizing Value of Household Wastes. PHILIP E. BROWNING.
11. The Effect of Fertilizers on the Hydrogen-Ion Concentration in Soils. FRED W. MORSE.
12. Some Suggestions Concerning the Preparation of Ammonium Citrate Solution and the Determination of Insoluble Phosphoric Acid. P. MCG SHUEY.
13. An Exact and Easy Method for Preparing a Neutral Ammonium Citrate Solution. J. M. MCCANDLESS.

A conference where the papers previously read will be freely discussed and general conditions affecting the fertilizer business from a chemical standpoint will close the meeting

RUBBER SECTION

L. E. WEBER, *Chairman* J. B. TUTTLE, *Secretary*

1. Report of the Chairman.
2. A Volumetric Method for the Determination of Free Sulfur. E. H. JOHNSON AND H. S. UPTON.
3. The Direct Determination of India-Rubber. JOHN B. TUTTLE AND LOUIS YUKOW.
4. The Increase in Gravity during the Vulcanization of Rubber. L. E. WEBER.
5. Effect of Copper Compounds on Crude Rubber. CHAS. P. FOX.
6. Symposium on the Best Methods for the Determination of Free and Total Sulfur.
7. The Use of Accelerators in the Vulcanization of Rubber.
8. The Rubber Chemist in the National Service.

Contributions to these last three topics are expected from D. SPENCER, E. H. JOHNSON, H. S. UPTON, C. R. BOGGS, L. J. PLUMB, DONALD CRANOR, RICHARD B. EARLE, L. E. WEBER, R. S. POSTMASTER, J. P. MILLWOOD, FREDERIC DANNERTH, JOHN B. TUTTLE and others.

WATER, SEWAGE AND SANITATION DIVISION

E. H. S. BAILEY, *Chairman* H. P. CORSON, *Secretary*

1. A Method for the Colorimetric Estimation of Small Amounts of Aniline. DEAN ELVOG. (See p. 955 this issue)
2. Copper in Sewage at the New Haven Sewage Experiment Station. (Lantern.) F. W. MCGHEE.
3. The Diffusion of Sea Water in the Puget Sound and Lake Washington Canal. THOMAS G. THOMPSON AND E. VICTOR SMITH.
4. The Bactericidal Efficiency of Soap Solutions in Power Laundering. H. G. REEBERG.
5. The Definition of Alkalinity. A. M. DUNWELL.
6. Manganese in Water Supplies. I. W. SEALE.

THE INDUSTRIAL CHEMIST IN WAR TIME

Conference held in Boston September 12, 1917, by the Division of Industrial Chemistry and Chemical Engineers, American Chemical Society.

This conference, the purpose of which was to emphasize the work which the industrial chemist can do in War time, was opened by H. E. HOWE, Chairman of the Division, who introduced DR. W. F. HILLER, of the Massachusetts Institute of Technology, who spoke on the supply of industrial chemicals.

Dr. Walker pointed out that chemists are already very scarce and indications are that there will continue to be a larger de-

mand than supply for some time. A course in chemical engineering is more expensive for the student than any of the other engineering courses and a fund is needed to help such men prepare themselves for industrial work. Dr. Walker believes that if industries would create a fund from which the proper men could borrow sufficient amounts to complete their education, the industries would be assured of a supply of trained men which at present is by no means certain. This money should be available without interest for the period of their educational course and could be repaid when the man is on an earning basis. Without such assistance, Dr. Walker believes that within a few years the chemist will be a very expensive institution for the manufacturer.

DR. W. F. HILLEBRAND, Chief Chemist of the Bureau of Standards, then spoke in general terms about the important work which the Bureau has undertaken in connection with war problems.

DR. L. H. BAEKELAND, of the Naval Advisory Board and National Research Council, then spoke on some of the problems and some of the suggestions which had been made to the Board. He pointed out that very plausible suggestions are carefully investigated by men qualified to pass upon the subject and that many impractical suggestions were made, apparently in a desire to be of assistance. A considerable number of citizens failed to consider properly the limitations and other features which rendered the suggestions of no value. Dr. Baekeland pointed out that War is not so much a question of research as of production and that new explosives cannot be introduced without very thorough testing and cannot be considered at all unless they can be produced readily in great quantities. He mentioned that in selecting cordite some years ago, in the making of plans for the use of that explosive, England thereby chose a course which now necessitates the production and utilization of great quantities of acetone. Acetone has become a determining factor and has made it difficult at times to reach the desired maximum production. Every successful explosive has been preceded by generations of research work. Dr. Baekeland spoke of some of the important accomplishments which have followed suggestions made by members of the Society or recommendations by the Advisory Board, and of the fact that appropriations have been obtained for a research laboratory which, however, will not be built while the War demands all of our energies. He further spoke of the need for such laboratories and jokingly pointed out that chemists need much apparatus for their work, with the exception of the physical chemists who can accomplish a great deal with a barrel of chalk. Dr. Baekeland paid tribute to the work of Dr. Whitney and the patriotic stand of the General Electric Company in allowing Dr. Whitney to devote all his time to the Government needs as well as backing him in his various experiments and undertakings.

DR. C. L. PARSONS, of the Bureau of Mines, then spoke concerning a great number of instances in which the Department of Mineral Technology is accomplishing things for the country. The importance of sulfuric acid at this time was emphasized, it being required for the production of fertilizers as well as for the manufacture of nitric acid. The efforts of the Bureau in locating and utilizing sulfur deposits in order that our sulfur might be conserved were pointed out. The work of the Bureau on manganese steel, synthetic gasoline and many other important things was outlined. In conclusion, Dr. Parsons paid a tribute to the very generous support of the General Chemical Company and the Nitrogen Products Company, both of which have offered the results of costly experiments to the Government without any return.

The W. H. BAKER, Chief Chemist of the National Research Laboratory, spoke on the nature of foods, showing by analysis the acids from the increased production and increased consumption.

vision of products to insure proper preservation and purity, the food chemist is not in a position to contribute anything fundamentally new at this time. He spoke of the shortage of tin plate and the unsatisfactory quality of sheet steel for tin plate now available and mentioned work carried on with an idea of determining the least amount of materials required for the proper canning of food products.

PROFESSOR L. A. OLNEY, of the Lowell Textile School, spoke regarding textiles, the dye situation, and the work which concerns the textile industry in providing the great quantity of cloth required for uniforms, etc., in addition to the usual demands. He spoke of the improved condition of the dye situation.

DR. L. F. HAWLEY, of the Forest Products Laboratory of the University of Wisconsin, spoke briefly on the work of the Forest Products chemists at the present time. He emphasized the necessity of producing large quantities of acetone and of providing ways in which acetone may be obtained from waste woods, not usually considered suitable for this process. In this connection he mentioned methods for increasing the production of acetone from calcium acetate. Besides the chemical work, the laboratory has been interested in timber testing and other physical experiments so important in determining the suitability of timber for use in shipbuilding, aeroplanes, etc.

DR. A. M. COMEY, Chairman of the Research Committee on Explosives (a sub-committee of the National Research Council) and Chief Research Chemist of the duPont Powder Company, said that there has been nothing new in explosives in the last three years. Production has been the thing upon which work has been concentrated and he gave some figures as to the usual production and exportation of various kinds of explosives. Research work is of course to be prosecuted with vigor and every effort made not only to make present explosives more efficient in use and safer for handling, but to find new materials which can be used to advantage.

MR. E. H. HOOKER, of the Hooker Electrochemical Company, gave a list of the electrochemical products now being produced at Niagara Falls, all of which are of fundamental importance to industry and the military establishment. These include artificial abrasives, chlorates, phosphorus compounds, graphite, caustic, chlorine, etc. Remarking that it was not necessary to give many details of this class of work to the audience present, Mr. Hooker then addressed himself to the Niagara water power situation. He pointed out again the absolute importance of products made by electrochemical processes, and the necessity of awakening the country to the realization that water power amounting to 5,000,000 horse power at Niagara Falls should be and must be utilized. He stated that the scenic beauty which many sought to preserve could be amply obtained by allowing about 20 per cent of the water to flow from the Falls, in fact the Falls are more beautiful when a minimum amount of water rather than high tide is passing over the brink. He urged chemists to make people acquainted with these facts in the hope that something could be done quickly and in the right direction.

MR. C. F. QUAINANCE then spoke on the work being done in America to provide industries and laboratories with the porcelain requisite for their work. Coors porcelain has now reached the point of perfection where it is not only just as good but actually better than the Teutonic ware which had become a most widely used material prior to the War. Great progress has been made in the last year and American manufacturers now stand ready to supply the American needs with a material satisfactory in every way.

MR. HENRY W. HESS, of the Libbey Glass Works, gave an outline of what the glass manufacturers are attempting to do to provide the necessary equipment and utensils. Two difficulties confront glass manufacturers, *vis.*, labor and fuel. Some of the companies have had to put their labor to the production of

tubing, incandescent lamp bulbs and other articles, which has meant a curtailment of chemical glassware production. Mr. Hess' statement, that chemical glassware of a superior quality to the German article is not only now obtainable from American manufacturers but has been at any time in the last ten years, was later substantiated by the report of Mr. P. H. Walker on his results in glassware testing. Mr. Hess emphasized that the American chemical glassware industry would have been even further advanced if the scientific men, especially the college professors, had supported the industry to anything like the extent they had supported the German industry.

DR. CHARLES BASKERVILLE, of the College of the City of New York, was called upon to report the oil and fat situation; he confined his remarks to the statement that notable progress is being made in the utilization of low-grade oil and fats to produce edible fats as well as material for manufacturing purposes. He expressed his belief that no greater progress was being made anywhere and that further remarkable achievements were about to be consummated.

PROF. CHARLES E. COATES, of the Louisiana State University, spoke briefly of the prosperity and optimism prevailing in the South and the work being done along the lines of sugar production. The sugar chemist is endeavoring to increase yields and at the time improve the color of the white sugars made directly from the Louisiana cane. While the slightly tinted sugars are not objectionable from any standpoint it is desirable to produce pure white sugars on account of market conditions.

DR. C. H. HERTY, Editor of the *Journal of Industrial and Engineering Chemistry*, spoke with enthusiasm of the work which had been done by the Publicity Committee of the Society in arousing the country to the appreciation of what chemistry means at the present time as well as at all times. He urged the chemists to support our publicity work not for the good of our profession so much as a public duty. The education of the public toward chemistry he considers a matter of great importance.

CAPTAIN A. H. WHITE, of the Bureau of Ordnance (and now on leave from the University of Michigan), spoke unofficially regarding the appreciation of the Government officials of chemistry and the exemplary attitude of the Regular Army officers and men toward professional men and civilians who have entered the service but are contributing from their experiments and training to the winning of the War. He pointed out the need for chemists in much of the Government work and said that it is hoped that chemists who had been drafted into the Army would be reported so that they might be used in this important branch of the work in serving the country. He stated that many men who desired to put on a uniform were prevented from doing so because of the importance of their present positions and he wanted it thoroughly understood that many of the men who were continuing in their present work were doing so because they could not be replaced and that their work was in many instances just as essential as that which many men in uniform were doing. Captain White hoped that some way would be found to designate such men in order that they would feel more at ease in pursuing their regular line of activity while their fellows were apparently more directly supporting Government work.

DR. T. B. FREAS, of Columbia University, made a plea for the continued support of the American manufacturers of scientific apparatus for the War. It is obvious that much of our trouble has been due to our failing to support these manufacturers and it is certainly up to the manufacturers and scientific men of America to continue to give the undivided support which the War has made necessary after the War. It is now possible to secure a majority of the required equipment made in the United States. We must do what we can to help these industries to become firmly established and to develop to that same high plane attained by American manufacturers in other fields.

NOTES AND CORRESPONDENCE

TWO LETTERS ON "SEASONAL DISTRIBUTION OF SOIL AND FECAL STRAINS OF THE COLON-AEROGENES GROUP IN SURFACE WATERS"

Editor of the Journal of Industrial and Engineering Chemistry:

In a very interesting article by M. Greenfield and W. N. Skourup on "The Seasonal Distribution of Soil and Fecal Strains of the Colon-Aerogenes Group in Surface Waters" published in the July, 1917, number of THIS JOURNAL, the conclusion is reached by the authors, on p. 678, that "there seems to be no difference between soil and fecal strains of organisms of the colon-aerogenes group from surface water supplies in their resistance to treatment." In interpreting the data submitted in the article, however, it would seem to the writer that the above conclusion is not quite justified. As far as can be judged, Miss Greenfield and her co-worker have based their conclusion upon an interpretation of the total percentages of soil and fecal strains without regard to the findings in the raw and treated waters of individual cities. If the data are analyzed with reference to particular sources and to the effect of treatment upon the different types of waters, a very complete selective action may be found to exist.

In order to make clear the presence of a distinct differentiation of action by treatment of these surface supplies, I have taken the liberty of summarizing the data found in the article, in Table I. The interpretation of these results may be made

TABLE I—DISTRIBUTION OF FECAL AND SOIL *B. Coli*. RESULTS IN PER CENT OF TOTAL BACILLI
(Adapted from Greenfield and Skourup, THIS JOURNAL, 9 (1917), 676)

City	RAIN				DROUTH			
	Fecal—Raw	Fecal—Treated	Soil—Raw	Soil—Treated	Fecal—Raw	Fecal—Treated	Soil—Raw	Soil—Treated
Independence.....	12.4	33.17	87.6	66.8	87.5	60.0	12.5	40.0
Chanute.....	50.0	59.9	50.0	40.1	36.5	45.7	43.5	54.3
Cherryvale.....	63.4	26.6	36.6	73.4	61.8	38.2	37.8	65.2
Humboldt.....	23.8	17.2	76.2	82.8	60.0	43.5	40.0	56.5
Coffeyville.....	13.3	40.1	86.7	59.9	52.4	66.7	47.6	33.3

NOTES—Humboldt raw water had by far the more sewage pollution. Cherryvale raw water collected after five days storage. Independence—only a small number of samples during drouth. Treatment of above waters consisted of coagulation with alum and rapid sand filtration. Independence also uses lime at times.

SOURCES OF POLLUTION—Cherryvale—raw sewage (20 mi.). Independence—raw sewage (24 mi.). Coffeyville—septic tank and contact bed effluents (24 and 30 mi.). Humboldt—septic tank effluent (8 mi.). Chanute—septic tank effluents (8 and 16 mi.).

considerably easier by using a numerical measure of selective action of treatment upon soil and fecal strains, which we shall name the "ratio of selection" and which may be defined as the numerical ratio of the percentage of total bacilli (fecal or soil, as the case may be) in the raw to that in the treated water. Using the above ratio, we may test the selective action of treatment in the case of the various cities cited in Table I. The presence or absence of this selective action will be evidenced equally as well by the use of the fecal or the soil strain percentages, since these are comparable, in each case, in an inverse degree. For the purpose of this discussion, the fecal strains only are considered.

In Table II the calculations of the "ratio of selection" have been made and arranged in the order of descending selective action. The table indicates at once, not only the presence of a well defined selective action, but also an apparent gradation of selection by treatment, an explanation for which may be found in a study of the five types of raw water used. Since these raw waters, in each case, have been subjected to approximately the same type of treatment, we can attribute probably the varying selection to the variable resistance of the raw water bacilli. A study of the data regarding the character and source of pollution in each of the raw waters seems to the writer to offer sufficient justification for a system of scoring of the bacilli in these surface supplies upon a basis of relative resistance. This has been

TABLE II—INTERPRETATION OF SELECTIVE ACTION BY TREATMENT OF CERTAIN KANSAS WATERS
(Wolman, July, 1917)

City	Probable Scoring of Degree of Resistance of Organisms in Raw Water	FECAL STRAINS ONLY		Drouth	Probable Scoring of Degree of Resistance of Organisms in Raw Water	Se-lection Ratio
		Se-lection Ratio	Se-lection Ratio			
Cherryvale.....	A—Least Resistant	2.4	A—Least Resistant	1.6		
Humboldt.....	B	1.4	B	1.4		
Chanute.....	C	0.8	C	1.2		
Independence.....	D	0.4	D or B	1.5		
Coffeyville.....	E—Most Resistant	0.3	E—Most Resistant	0.8		

done in Table II. That the gradation of the scoring is a reasonable one, we may venture to assert because of the following conditions. The raw water of Cherryvale would probably contain the least resistant forms of bacilli because it is polluted by raw sewage at a distance of only 20 miles. The effect of the storage of five days on the Cherryvale supply is problematical in this connection, although it would tend possibly to increase the resistance of the surviving bacilli. The scoring of the Humboldt supply seems reasonable when it is noted that the source of its pollution (even though subjected to preliminary treatment) is only 8 miles away and also relatively great in its extent. It would appear, therefore, that this raw water should contain bacterial forms of quite low resistance. The Chanute raw water, upon a similar basis, should show a slightly higher degree of resistance in its bacilli. Independence and Coffeyville may be assigned fourth and fifth places in this system of scoring, since the former has been exposed to raw sewage pollution, but at a distance of 24 miles, while the latter should undoubtedly contain the most resistant forms of bacilli, since its sewage pollution is farthest away and subject to the highest degree of treatment of any of the five contributory sewages, factors which would tend to inhibit the appearance of less resistant forms in the Coffeyville raw water supply. In periods of drouth, a similar grading of resistance and selective action is possible, but modifications in interpretation are necessary in order to readjust the probable degree of resistance of surviving forms of raw water bacilli.

The conclusion which the writer would like to indicate, therefore, is that the treatment of these Kansas surface water supplies apparently does exhibit a degree of selection between fecal and soil strains of bacilli, which may be correlative with the resistance of the particular forms and with the nature of their origin. Since the action of a rapid sand filter upon resistant and non-resistant forms of bacteria would be, in all probability, non-selective, it might be well to search for the selective actions illustrated above in the devitalization effect arising in the process of coagulation and sedimentation preliminary to the actual filtration.

MARYLAND STATE DEPT. OF HEALTH
16 W. SAKATOGA ST. BALTIMORE, MD.
July 12, 1917

ABEL WOLMAN,
Mechanical Engineer

Editor of the Journal of Industrial and Engineering Chemistry

The note from Abel Wolman, Division Engineer, Maryland State Department of Health, in which he criticizes the article on "The Seasonal Distribution of Soil and Fecal Strains of the Colon Aerogenes Group in Surface Waters" published in the July, 1917, number of THIS JOURNAL, is very interesting. Unfortunately Mr. Wolman misinterpreted the terminology of the authors. A treated water is one coagulated with alum only, and a tap water is the finished product, that is, a water coagulated with alum and filtered through a rapid sand filter. By using the numerical ratio of the percentage of total fecal bacilli in the raw to that in the tap water, very different results are obtained.

Table I gives the percentage of fecal strains in the raw and tap water, Mr. Wolman's scoring of the degree of probable resistance of organisms in the raw water, and the selection ratio.

I agree with Mr. Wolman's scoring of the degree of resistance of organisms in raw water with the exception of Cherryvale. It seems reasonable to assume that only very resistant organisms would remain after five days storage.

TABLE I—INTERPRETATION OF SELECTIVE ACTION BY TREATMENT OF CERTAIN KANSAS WATERS

CITY	Wolman's scoring of probable degree of resistance of organisms in raw water	FECAL STRAINS ONLY					
		Rain			Drought		
		Per cent Raw	Per cent Tap	Selection Ratio	Per cent Raw	Per cent Tap	Selection Ratio
Cherryvale....	A—Least resistant	63.4	21.2	3.1	61.8	78.6	0.785
Humboldt....	B	23.8	38.1	0.626	60.0	66.7	0.91
Chanute....	C	50.0	39.2	1.28	56.5	63.8	0.885
Independence....	D	12.4	25.45	0.48	87.5	70.1	1.24
Coffeyville....	E—Most resistant	13.3	16.68	0.79	52.4	73.3	0.715

Table I shows that there is a difference in the resistance of the fecal strains from the several cities but that this selective action is not consistent with the variable resistance of the raw water bacilli. In other words, there is no way to prophesy, given the source of pollution, the percentage of fecal bacilli that will resist the treatment.

M. GREENFIELD AND W. N. SKOURUP

STATE BOARD OF HEALTH
LAWRENCE, KANSAS

NITRATE SUPPLY COMMITTEE—CORRECTION

Owing to a typographical error, the investment cost of the Haber Process when ammonia is the product [see table, *THIS JOURNAL*, 9 (1917), 841] was made to read \$540, when it should read \$340.

CHARLES L. PARSONS

WASHINGTON LETTER

By PAUL WOOTON, Metropolitan Bank Building, Washington, D. C.

With such matters on the tapis as the location of the nitrate plant; the investigation of the defective primers manufactured at the Frankford arsenal; the important progress being made in the study of noxious gases and the materials used in the manufacture of submarines, aeroplanes and balloons; the pyrite and manganese situation and the important information gleaned at the Boston meeting of the American Chemical Society, Washington chemists have had much food for thought and subject matter for discussion during the past month.

Rarely has there been such a demand in Washington for a publication as that evinced for the September issue of *THIS JOURNAL*. Despite the fact that proofs of the article on the nitrate report had been delivered in advance to the four daily newspapers published in the capital, nothing in regard to the report was published. The only available copies of the report were those contained in the *Journal*. The demand for the report became so great that a week following its publication in the *Journal*, the Committee on Public Information issued a statement containing some of the more important phases of the matter.

The failure of the newspapers to print the results of the nitrate investigation led Representative Longworth, of Ohio, on September 14, to address the House on the subject and to have the complete report printed in the *Congressional Record*. Mr. Longworth considered the action taken "of vast, if not vital, importance to the safety of the nation and to our continuance as a potent factor in this war."

Continuing, Representative Longworth said: "My other object, far more important, is to show that a situation has been brought about by the intelligent action of this Government, with the assistance of a number of prominent American engineers and scientists and chemists, by which the country is assured during this war, no matter what may happen, regardless of whether or not we may by some chance be cut off from the Chile nitrate supply, of an absolutely sufficient and cheap supply of nitric acid, without which it is impossible to make ammunition or explosives of any kind, without which we would be impotent in the conduct of a war, either defensive or offensive, and without which the enormous amount of money appropriated in this bill would be absolutely useless. This happy situation is better summed up than I could sum it up in a letter written by Dr. Herty, formerly the president of the AMERICAN CHEMICAL SOCIETY, now the editor of the official organ of the AMERICAN CHEMICAL SOCIETY, known as the *Journal of Industrial and Engineering Chemistry*, and a member of the committee appointed by the Secretary of War to investigate this question. In a letter written to the editor of the *Manufacturers Record* and published a few days ago he says: 'Representative Longworth then read excerpts from the letter.

After recounting how Dr. Chas. L. Parsons (secretary of the American Chemical Society), whom he designated as "one of the great chemists of the country," has investigated nitrate manufacturing methods in Europe, Mr. Longworth said: "The outstanding feature of the action officially taken is the postponement indefinitely of the proposition to make nitrogen in any form by the use of water power. This, thank goodness, gentlemen, sounds the death knell of that Muscle Shoals \$20,000,000 nitrate scheme."

Accustomed as he is to the high standard of efficiency in his own organization, Dr. W. H. Nichols, chairman of the Com-

mittee on Chemicals of the Council of National Defense, finds it difficult to understand the delays in official action. The fact that the selection of the site for the nitrate plant is being deferred from week to week is giving much concern to Dr. Nichols, who characterizes the handing over to the government of the General Chemical Company's synthetic ammonia processes as the greatest sacrifice he ever made. He pointed out that the General Chemical Company has been working on this process since 1911 and, at the time of the government's appeal, had allotted a large sum of money to build a plant for the carrying out of the process on a large scale. He said the only condition which the company had stipulated was that the government take adequate steps to safeguard the company's confidences. He also called attention to the fact that the company is not receiving a penny for the use of its processes and that they had been turned over with the sole intention of being helpful to the country.

That a knotty chemical problem which will have to be solved by the special board consisting of Col. Worth Robinson, professor of chemistry at the U. S. Military Academy, Dr. H. P. Talbot of Massachusetts Institute of Technology and Dr. Chas. L. Parsons, secretary of the American Chemical Society is involved in the failure of certain primers manufactured at the Frankford arsenal became very evident during the course of the investigation conducted by a special congressional committee. H. C. Pritham, the chief chemist of the technical staff at the arsenal, testified that a number of causes contributed to the failure of the primers. Principal among these were: the presence of impurities in the ingredients; improper granulation of materials; overcrowding in the dry houses; and irregularities in manufacture. The particular impurity which Mr. Pritham held largely responsible for the trouble was potassium bromate in the potassium chlorate. "Primers may shoot fine when made," said Mr. Pritham, while on the stand, "but the potassium bromate will cause a slow deterioration. We do not know whether it is a catalytic action or whether it is simply a decomposition with the liberation of the bromine and the generation of sulfuric acid. The presence of the bromate is a result of impurities in the original potassium chloride from which the chlorate was made."

After explaining how war conditions have cut off the supplies of chlorate usually relied upon in this country, Mr. Pritham said: "The chlorate made in the United States carries a higher percentage of impurities. During manufacture the bromate is not eliminated; that is, it occurs as bromide and is oxidized to the bromate and crystallizes out with the chlorate in the ordinary process of manufacture. The improved process which Major Cushman has been working on, will be a very simple way of getting rid of the bromate. All the chlorate on hand at the arsenal has been shipped away to be treated by the new process. Previously no one had paid any particular attention to this matter because nobody had any information or had demonstrated that bromates formed a deleterious ingredient in a primer."

Mr. Pritham was graduated from the Chemical and Engineering Department of the University of Maine in 1901.

Walter Arthur, the research metallurgist for the Titanium Alloys Manufacturing Company, who made an examination of some of the primers for the War Department, told the committee that the trouble resulted wholly from too coarse granulation of the antimony sulfide and the potassium chlorate. "No

progressive action of any sort was observable," he said, "and it is firmly believed that none occurred."

Some of the matters receiving attention at the Bureau of Standards are as follows: Permeability, bursting strength, and endurance under service of balloon and aeroplane fabrics; investigation of apparatus for generating hydrogen; procedure in balloon filling; methods of detecting inflammable gases; study of aeroplane dopes and varnishes, glue, oils, metallic coatings, and cleaning materials; investigation of fire-retarding paints, and paints for helmets.

Experimentation on sugar looking to the production of glycerin is being continued in the laboratory of the Internal Revenue Service. A statement to the effect that this work had been transferred to the Food Administration is denied by Dr. A. B. Adams, the chief chemist at the Treasury Department's laboratory.

Exporters of chemicals have filed scores of protests growing out of delays incident to the operation of the export licensing

provisions. A number of prominent exporters have come to Washington to investigate the matter in person. Several of those who called at the offices of the Exports Administrative Board went away convinced that everything humanly possible is being done at the Bureau of Export Licenses to facilitate the movement of traffic. The business of the country is so extensive that the Bureau is literally buried in the applications for licenses which are coming in.

The Chemistry Committee of the National Research Council has submitted to the Executive Committee of the Council the following resolution: "That the Executive Committee of the Research Council be requested to take immediate steps to organize an informal conference or committee composed of chemists representing the Research Council and the Government bureaus with a view to avoiding the isolation of the several groups engaged in chemical work for the government, and with a view of securing the most efficient prosecution of the work of the Chemistry Committee." Favorable action on the resolution is said to be assured.

PERSONAL NOTES

Dr. Lloyd Balderston has been appointed professor of leather chemistry and technology at the College of Agriculture of the Tohoku Imperial University at Sapporo, Japan. Dr. Balderston is at present with the Elk Tanning Company at Ridgway, Pa. He is associate editor of the *Journal of the American Leather Chemists Association* and editor of the leather and glue section of *Chemical Abstracts*.

Dr. Colin G. Fink, for the past ten years in the Research Laboratories of the General Electric Company, has been appointed head of the new laboratories of the Chile Exploration Company, located at 202nd Street and 10th Avenue, New York City.

Abraham Henwood, professor of chemistry at Drexel Institute and presiding officer of the Philadelphia Section of the A. C. S., has received the degree of doctor of science from Muhlenberg College.

Regular monthly sessions of the Philadelphia Section of the A. C. S. will be resumed at the Engineers' Club, in Spruce Street, that City, this month. During the summer vacation period the membership was increased beyond 700.

Richard H. Chapman, Jr., is head of the Sanazone Manufacturing Company which has just been incorporated in Pennsylvania with a capital of \$100,000 for the manufacture of chemicals.

H. J. Broderston, instructor in industrial chemistry at the University of Illinois, Urbana, has accepted a position with the Standard Oil Company at Whiting, Ill.

Dr. Edgar T. Wherry, for the past four years connected with the U. S. National Museum, Washington, D. C., has been transferred to the position of crystallographer in the Bureau of Chemistry of the U. S. Department of Agriculture.

L. W. Bahney has severed his connection with Yale University to accept a position as metallurgical engineer with the Scovill Manufacturing Company, Waterbury, Conn.

Mr. A. W. Phillips, for the past year general superintendent of the Aetna Chemical Company's Canadian smokeless plant at Drummondville, P. Q., has resigned to become superintendent of the Canadian Electro-Products Company's synthetic acetone plant at Shawinigan Falls, Quebec.

The U. S. Civil Service Commission announces the following open competitive examinations: *Chemist in Forest Products* (made), salary \$2000 to \$2400, applications received until October 10; *Mitochondrion* (made), salary \$2000 to \$2400; *Assistant Chemist* (made), salary \$2000 to \$2400. Until further notice, and on account of the urgent need of the service, applications for the first two positions will be received at any time. Papers will be rated promptly and certification made as the needs of the service require.

The *Abstract* announces the appointment of Mr. M. D. L.monds as its Associate Editor. Mr. Lmonds, who has recently become a member of the A. C. S., is the editor of the Bureau section of the *Pacific Leader* of Philadelphia. He has devoted a great deal of attention to the growth of chemical industry within the past three years, and his paper has published more authentic chemical news than any one paper in the country.

H. D. Batchelder has been appointed head of the Cleveland Laboratories of the National Carbon Company.

Dr. Charles K. Francis, for the past seven years chemist and professor of petroleum technology in the Oklahoma Agricultural and Mechanical College, has resigned to become chief chemist for the Cosden Oil Company, Tulsa, Oklahoma.

Mr. Charles R. Oberfell has resigned the position of Chemical Director of England Walton Co. to accept a similar one with the firm of John H. Heald, Inc., of Lynchburg, Va., manufacturers of tanning and dyewood extracts. Mr. Oberfell is president of the American Leather Chemists Association, and is one of the foremost investigators in the field of leather chemistry.

Robert A. Hall, Ph.D., formerly assistant professor in physiological chemistry at the University of Minnesota, has been appointed to a lieutenantcy in the army and is now on his way to France for immediate service.

Dr. Frank C. Gephart, chemist at the Russell Sage Institute of Pathology, New York City, has received a commission as Captain, Sanitary Corps, United States National Army, with headquarters at the Surgeon-General's office, Washington, D. C.

Dr. J. H. Matthews, of the University of Wisconsin, has been appointed captain in the Ordnance Department.

Dr. Leon I. Shaw, of the department of chemistry of Northwestern University, has been advanced to the position of assistant professor of chemistry on leave of absence for one year for service with the government. He has received the appointment of first lieutenant in the Ordnance Officers' Reserve Corps.

Mr. Ernest E. Follin, of Detroit, has received the Commission of First Lieutenant, U. S. Army.

The death is announced of Dr. Eduard Buchner, professor of chemistry at Wurzburg, who died from wounds received while serving as major at the front. Dr. Buchner was distinguished for his work on the chemistry of fermentation, and was the recipient of the Nobel prize for chemistry in 1907.

Word has just been received of the death of Francis Sutton, author of *Sutton's Systematic Analysis of Volatile Organic Analysis*, at Great Plimouth, England, April 15, 1917, just at the age of 80.

Adolf Ritter von Baeyer, professor of chemistry at the University of Munich, has been elected to the A. C. S. and one of Germany's best known organic chemists died in Germany the latter part of August of the year 1916. He was distinguished for his work in acid and base chemistry, especially that in aliphatic and cyclic acids. He was president of the German Chemical Union in 1906, at the time of the war, and was elected to the A. C. S. In 1908, he was the recipient of the Nobel prize for chemistry.

We learn from the *London Times* that the death of Mr. Clayton B. Leach, of the University of California, at the age of 60. He was particularly known for his work in the field of organic chemistry, and his work was of a high order. He was elected to the A. C. S. in 1910. Among the honors conferred upon him were the John Scott Legacy Medal and Premium of the Franklin Institute in 1910, the Distinguished Service Award of the American Chemical Society in 1911, and the Distinguished Service Award of the American Chemical Society in 1912.

INDUSTRIAL NOTES

Plans have been perfected for a "Don't Waste Gasoline" campaign, which has the support of Government authorities at Washington. Van H. Manning, of the Bureau of Mines, says that there is ample gasoline for all our needs, but the uncertainties of war are such that a campaign against waste is regarded as a patriotic measure.

It is reported that the Grasselli Chemical Company has entered the field of high explosives. The Grasselli Powder Company has been incorporated in Ohio with \$5,000,000 capital to take over the American Explosives Company, the Burton Powder Company and the Cameron Manufacturing Company, all at present active makers of high explosives.

Part of the plant of the Grasselli Chemical Works at Tremley Section, Linden, N. J., was destroyed by fire on August 17 with an estimated loss of \$30,000.

The Dupont Chemical Works, 120 Broadway, New York City, has acquired the plant of the Pan Chemical Company, Hastings-on-Hudson, N. Y. The plant will be moved to Hopewell, Virginia, and the present capacity largely increased.

According to the Japan *Times* sulfur production in Japan has increased 219 per cent during the past ten years.

Imports of chemicals, drugs and dyes into the United States during the fiscal year ending June 30 were valued at \$127,770,000, against \$109,123,000 in the previous fiscal year and \$88,039,000 two years ago.

From *The Journal of Commerce* of September 5 we learn of the installation of a potash plant on the Queen Charlotte Islands, British Columbia. The enterprise has for its purposes the manufacture of potash from kelp, the extraction of oil from fish, the manufacture of fertilizer and the sale of edible fish. The plant is to be operated by the International Chemical Company, a concern financed by the National Chemical Company. It is controlled by Cleveland and Chicago capital. The firm has exclusive licenses from the Government on what are said to be the most extensive kelp beds on the Pacific Coast. The new company claims that even at the pre-war prices it will be able to operate successfully in the Queen Charlotte Islands, owing to the richness of the kelp beds and its convenient location.

The Kalbfleisch Corporation claims a greatly increased output of permanganate of soda solution, a sample of which was shown at the National Exposition of Chemical Industries at the Grand Central Palace, New York.

We learn from *Science* that at Liverpool University an advisory committee of ten members has been formed in order to develop the chemical industry after the war; it consists of four members of the chemical staff of the university and six others representing the chemical industries.

The Monsanto Chemical Company, St. Louis, will, it is announced, shortly begin the construction of a plant costing \$1,500,000, for the production of crude medicinal coal-tar products, on the Illinois Bank of the Mississippi River. The plant is intended to make the Monsanto Chemical Company independent of Europe after the war.

We learn from the *Textile World Journal* that the Paris Chamber of Commerce has written the Philadelphia Bourse giving details regarding plans for developing a self-contained dyestuff industry in France without dependence upon outside countries. This trade body tells of the organization of powerful associations of chemists, engineers and manufacturers, one of which, with a capital of \$8,000,000, is to receive from the Government at the end of the war a number of munition plants which in a short time can be turned into great dye and chemical manufacturing. In the past three years, it is stated, France has succeeded in turning out in large quantities and with many improvements articles for home consumption which before the war came entirely from across the Rhine and which the French did not believe they could manufacture. The French manufacturer now has the necessary confidence and organization and means with which to produce in almost unlimited amounts.

The Curtis Bay Chemical Company, subsidiary of the United States Industrial Alcohol Company of New York, at Stone House Cove, Maryland, has begun the manufacture of potash from molasses, and has ceased to manufacture acetone which has been made for two years for use in the manufacture of high explosives.

The Texas Nitrate and Fertilizer Co. of Alpine, Texas, has been formed for the purpose of developing a large deposit of nitrate in Presidio County, West of Alpine, in one of the most arid parts of the upper border region of that State, with an area two miles long and one-half mile wide and a depth of five to twelve feet. The company has obtained a lease upon 2700 acres of land including and surrounding the deposit.

The Journal of Commerce states that in the thirty-two months since January 1, 1915, the total indicated investments in new drug, chemical and dye companies is \$230,670,000. Of this amount \$65,861,000 has been contributed during the first eight months of 1917, which is slightly more than the total authorized capital involved in the formation of similar concerns during 1915, but well below the figure for 1916. It compares with \$60,523,000 during the first eight months of last year. Four concerns were organized in August of this year with an authorized capital of \$1,000,000 or more, as follows: Mason Coal and Chemical Company, \$5,000,000; United Oil and Chemical Corporation, \$2,000,000; Marden, Orth and Hastings Corporation, \$1,950,000; and the Nitrogen Fixation Corporation, \$1,000,000.

At the suggestion, and under the advice of the Department of Commerce, says the *Commercial Fertilizer*, an organization known as the Chemical Alliance, Inc., has been incorporated under the laws of the State of Connecticut. The directors of this alliance are the eleven members of the Committee on Chemicals. The officers of the Alliance, and the Executive Committee of the Board of Directors are as follows: *President*, Dr. Wm. H. Nichols; *Vice-President*, Horace Bowker; and *Secretary-Treasurer*, J. D. C. Bradley; *Executive Committee*, Dr. Wm. H. Nichols, Horace Bowker, Henry Howard, E. R. Grasselli and J. D. Pennock. A detailed statement of the organization and purposes of the Chemical Alliance, Inc., will be furnished just as soon as the Department of Commerce formally approves of the organization.

A cablegram from the American Consul-General at London informs the American Government that the Ministry of Munitions from September 1 takes possession of all pig lead, virgin remelted, old scrap and residues in United Kingdom, except such lead as may be in possession of manufacturer for use in his own works, or specially excepted under written authority.

An alcohol explosion in the laboratory of the Bayway Chemical Company plant at Elizabeth, N. J., caused a fire which wrecked the building and destroyed chemicals valued at \$10,000.

The Morris Fertilizer Company of Atlanta, Ga., will build three buildings to cost \$125,000 at Navassa, N. C. Equipment for the manufacture of sulfuric acid, acid phosphate and complete fertilizers will be installed. The plant will cover eight acres.

We learn from the *Oil, Paint and Drug Reporter* that a Danish chemist has invented a process by which fish oil may be made to yield not only oil, but also a solid substance named "corimite" which is specially suitable for electrical insulation. A company capitalized at 70,000 kroner has been formed to work the process, and production is expected to begin during the present year.

By royal orders the Spanish government prohibits exports of chloride of lime, except shipments already booked for export.

Capron Neutral Sulfate of Ammonia Syndicate, Ltd., of London, has been incorporated with the object of taking over the Capron process for the manufacture of sulfate of ammonia, and carrying on the business of manufacturers of, dealers in, and agents for chemicals, manures, dyes, colors, oils, coal tar, ammoniacal liquor, residual products, etc.

The U. S. Geological Survey reports that more potash has been produced during the first six months of 1917 than was made during the entire year of 1916. The Nebraska alkali lakes have yielded about one-third of the entire production. No production is reported from feldspar on other silicate rocks, but considerable quantities of potash salts and potash-bearing fertilizers were obtained from the dusts in cement mills and blast furnaces.

Imports of chemicals, dyes and colors into the United Kingdom in July showed a decrease, while there was a notable increase in the exports for that month of oil seeds and fats.

GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

CONGRESSIONAL COMMITTEES

American Academy of Engineers. Senate Report 86 to accompany Senate Bill 2360, which proposes to incorporate an American Academy of Engineers submitted July 21. 7 pp.

Manufacture of Explosives. Senate Report 85, 4 pp., dated July 17th, submitted to accompany House of Representatives Bill 3932, which proposes to control and regulate the manufacture and use of explosives in the time of war. The second part of the report on hearings on this bill by the Senate Committee on Mines and Mining is also available dated July 6th.

Mineral Lands. Senate Report 74, 1 p., dated June 30. A report to accompany Senate Joint Resolution 78 suspending mining assessment work on mining claims during the present war under certain conditions there defined.

COUNCIL OF NATIONAL DEFENSE

Laboratory Utensils. 26 pp. Part 3 of the list of staple medical and surgical supplies selected to meet war conditions by the Committee on Standardization appointed by the Council of National Defense. Available only through the Council.

GEOLOGICAL SURVEY

The Coal Fields of the United States. General Introduction. M. R. CAMPBELL. Professional Paper 100-A, 33 pp. and 2 maps. The growing demand for fuel and the probability that sooner or later the United States will be called upon to furnish supplies to less favored countries has made it desirable for the Geological Survey to take stock of the country's fuel and to determine the quantity, quality, and geographic distribution of the coal still in the ground and available for future use. This report is intended to supply such information regarding the coal fields of the United States, arranged according to the States within which they lie.

Structure of the Northern Part of the Bristow Quadrangle, Creek County, Oklahoma. With Reference to Petroleum and Natural Gas. A. E. FATH. Bulletin 661-B. From Contributions to Economic Geology, 1917, Part II, 30 pp. Published July 26. A few of the anticlines appear to be sufficiently large to be well worth prospecting with the drill. Several others, which are comparatively small and closely related to faults, are not considered to be worth prospecting until after the larger ones have been developed and prove their value. Although faults alone may cause accumulations of petroleum and natural gas, those in this quadrangle are probably of little value for this purpose. As the information collected in the northern part of the quadrangle is valuable at the present time, it is being published at an early date rather than withheld until the examination of the remainder of the quadrangle is completed.

The De Soto-Red River Oil and Gas Field, Louisiana. G. C. MATSON AND O. B. HOPKINS. Bulletin 661-C, from Contributions to Economic Geology, 1917, Part II, 30 pp. Published June 28.

Alaska's Mineral Supplies. A. H. BROOKS. Bulletin 666-P, 14 pp. "For the purpose of the present paper Alaska's mineral reserves may be roughly divided into three groups: One group includes those so inaccessible at the present time as not to form a part of the available supply: this group includes a considerable part of the mineral wealth of the territory but needs no discussion here. A second group includes the mineral reserves which, though now inaccessible and undeveloped, could be made available by one or two years of preparatory work: this group includes much of the coal and oil and a part of the copper, gold and other metalliferous deposits. In general, most of the mineral deposits that are far from tidewater fall in this category, though exception must be made of some tributary to the existing railroads. Undeveloped deposits, even though they are located close to the seaboard, also belong to this group in so far as they require extensive mine equipment before productive operations can be begun. The third group, constituting the most available but much the smallest part of Alaska's mineral wealth, includes developed deposits lying on or near established transportation routes. In this group fall not only the deposits on tidewater and railroads but also those in inland districts that are accessible for a part of the year by river transportation."

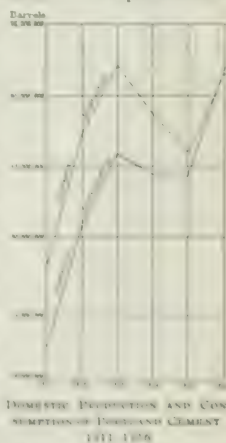
This report includes a discussion of the resources for the following minerals: gold and silver, copper, tin, tungsten, antimony, lead, platinum, chromite, nickel and cobalt, quicksilver, molybdenite and bismuth, iron, coal, petroleum and miscellaneous minerals.

Limestone and Lime. G. F. LOUGHLIN. Bulletin 666-R, 6 pp. Limestone, including high magnesium limestone or dolomite, has been demonstrated by work of the United States Geological Survey to be so widely distributed and so abundant in the United States that there is no doubt whatever of an adequate supply to meet all unprecedented demands, even though it is realized that stone sufficiently pure to yield lime of the highest grades forms but a small fraction of the whole. Limestone is quarried and lime is manufactured in 43 of the 48 States, and large deposits are favorably situated with respect to industrial centers, especially in the Central and Eastern States.

Portland Cement. E. F. BURCHARD. "The production of Portland cement in the United States from 1912 to 1916 has ranged between 82,000,000 barrels and 92,000,000 barrels annually, an output far exceeding that of any other country. Average prices have been relatively low, ranging between 80 cents and \$1.10 a barrel in bulk at the mills, yielding only small profits, but much higher prices are reported to have prevailed in the early months of 1917."

"The imports of hydraulic cements into the United States are normally very small, but in 1916 they were almost negligible, having dropped to 1,800 barrels, compared with 1,000 barrels in 1915."

"The export has never been great, the largest quantity—that in 1912—having been only 4,000,000 barrels. In 1914,



1915 and 1916 the exports were, respectively, 2,140,197, 2,565,031 and 2,563,976 barrels."

Among the present needs of the cement industry is more comprehensive and accurate information with regard to the distribution of materials suitable for concrete aggregates—especially for concrete roads—such as good clean sand, gravel, and stone available for crushing.

Iron. E. F. BURCHARD. Bulletin 666-V. 12 pp. This article gives brief statistical data for the iron and steel raw materials and manufacturing industries.

Mica, Monazite, and Lithium Minerals. W. T. SCHALLER. Bulletin 666-X. 6 pp. "The imports of sheet mica exceed the domestic output in both quantity and value. In 1916 more than \$1,000,000 worth of sheet mica, unmanufactured and manufactured, was imported. More mica is imported from Canada than from India, but the value of the India mica is greater. The mica from India comes both direct and through England. The demand for mica in 1915 was brisk, and in the United States the average price of sheet mica, rough trimmed and cut, was 68 cents a pound, the highest since 1911. Since 1915 similar or slightly higher prices have prevailed. Until 1916 there was a slight, steady increase in the percentage of the total produced by the United States. The decline in the percentage for 1916 is, however, slight. The mica obtained in this country and from India is muscovite; that from Canada is phlogopite. For certain pieces of electric machinery phlogopite is preferable to muscovite, and deposits of phlogopite in New York and New Jersey are now being examined. The mica from these two deposits is of good quality and it is hoped that they will become commercial sources.

"There is still an abundance of monazite sand in the Carolinas, but the Carolina deposits cannot be worked extensively in competition with foreign sand. As the United States consumes about one-fourth of the thorium nitrate used in the world, it requires a yearly production of about 2,000,000 lbs. of monazite sand (90 per cent), monazite containing 5 per cent thorium. Even in its most prosperous times the domestic output did not reach that figure. Whether such a domestic production could be sustained year by year if all imports were cut off cannot be told. The Carolinas, however, could produce enough monazite sand to make this country independent of other sources for several years at least, and if the ashes of broken mantles were conserved by consumers, enough thorium nitrate could be obtained from domestic sources to serve for some time.

"The factors that have prevented a thorough test of the extent of the domestic deposits in recent years are the better quality and cheapness of the imported foreign sands. Both the Brazilian sand and that of India contain a higher natural concentration of monazite and a higher content of thorium oxide than the American sand, the sand from Brazil averaging about 6 per cent thorium and that from India about 9 per cent. The cheapness of labor and transportation in these foreign countries has also deterred domestic exploitation. The market price of thorium nitrate is a good indicator for domestic production of monazite sand, for only at a high price for this manufactured salt can the domestic sands be profitably worked. The importation of large quantities of foreign sand rich in thorium prevents a very high price being paid for thorium nitrate.

"The chemical products derived from lithium minerals cannot be considered necessary for every-day life. Such products, however, find several applications, especially in military uses, in which they serve a useful purpose. Lithium minerals are produced in this country in varying amounts up to 1,000 tons a year."

Nitrates. H. S. GALE. Bulletin 666-Z. 4 pp. "The rated values given with import returns, which perhaps represent cost exclusive of freight, are lower than the usual market quotations. For instance, the normal New York quotations

for sodium nitrate, 95 per cent pure, ranged from \$44 to \$52 a short ton in 1912 and from \$44.40 to \$52.40 in 1913. At the end of 1916 or early in the spring of 1917 sodium nitrate was quoted at \$75 a ton in Atlantic ports.

"The import figures show a war-time stimulus, the normal annual domestic consumption of about 600,000 tons of sodium nitrate increasing to more than double this amount in 1916. Of this large increase between 100,000 and 200,000 tons are believed to be in storage as a reserve for the time when access to a foreign supply may be cut off. The remainder of the increase, probably 600,000 tons, may be assumed to have gone into munition manufacture, chiefly for export.

"The amount of nitrates consumed in fertilizers is not known exactly, but about 280,000 short tons (250,000 long tons) of sodium nitrate were used in 1916 for direct application to the soil as fertilizer. It is said to be applied chiefly as a top dressing, by itself, to promote or hasten growth at certain seasons, usually in the spring, after the crop has made a start.

"A very important use for sodium nitrate is in the manufacture of sulfuric acid by the chamber process. In this process, by which the greater part of the acid of low gravities produced in this country is made, the nitric acid is required for the oxidation of the sulfurous gases to sulfuric form. The weight of sodium nitrate used in this way is estimated to be about 5 per cent of the weight of the sulfur consumed to make the sulfuric acid. The production in 1916 of 4,500,000 tons of sulfuric acid of strengths less than 66° Baumé therefore required 75,000 long tons (nearly 85,000 short tons) of sodium nitrate.

"There are many other industrial uses of nitrates for which, at present, accurate statistics are not available. The following estimated summary is therefore given in general terms:

"SODIUM NITRATE CONSUMED IN THE UNITED STATES IN 1916

	Quantity Short tons	Approximate Percentage
Explosives.....	600,000	45
Fertilizers.....	280,000	20
Manufacture of sulfuric acid.....	85,000	5
Miscellaneous, including stocks in storage..	400,000	30
	1,365,000	100"

Lead. C. E. SIEBENTHAL. Bulletin 666-AA. 3 pp. The annual progress and developments in the lead-mining industry are shown in the mine reports for the several producing States published in "Mineral Resources of the United States." Detailed reports on the ore deposits of many lead-producing districts have also been published by the United States Geological Survey.

Magnesite. H. S. GALE. Bulletin 666-BB. 3 pp. "The production of magnesite in the United States in 1916 far exceeded that of any preceding year. The increase was due to the larger demand for refractory magnesite products and to the decline in imports. Though more magnesite was used in the United States in 1916 than in 1915, the consumption was less than that of any of the three years preceding 1915, and the use of the mineral has now been greatly curtailed by its relative scarcity and high cost.

"It is estimated that normally about 6 lbs. of magnesite were formerly used for every ton of steel made by the basic open-hearth process, but not more than half a pound for every ton is now being used, and at some steel plants cheaper and less satisfactory refractories have been substituted for magnesite. Owing to its use in the steel and copper industries, magnesite is an important though a minor war commodity, and the need for it in these industries is so great that its lack has at times been viewed with serious apprehension."

Platinum and Allied Metals in 1916. J. M. HILL. Separate from Mineral Resources of the United States in 1916, Part I. 20 pp. Published July 12th. The United States alone apparently uses about 165,000 fine ozs. of platinum a year. The known supply of platinum is small: possibly 5,000,000 ozs. have been produced in the world to date.

Probably 500,000 ozs. of this total output of platinum is in use as a catalyzing agent. The quantity manufactured in the form of chemical and physical equipment cannot be readily ascertained but may be roughly estimated at 1,000,000 ozs. Electrical devices may have required 500,000 ozs., but perhaps 250,000 ozs. would cover that use. The jewelry industry has probably consumed 1,000,000 ozs., and the dental industry also about 1,000,000 ozs. Minor uses and hoarded platinum will account for the remainder of the total supply derived from the known placer deposits.

The production of crude platinum in California and Oregon in 1916, as reported by miners, was 710 troy oz valued at \$35,490. Buyers and refiners, however, report purchases of 890 oz. of crude platinum from these States, which, at the average price of crude platinum (\$45.50 an oz.), would have a value of \$40,495.

Reports from refiners of platinum indicate that 25,945 oz. of foreign crude platinum were refined. Most of this material came from Colombia and a little from British Columbia.

The price of refined platinum in the New York market has been very erratic. Beginning at \$90 a troy oz. in Jan. 1916, the price increased 75 cents an oz. to March, when it began to decline and reached \$55, the lowest for the year, in August. Buying for the Christmas jewelry trade in September brought a strong reaction and quotations rose to an average of \$101.25 for November, with a maximum of \$105 at the end of the month. In December quotations were easier and the year closed with platinum at about \$82 per oz.

Lithium Minerals in 1916. W. T. SCHALLER. Separate from Mineral Resources of the United States, 1916, Part II. 10 pp. Published July 9th. This is a full discussion of the mineral sources of lithium and the characteristics of these minerals, with a description of the occurrence, production, and uses of lithium salts.

Asbestos in 1916. J. S. DILLER. Separate from Mineral Resources of the United States, 1916, Part II. 5 pp. Published July 21. "The asbestos industry of the United States is in good condition as to both production and manufacture. The output of raw material in this country is far less than the demand, but the needed supply is readily drawn from Canada. The supply of asbestos of all grades, in Quebec, is so large, so conveniently obtained, and of a quality so excellent as to delay the development of asbestos deposits in the United States, except as to the lowest grade, which will not bear transportation, and as to the highest grade, the domestic supply of which for certain purposes is superior to the best grade of a asbestos from Canada. The demand for high grade asbestos has always been active, but under the stimulus of war conditions the available supply is not equal to the demand.

"The marketed production of asbestos in the United States in 1916 was 1,479 short tons, valued at \$448,214. As compared with the production of 1915, this was a decrease of 282 tons, or nearly 15 per cent in quantity, but a gain of 482 per cent in value. The decrease in quantity was wholly in the lower grade. The output of higher grades increased both in quantity and in value.

"Five States now produce asbestos: Arizona, California, Idaho, Georgia, and Virginia. Arizona and Georgia produce the largest quantities, Arizona of high-grade fiber and Georgia of fiber below the spinning grade. In Arizona there were three producers, but in each of the other States there was only one producer in 1916."

Talc and Soapstone in 1916. J. S. DILLER. Separate from Mineral Resources of the United States, 1916, Part II. 3 pp. Published July 21. The sales of talc in 1916 amounted to 193,309 tons, valued at \$1,762,842, a gain, as compared with

1915, of 16 per cent in quantity and of about 26 per cent in value.

As noted in the following table, talc is marketed in three forms. About 5 per cent is sold rough as it comes from the quarry or mine in California, Georgia, Maryland, North Carolina, Pennsylvania, and Virginia; a small quantity is manufactured, and the bulk is ground and sold for various purposes.

CLASSIFICATION OF TALC SOLD IN THE UNITED STATES IN 1916

CONDITION IN WHICH MARKETING	Quantity Short tons	Value	Av. Price per Ton
Rough	11,269	\$ 406,927	\$ 36.46
Manufactured into pencils and blanks ¹	828	102,674	124.00
Ground ²	181,182	1,553,240	8.57
	193,309	1,762,841	9.12

¹ Includes slate pencils and metal workers' crayons and blanks used in making acetylene burners and other objects.

² For foundry facings, filler for paper, paint, and rubber goods, toilet powder, foot dyes, lubricators for dressing skins and leather, etc.

There was a small production of soapstone in California, but almost the entire output of the United States came from Virginia, where there were four producing quarries. The total yield, including that of California, is 19,652 short tons.

CLASSIFICATION AND VALUE OF SOAPSTONE MINED AND SOLD IN THE UNITED STATES IN 1916

CLASS	Quantity Short tons	Value	Av. Price per Ton
Crude	525	\$ 1,355	\$ 2.58
Sawn into slabs	3,538	72,501	20.48
Manufactured	15,569	417,108	26.79

Phosphate Rock in 1916. R. W. STONE. Separate from Mineral Resources of the United States, 1916, Part II. 13 pp. Published August 13. "The quantity of phosphate rock marketed in the United States in 1916 was 1,682,385 long tons, valued at \$5,896,993, an increase of 149,718 tons in quantity and of \$483,544 in value over the production of 1915. This increase was comparatively small, but it indicates an improvement in the industry, and suggests that in spite of the curtailment in the exports, the production of former years may in time be approached. The output in 1916 was less than two-thirds that in 1913, the year before the European war began."

Graphite in 1916. H. G. FERGUSON. Separate from Mineral Resources of the United States, 1916, Part II. 16 pp. Published Aug. 13. This is a full statistical report.

Slate in 1916. G. F. LOUGHLIN. Separate from Mineral Resources of the United States, 1916, Part II. 11 pp. Published August 11.

Feldspar in 1916. F. J. KAY. Separate from Mineral Resources of the United States, 1916, Part II. 11 pp. Published August 15. The marketed production of domestic feldspar in 1916 was nearly 2 per cent lower in quantity than in 1915, but greater than in any other previous year and 46 per cent greater than in 1914. The production in 1916, 2.2 per cent and 3.2 per cent in quantity below 1915 and 1914, respectively, but was greater than in any other preceding year. An increase reported the values of the yearly production have expressed the combined sales of feldspar and ground felspar, and have, therefore, shown wider fluctuations than the quantities because of changes from year to year of the relative proportions of feldspar sold as crude or ground.

The average price for ground felspar in 1916 was \$4.44 a long ton, as compared with \$4.21 in 1915 and \$3.43 in 1914. The range in price is given, reported to the Bureau of Mines, and prices being from \$3.00 to \$6. The average price of ground felspar in 1916 was \$3.21 a short ton, compared with \$3.13 in 1915 and \$3.43 in 1914. The sales in 1916 in prices expressed in the United States Geological Survey being from \$2.00 to \$11.50 a ton. Of the total marketed production about 50 per cent was acid grade and 50 per cent was ground in 1916, compared with 85 per cent acid and 15 per cent, respectively, in 1915.

Salt, Bromine, and Calcium Chloride in 1916. R. W. STONE. Separate from Mineral Resources of the United States, 1916, Part II. 8 pp. Published September 8. Full statistics of the salt industry are given. The quantity of bromine marketed in 1915 was an increase of nearly 50 per cent over the production of each of the two preceding years, but in 1916 there was a decrease of nearly 20 per cent. The increased price caused a considerable increase in total value in 1916. The price of bromine in New York during the first half of 1916 ranged from \$4.75 to \$6.50 per lb., as a result, at least in part, of the unprecedented demand from abroad. These prices include cost of transportation and dealers' profits. In March, 1917, the price of bromine in New York had fallen to \$1.30 per lb.

Calcium chloride is made from natural brines at Mount Pleasant and Saginaw, Mich.; Pomeroy, Ohio; and Mason, Hartford, and Malden, W. Va. As the same brines yield salt and bromine, practically every constituent in them is turned to profit. The quantity of calcium chloride produced from natural brines and sold in the United States has recently been about 20,000 short tons a year, valued at \$6 to \$7 a ton. Since the first half of 1916 there has been a demand for this material which has raised the price.

Fuller's Earth in 1916. J. MIDDLETON. Separate from Mineral Resources of the United States, 1916, Part II. 2 pp. Published September 4. The fuller's earth industry showed considerable progress in 1916, and the quantity, value, and average price per ton of the product sold in that year were the largest ever recorded by the United States Geological Survey. The increase in quantity was 19,921 short tons, or 42 per cent, and in value \$217,732, or 45 per cent, over 1915, the previous leading year. Almost from the beginning of the industry in this country the quantity and value and the average price per ton of the domestic product have exceeded those of the imports. The quantity and the value of the earth produced in the United States in 1916 were more than four times as great as those of the earth imported, and the average price per ton of the domestic earth was \$2.11 more than that of the imported earth. Notwithstanding a continued decrease in imports, the apparent consumption—production plus imports—increased from 57,222 short tons in 1913 to 84,623 in 1916. The domestic fuller's earth formed 80 per cent of the consumption in 1916 and 67 per cent in 1913.

The imports of fuller's earth for consumption in 1916 continued to decline. The decrease in quantity was 14 per cent and in value 8 per cent. The average price per ton of imported earth was 47 cents higher than in 1915. The imports are nearly all (93 per cent in 1916) of wrought or manufactured earth.

BUREAU OF MINES

The Primary Volatile Products of the Carbonization of Coal. G. B. TAYLOR AND H. C. PORTER. Technical Paper 140, 59 pp. Paper, 10 cents. This report is a continuation of the work described in Bulletin 1 of the Bureau of Mines on the character of the volatile matter of coal. The experimental methods have been refined and more precise results obtained.

The importance of an exact knowledge of the reactions taking place when coal is heated need not be dwelt upon at length. The subject of carbonization is important in all industrial applications of coal, whether it be in gas manufacture or coke making, where it is paramount, or in those processes where coal is burned, such as in boiler furnaces, gas producers, and metallurgical furnaces. The results presented here are more or less of a fundamental character—a study of basic phenomena in carbonization, rather than of the ultimate results of these phenomena as a whole.

The Ores of Copper, Lead, Gold, and Silver. C. H. FULTON. Technical Paper 143, 41 pp. Paper, 5 cents. This report discusses the various minerals which constitute these ores and describes the characteristics of the ores themselves.

Limits of Complete Inflammability of Mixtures of Mine Gases and of Industrial Gases with Air. G. A. BURRELL AND A. W. GAUGER. Technical Paper 150, 13 pp. Paper, 5 cents.

Carbon Monoxide Poisoning in the Steel Industry. J. A. WATKINS. Technical Paper 156, 19 pp. Paper, 5 cents. The object of this paper is to set forth briefly the liability to carbon monoxide poisoning of those employed in the various departments of a steel plant; the sources of the gas; the extent to which it is present; its effect on workers; and to make certain recommendations for the prevention and remedy of such conditions. This report, prepared through the coöperation of the Public Health Service and the Bureau of Mines, is published as a contribution to the literature dealing with the improvement of conditions affecting the health of persons employed in the metallurgical industries. Attention is given primarily to the liability to chronic poisoning—that is, the daily exposure of employees to small quantities of this gas over an extended period of time—rather than to that of acute poisoning, or "gassing," as prevention of this accident is a problem of safety engineering rather than of industrial hygiene.

The Determination of Nitrogen in Substances Used in Explosives. W. C. COPE AND G. B. TAYLOR. Technical Paper 160, 46 pp. Paper, 10 cents. This article discusses particularly the Dumas method for nitrogen and gives a large number of useful tables to assist in the computations of this method.

Permissible Explosives, Tested Prior to Jan. 1, 1917. S. P. HOWELL. Technical Paper 169, 19 pp. Paper, 5 cents.

Production of Explosives in the United States during the Calendar Year 1916. A. H. FAY. Technical Paper 175, 24 pp. Paper, 5 cents.

"The production figures tabulated are classified as follows:

"(1) *Black Blasting Powder*—All black powder with sodium or potassium nitrate as a constituent is here classified as black blasting powder.

"(2) *High Explosives*—Dynamite and all other high explosives of various trade names and compositions, except permissible explosives, are put in this class.

"(3) *Permissible Explosives*—In this class are included ammonium nitrate explosives, hydrated explosives, organic nitrate explosives, and certain nitroglycerin explosives containing an excess of free water or carbon. All permissible explosives have passed certain tests of the Bureau of Mines and are not to be regarded as permissible unless used in the manner specified by the bureau.

"The total production, excluding exports, of explosives in the United States during the calendar year 1916, according to figures that the Bureau of Mines has received from manufacturers, was 505,415,052 lbs. (252,708 short tons), as compared with 460,900,796 lbs. (230,450 short tons) in 1915.

"The production for 1916 is segregated as follows: Black powder, 215,575,025 lbs.; "high" explosives other than permissible explosives, 255,154,787 lbs.; and permissible explosives, 34,685,240 lbs. These figures represent an increase of 17,852,725 lbs. of black powder, 19,326,200 lbs. of high explosives and 7,335,331 lbs. of permissible explosives, as compared with figures for 1915."

Preparation of Ferro-Uranium. H. W. GILLET AND E. L. MACK. Technical Paper 177, 46 pp. Paper, 5 cents. (See THIS JOURNAL, 9 (1917), 342.)

The Wet Thiogen Process for Recovering Sulfur from Sulfur Dioxide in Smelter Gases—A Critical Study. A. E. WELLS. Bulletin 133, 66 pp. Paper, 10 cents. (See THIS JOURNAL, 9 (1917), 872.)

BUREAU OF STANDARDS

Testing of Clinical Thermometers. Circular 5, third edition. 19 pp. Issued July 16th. The procedure for testing clinical

thermometers and regulations and schedule of fees for this work are given. There is also included a description of revised methods of testing and a new form of certificates for certifying thermometers that fall within the acceptable range of tolerance for their class.

Gas Calorimetric Tables. Circular 65. 19 pp. Issued June 25. "This publication is in response to numerous requests for a brief and concise set of operating directions for a gas calorimeter, and for a convenient set of correction tables. It may be regarded as a supplement to Bureau Circular No. 48 on 'Standard Methods of Gas Testing.' It is hoped that this will promote greater uniformity in operating methods and in records and facilitate the application of proper corrections.

"It is assumed that the operator is thoroughly familiar with directions and precautions as outlined in Circular No. 48. The directions given here are a brief summary of the full instructions contained in that circular, together with the tables needed for daily laboratory use."

Standard Samples for Thermometric Fixed Points. Circular 66. 13 pp. Issued July 25. "In response to many urgent requests for a concrete realization of a series of standard temperatures, which would be available to anyone anywhere for the standardization of pyrometers and for the reproduction of the standard scale of temperature for use in laboratory and industrial works, the Bureau has had prepared a series of pure metals, of which it has made chemical analyses as a check on the degree of purity realized, together with exact determinations of the respective melting or freezing points.

"In this, the first Bureau circular relating to the subject, are described the samples of tin, zinc, aluminum, and copper which are now available for distribution as standard temperature samples. Preparations are under way to add samples of pure lead to this list. As soon as opportunity permits, palladium and platinum samples in the form of wires will be added to serve for the reproduction of the temperature scale up to 1755° C., and it is expected that others will be added as the demand for them may arise. Pure samples of naphthalene, benzophenone, and sulfur would serve, by means of their boiling points, taken under carefully specified conditions, as excellent standard temperature samples for the reproduction of the lower range (to 450° C.) of the temperature scale with the highest attainable accuracy."

The Relative Sensibility of the Average Eye to Light of Different Colors, and Some Practical Applications to Radiation Problems. W. W. COBLENTZ AND W. B. EMERSON. Scientific Paper 303. 83 pp. "In the present investigation the methods are practically the same as used by previous experimenters. In the visual measurements, the spectral light was compared with a standard white light both by means of a flicker photometer and by means of an equality of brightness photometer. The source of white light was a standardized vacuum tungsten lamp. A cylindrical acetylene flame was used as a source of spectral light. The distribution of energy in the spectrum of the acetylene flame was determined with great care. Visibility curves were obtained on 130 persons, of which number seven were known to be color blind. The visibility curve of the average eye is wider than previously observed. A mathematical equation of the average visibility is given and applications of these data to physical photometry are made. It is shown that the eye responds to light having an intensity less than 1×10^{-16} watt."

An Experimental Study of the Fahy Permeameter. C. W. HEDGECOCK AND R. L. SANDFORD. Scientific Paper 304. 31 pp. Issued Aug. 17th. This permeameter was devised by F. P. Fahy, of the Pennsylvania Railroad Company, for the purpose of comparing the magnetic properties of two similar specimens of steel. In the fall of 1914 a comparative investigation of the

magnetic-mechanical properties of steel was begun by the above-named company and the Bureau of Standards at the Bureau laboratories in which the Fahy apparatus was used for comparative magnetic measurements. Early results obtained with the apparatus, however, indicated the possibility of its development as a permeameter and this was immediately undertaken. In order to ascertain the degree of accuracy that has been attained, as well as its fitness for general laboratory use, a critical experimental study has been made of the instrument in its present improved form.

Note on Electrical Conduction in Metals at Low Temperatures. F. B. SILLBEE. Scientific Paper 307. 6 pp. Issued July 23.

Reflecting Power of Tungsten and Stellite. W. W. COBLENTZ AND W. B. EMERSON. Scientific Paper 308. 10 pp. Issued August 10. This paper gives the results of a critical examination of the reflecting power of tungsten in the region of the spectrum from 0.5 to 6.0 μ .

The reflecting power of tungsten in the form of plane, highly polished mirrors was determined by comparison with silver and by a new method employing a total reflection prism.

The results obtained are based upon an examination of three samples of pure tungsten and a sample of unknown purity.

DEPARTMENT OF AGRICULTURE

The Seasoning of Wood. H. S. BETTS. Department Bulletin 552. 28 pp. Paper, 10 cents. Issued July 9th. This is a description of various methods of seasoning wood that are of interest to manufacturers of wood products.

Articles from the Journal of Agricultural Research

Daily Variation of Water and Dry Matter in the Leaves of Corn and the Sorghums. E. C. MILLER. 10, 11-46 (July 2).

A Neglected Factor in the Use of Nicotine Sulfate as a Spray. W. MOORE AND S. A. GRAHAM. 10, 47-50 (July 2).

Isolation of Cyanuric Acid from Soil. L. E. WISE AND E. H. WALTERS. 10, 85-92 (July 9).

A Substitute for Litmus for Use in Milk Cultures. W. M. CLERK AND H. A. LUBS. 10, 105-112 (July 10).

Movement and Distribution of Moisture in the Soil. F. S. HARRIS AND H. W. TURPIN. 10, 113-55 (July 10).

Physiological Effect on Growth and Reproduction of Rations Balanced from Restricted Sources. E. B. HART, E. V. MCCOLLUM, H. STERNHOCK AND G. C. HUMPHREY. 10, 175-94 (July 23).

Toxic Value and Killing Efficiency of the Arsenates. A. L. LOVETT AND R. H. ROBINSON. 10, 190-207 (July 23).

Evaporation from the Surface of Water and River-Bed Materials. R. B. SLEDGE. 10, 208-215 (July 30).

Influence of Grading on the Value of Fine Aggregate Used in Portland Cement Concrete Road Construction. F. H. JACKSON, JR. 10, 263-74 (July 30).

Chemical Studies in Making Alfalfa Silage. C. O. SWANSON AND E. L. TAYLOR. 10, 275-92 (August 6).

Toughness of Bituminous Aggregates. C. S. KEEFE AND R. H. LEWIS. 10, 315-30 (August 13).

Origin of Alkali. E. STEWART AND W. PETERSON. 10, 331-34 (August 13).

Effect of Paraffin on the Accumulation of Ammonia and Nitrates in the Soil. P. L. CLARK. 10, 331-64 (August 13).

Volatility of Organic Compounds as an Index of the Toxicity of Their Vapors to Insects. W. MILLER. 10, 366-71 (August 13).

Relation of Movement of Water in a Soil to Its Hygroscopicity and Initial Moisture. F. J. ARDAY AND G. B. MATHIAS. 10, 369-478 (August 13).

BOOK REVIEWS

Water Supply. 4th Ed. By WILLIAM P. MASON, Professor of Chemistry, Rensselaer Polytechnic Institute. 8vo, and 528 pp. John Wiley & Sons, Inc., New York, 1916. Price, \$3.75 net.

The first edition of this book was issued in 1896, the third in 1902. Since the appearance of the third edition so many improvements and changes have been made in waterworks practice that considerable portions of this edition have been changed and many additions have been made. The same arrangement of chapters has been followed.

Under the title "Drinking Water and Disease" is shown the distinction between normal and polluted waters, and the relation of water supply to public health. Among the additions are the following: typhoid-fever death rates; the occurrence of the typhoid bacillus in carbonated waters, sewage, soil, dust, growing plants, river and lake water, and the Chicago drainage canal; the distribution of typhoid fever by milk, flies, shell fish and typhoid carriers; and vacation typhoid. The author discusses the value of *B. coli* as an indicator of pollution, and the use of a pure or purified water as illustrated by the Bubbly Creek, Chicago case. Distilled water is shown to be wholesome.

Under the title "Artificial Purification of Waters," methods of filtration are described. Owing to the progress in filtration more emphasis has been placed on American or mechanical filtration than in previous editions. Drifting sand filters, Peuch-Chabal system and non-submerged filters, sterilization by bleaching powder, liquid chlorine, ozone, and ultraviolet light are discussed. Plants for the removal of iron, manganese, and carbon dioxide are described. Emergency purification and purification for army encampments are also included.

A new and striking example of natural purification by aeration is given in the Kensico aerator of the New York water supply. For purification of streams the Chicago drainage canal case is cited in considerable detail.

There is additional information concerning purification due to freezing and storage. Specific investigations have shown the effect of freezing upon typhoid bacilli. Ice-borne typhoid epidemics are very rare.

The author has taken advantage of investigations by the United States Geological Survey which furnish interesting data concerning the amount of substances carried in suspension by Mississippi River. He lays special stress on sewage pollution of rivers, a point made necessary because of the great increase in the amount of sewage and trade wastes emptied into our streams. Sewage pollution not only causes nuisances in varying degree, but destroys the value of the streams for fish life.

The pollution of the Great Lakes is increasing. The Chicago drainage canal is given as an illustration of one method of protecting the purity of the Great Lakes water. The advantages of storage for purification and as a preliminary to a filtration are indicated. The new and very successful method for destroying algae by copper sulfate is described. Stripping of reservoirs is considered of less importance than formerly. Inspection and care of watersheds, especially when the water is used without further treatment, is shown to be of the utmost importance. Special emphasis is laid on water supplies and sanitation of camps, not only for the military, but, also for unorganized gangs of laborers. The report of the International Joint Commission on the care of the water of the Great Lakes is suggestive of future methods of protecting the purity of this water supply.

The distinction is made between the water from shallow wells not entering rock and those which enter rock. The principal addition to methods of obtaining water are the subsurface dams. Additional information concerning the carrying of pollution to wells is given and specific examples shown.

Deep-seated water includes water from deep rock-wells and springs having a temperature different from that of the subsoil. Methods of securing deep-seated water are given and the very interesting sea mills of Greece are described.

Much water is wasted when an unlimited amount is allowed. Meters prevent this waste and are shown to be unobjectionable from a sanitary standpoint. As cities increase in size, it is shown that the proportional draft for fires decreases.

Additional examples of trouble from lead and zinc are given. Iron pipes corrode or become tuberculated. Special methods of cleaning have been devised. The recently discovered processes for the softening of water for boilers, especially the Permutit process, are described.

The book is written in a very pleasing style which adds to the pleasure of reading it. The use of heavier type than in previous editions improves the appearance of the pages.

EDWARD BARTOW

Calculations Used in Cane Sugar Factories. By IRVING H. MORSE. 2nd Edition, Rewritten, 185 pp. John Wiley and Sons, New York, 1917.

The first edition of this book made its main appeal to the technical superintendent or chief chemist of sugar houses of the old type in which the chemical control was rather loose and the chemical bookkeeping rather incomplete. To these men it offered convenient formulae and tables for rapid calculations, and it served its purpose fairly well. This new edition is practically a new book and a much better one in every respect than the old one. It is well printed on good paper with flexible leather covers and is small enough to go into the pocket. It does not compete with such standard books on sugar analysis as those of Spencer and Prinsen-Geerlings, but it supplements them by giving a practical, intelligible and thorough system of interpreting the analytical results, together with model form sheets for report work.

Both the system and the reports accord with the best modern practice in the most efficiently run sugar centrals, in Louisiana as well as in the tropics. The book also contains numerous convenient tables which it is difficult to find elsewhere and a complete set of standard formulae for ordinary sugar house calculations. Both the tables and the formulae are accompanied by sufficiently detailed directions and examples of practical application to render them intelligible even to the non-technically trained man. The system of laboratory reports and calculations of yields is convenient and well considered.

The chapter on Manufacturing Economy is of particular interest. It shows by simple calculation the actual financial returns of certain sugar house procedures which are frequently accepted or rejected by the superintendents almost at haphazard, such as the effect of increased maceration on yield. It also touches upon the subject of turning out products from the sugar house which will give the greatest net gain rather than running the house in a groove with no regard for market prices or for supply and demand.

The last chapter has to do with the purchase of cane by the unit system. As the purchase of cane by rich sugar house owners from poor cane growers is a problem which involves not only chemistry but psychology as well, Mr. Morse's particular solution will probably not be accepted without discussion, at least.

In spite of some hasty proof-reading and careless construction, the book on the whole is clearly written and intelligible. It will undoubtedly prove of much value in sugar laboratories, both of Louisiana sugar houses and tropical sugar houses as well.

CHARLES E. COATES

MARKET REPORT—SEPTEMBER, 1917

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON SEPT. 20

INORGANIC CHEMICALS

Acetate of Lime.....	100 Lbs.	6.00	@	6.05
Alum. Ammonia, lump.....	100 Lbs.	4.25	@	4.50
Aluminum Sulfate, high-grade.....	Ton	70.00	@	75.00
Ammonium Carbonate, domestic.....	Lb.	10 1/4	@	11
Ammonium Chloride, white.....	Lb.	—	@	—
Aqua Ammonia, 26°, drums.....	Lb.	12 1/4	@	13
Arsenic, white.....	Lb.	16	@	16 1/2
Barium Chloride.....	Ton	80.00	@	90.00
Barium Nitrate.....	Lb.	11 1/4	@	12
Barytes, prime white, foreign.....	Ton	28.00	@	30.00
Bleaching Powder, 35 per cent.....	100 Lbs.	1.50	@	2.00
Blue Vitriol.....	Lb.	9 1/4	@	10
Borax, crystals, in bags.....	Lb.	7 1/4	@	8 1/4
Boric Acid, powdered crystals.....	Lb.	13	@	13 1/4
Bromine, crude, domestic.....	Long Ton	60.00	@	65.00
Bromine, technical, bulk.....	Lb.	55	@	60
Calcium Chloride, lump, 70 to 75% fused.....	Ton	30.00	@	35.00
Caustic Soda, 76 per cent.....	100 Lbs.	9.90	@	10.00
Chalk, light precipitated.....	Lb.	4 1/4	@	4 1/4
China Clay, imported.....	Ton	18.00	@	30.00
China Clay, imported.....	Ton	8.00	@	15.00
Fuller's Earth, foreign, powdered.....	Ton	—	@	35.00
Fuller's Earth, domestic.....	Ton	8.50	@	15.00
Glauber's Salt, in bbls.....	100 Lbs.	80	@	85
Green Vitriol, bulk.....	100 Lbs.	1.00	@	1.05
Hydrochloric Acid, commercial, 18°.....	Lb.	1 1/4	@	1 1/4
Hydrochloric Acid, C. P. conc., 22°.....	Lb.	1 1/4	@	2
Iodine, resublimed.....	Lb.	3.50	@	3.55
Lead Acetate, white crystals.....	Lb.	16	@	16 1/2
Lead Nitrate.....	Lb.	15 1/4	@	16
Litharge, American.....	Lb.	11	@	11 1/4
Lithium Carbonate.....	Lb.	—	@	1.25
Magnesium Carbonate, U. S. P.....	Lb.	18	@	20
"Magnesite," "Calcined".....	Ton	60.00	@	65.00
Nitric Acid, 36°.....	Lb.	7 1/4	@	7 1/4
Nitric Acid, 42°.....	Lb.	8	@	8 1/4
Phosphoric Acid, sp. gr. 1.710.....	Lb.	33	@	37
Phosphorus, yellow.....	Lb.	2.20	@	2.25
Plaster of Paris.....	Bbl.	1.50	@	1.70
Potassium Bichromate, cakes.....	Lb.	44	@	45
Potassium Bromide, granular.....	Lb.	1.35	@	1.36
Potassium Carbonate, calcined, 80 to 85%.....	Lb.	70	@	75
Potassium Chlorate, crystals, spot.....	Lb.	54	@	55
Potassium Cyanide, bulk, 98-99 per cent.....	Lb.	2.30	@	2.40
Potassium Hydroxide, 88 to 92%.....	Lb.	83	@	85
Potassium Iodide, bulk.....	Lb.	—	@	2.90
Potassium Nitrate.....	Lb.	29	@	31
Potassium Permanganate, bulk.....	Lb.	4.00	@	4.25
Quicksilver, flask.....	75 Lbs.	110.00	@	112.00
Red Lead, American, dry.....	Lb.	13	@	13 1/4
Salt Cake, glass makers.....	Ton	22.00	@	24.00
Silver Nitrate.....	Oz.	64	@	66
Soapstone, in bags.....	Ton	10.00	@	12.50
Soda Ash, 58%, in bags.....	100 Lbs.	3.60	@	3.75
Sodium Acetate.....	Lb.	11	@	11 1/4
Sodium Bicarbonate, domestic.....	100 Lbs.	2.45	@	2.60
Sodium Bichromate.....	Lb.	26	@	27
Sodium Chlorate.....	Lb.	23 1/4	@	24 1/4
Sodium Fluoride, commercial.....	Lb.	18	@	19
Sodium Hyposulfite.....	100 Lbs.	1.75	@	1.85
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	5.00	@	5.10
Sodium Silicate, liquid, 40° Bé.....	100 Lbs.	2.10	@	2.20
Sodium Sulfide, 60%, crystals, in bbls.....	Lb.	3 1/4	@	3 1/4
Sodium Bisulfite, powdered.....	Lb.	6 1/4	@	7
Strontium Nitrate.....	Lb.	28	@	30
Sulfur, flowers, sublimed.....	100 Lbs.	4.05	@	4.06
Sulfur, roll.....	100 Lbs.	3.70	@	4.15
Sulfuric Acid, chamber, 66° Bé.....	Ton	34.00	@	35.00
Sulfuric Acid, oleum (fuming).....	Ton	40.00	@	50.00
Talc, American white.....	Ton	15.00	@	18.00
Terra Alba, American, No. 1.....	100 Lbs.	85	@	90
Tin Bichloride, 50°.....	100 Lbs.	19.25	@	19.50
Tin Oxide.....	Lb.	64 1/4	@	65
White Lead, American, dry.....	Lb.	11 1/4	@	12
Zinc Carbonate.....	Lb.	25	@	25 1/4
Zinc Chloride, commercial.....	Lb.	16 1/4	@	17
Zinc Oxide, American process XX.....	Lb.	16 1/4	@	16 1/4

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	55	@	56
Acetic Acid, 56 per cent, in bbls.....	Lb.	11	@	11 1/4
Acetic Acid, glacial, 99 1/4%, in carboys.....	Lb.	37	@	38
Acetone, drums.....	Lb.	35	@	36
Alcohol, denatured, 180 proof.....	Gal.	1.00	@	1.01

Alcohol, grain, 188 proof.....	Gal.	4.26	@	4.28
Alcohol, wood, 95 per cent, refined.....	Gal.	1.10	@	1.12
Amyl Acetate.....	Gal.	4.50	@	4.60
Aniline Oil.....	Lb.	26 1/4	@	27
Benzoic Acid, ex-toluol.....	Lb.	2.00	@	2.50
Benzol, 90 per cent.....	Gal.	51	@	54
Camphor, refined in bulk, bbls.....	Lb.	79 1/4	@	80
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	42	@	43
Carbon Bisulfide.....	Lb.	7	@	7 1/4
Carbon Tetrachloride, drums, 100 gals.....	Lb.	16 1/4	@	17
Chloroform.....	Lb.	60	@	61
Citric Acid, domestic, crystals.....	Lb.	72	@	75
Cresote, Beechwood.....	Lb.	1.90	@	2.00
Cresol, U. S. P.....	Gal.	1.25	@	1.30
Dextrine, corn (carloads, bags).....	100 Lbs.	6.85	@	6.90
Dextrine, imported potato.....	Lb.	—	@	—
Ether, U. S. P. 1900.....	Lb.	31	@	39
Formaldehyde, 40 per cent.....	Lb.	16	@	16 1/4
Glycerine, dynamite, drums included.....	Lb.	66	@	67
Oxalic Acid, in casks.....	Lb.	46	@	47
Pyrogallie Acid, resublimed, bulk.....	Lb.	3.25	@	3.50
Salicylic Acid.....	Lb.	1.40	@	1.50
Starch, cassava.....	Lb.	—	@	—
Starch, corn (carloads, bags) pearl.....	100 Lbs.	5.55	@	5.60
Starch, potato.....	Lb.	13	@	14
Starch, rice.....	Lb.	10	@	12
Starch, "sago flour".....	Lb.	6	@	6 1/4
Starch, wheat.....	Lb.	5 1/4	@	6 1/4
Tannic Acid, commercial.....	Lb.	80	@	95
Tartaric Acid, crystals.....	Lb.	78 1/4	@	79

OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	65	@	68
Black Mineral Oil, 29 gravity.....	Gal.	13 1/4	@	14
Castor Oil, No. 3.....	Lb.	2 5/4	@	26
Ceresin, yellow.....	Lb.	14	@	14
Corn Oil, crude.....	Lb.	—	@	—
Cottonseed Oil, crude, f. o. b. mtl.....	Gal.	1.05	@	1.06
Cottonseed Oil, p. s. y.....	Lb.	16 1/4	@	16 1/4
Menhaden Oil, crude (southern).....	Gal.	—	@	—
Neat's-foot Oil, 20°.....	Gal.	1.90	@	2.00
Paraffin, crude, 118 to 120 m. p.....	Lb.	7 1/4	@	7 1/4
Paraffin Oil, high viscosity.....	Gal.	29 1/4	@	30
Rosin, "F" Grade, 280 lbs.....	Bbl.	—	@	6.25
Rosin Oil, first run.....	Gal.	35	@	35
Shellac, T. N.....	Lb.	55	@	55
Spermaceti, cake.....	Lb.	25	@	25
Sperm Oil, bleached, winter, 38°.....	Gal.	—	@	1.55
Spindle Oil, No. 200.....	Gal.	24	@	25
Stearic Acid, double-pressed.....	Lb.	26	@	27
Tallow, acidless.....	Gal.	—	@	1.50
Tar Oil, distilled.....	Gal.	33	@	34
Turpentine, spirits of.....	Gal.	44	@	44

METALS

Aluminum, No. 1, ingots.....	Lb.	41 1/4	@	42 1/4
Antimony, ordinary.....	Lb.	15	@	15 1/4
Bismuth, N. Y.....	Lb.	2.85	@	2.90
Copper, electrolytic.....	Lb.	27	@	27 1/4
Copper, lake.....	Lb.	27	@	29 1/4
Lead, N. Y.....	Lb.	9	@	9 1/4
Nickel, electrolytic.....	Lb.	55	@	56
Platinum, refined, soft.....	Oz.	—	@	105.00
Silver.....	Oz.	—	@	1.03 1/2
Tin, Straits.....	Lb.	62 1/4	@	62 1/4
Tungsten (W.O.).....	Per Unit	23.00	@	25.00
Zinc, N. Y.....	Lb.	8 1/4	@	8 1/4

FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	7.10	@	7.25
Blood, dried, f. o. b. Chicago.....	Unit	—	@	6.50
Bone, 4 and 50, ground raw.....	Ton	35.00	@	40.00
Calcium Cyanamid.....	Unit of Ammonia	—	@	4.00
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	—	@	nominal
Phosphate, acid, 16 per cent.....	Ton	16.00	@	18.00
Phosphate rock, f. o. b. mine.....	Ton	—	@	—
Florida land pebble, 68 per cent.....	Ton	3.15	@	3.25
Tennessee, 78-80 per cent.....	Ton	5.50	@	6.00
Potassium "muriate," basis 80 per cent.....	Ton	330.00	@	340.00
Pyrites, furnace size, imported.....	Unit	—	@	nominal
Taukage, high-grade, f. o. b. Chicago.....	Unit	6.00	@	10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

AT EASTON, PA.

Volume IX

NOVEMBER 1, 1917

No. 11

Editor: CHARLES H. HERTY

Assistant Editor: LEOLA E. MARRS

Advertising Manager: G. W. NOTT

ADVISORY BOARD

H. E. BARNARD, H. K. BENSON, F. K. CAMERON, B. C. HESSE, A. D. LITTLE, A. V. H. MORY, M. C. WHITAKER

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly; single copy, 60 cents

Price per single copy to American Chemical Society members, 50 cents. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted

Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879

All communications should be sent to The Journal of Industrial and Engineering Chemistry,

Telephone: Vanderbilt 1930

35 East 41st Street, New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

War Service for Chemists.....	1002
Toluol, Toluol, and then Toluol!.....	1002
Explosives and Dyestuffs—A French Confirmation....	1003
Dr. Roerber.....	1004
The Exposition.....	1004
The Slacker Ring Again.....	1004

THIRD EXPOSITION OF CHEMICAL INDUSTRIES:

Opening Addresses:

The Battle of the American Chemical Industries. Chas. H. Herty.....	1005
American Chemical Industry and the American Chemical Society. Julius Stieglitz.....	1005
Greeting from the Electrochemists. Colin G. Fink. The Progress of American Chemical Engineering. G. W. Thompson.....	1006
National Research Council and U. S. Tariff Com- mission Addresses:	1007

Introductory. B. C. Hesse.....	1008
National Research Council, Chemistry Committee, Second Report. Marston Taylor Bogert.....	1009
The Tariff Commission and Our Chemical Indus- tries. William S. Culbertson.....	1013
The Tariff Commission and Its Operation with Reference to the Chemical Schedule. Grinnell Jones.....	1016
The Development of Our Export Trade. W. S. Kies. The Future of Chemical Industry in the United States. L. H. Backlund.....	1020
Russia and Its Relationships to the United States. C. H. Rowton.....	1022

Natural Resources Symposium: Ahoppa Awan Tewa (The Dead Their Day). C. H. Crawford.....	1022
Building a Complete Cycle of Chemical Industries on the Clinchfield. Victor V. Kelsey.....	1023

Development of Chemical Industries along the Norfolk and Western Railway: Natural Re- sources Developed and Undeveloped. E. A. Schubert.....	1025
Alloy Metals, Production and Uses, Especially in Relation to the War. Notes on Observation Made Abroad. Geo. K. Burgess.....	1026
Symposium—The Chemist and the Banker The Chemist. Arthur D. Little.....	1027
The Banker. G. A. O'Reilly.....	1028

ORIGINAL PAPERS:

The Deposition of Silver Films on Glass. Alex- ander Silverman and Raymond M. Howe.....	1032
The Recovery of Water Soluble Potash as a By- Product in the Cement Industry. William H. Ross and Albert R. Mery.....	1035

Solvent Gasoline. C. Olin North.....	1038
The Composition of Loganberry Juice and Pulp Milo Reason Daughters.....	1043
The Fertilizing Value of Some Household Wastes Philip E. Browning.....	1043

LABORATORY AND PLANT:

Method of Staining to Distinguish between Bleached and Unbleached Sulfite Pulps. Charles G. Bright.....	1044
Some Suggestions Concerning the Preparation of Am- monium Citrate Solution and the Determination of Insoluble Phosphoric Acid. Philip McG. Shuey.....	1045
A Suggested Form of Viscosimeter. W. C. Cope.....	1046
A Convenient Automatic Device for Rapidly Wash- ing Pipettes. Aubrey Vail Fuller.....	1046
An Asbestos Stopper. Joseph B. Nichols.....	1047
A New Form of Safety Pipette. A. S. Behrman.....	1047

ADDRESSES:

Analysis and Testing of Prepared Roofings. Herbert Abraham.....	1048
Technical Photography and Its Use in Industrial and Commercial Organizations. John H. Graff.....	1052
Chairman's Address: Fertilizer Division, American Chemical Society. J. E. Breckenridge.....	1054

METALLURGICAL SYMPOSIUM:

Physico-Chemical Data Needed by Metallurgists. J. W. Richards.....	1056
Recent Developments in Connection with the Use of Sulfur Dioxide in Hydrometallurgy. Edward R. Weddell.....	1057
The Importance of the Flotation Process in the Metallurgy of Copper. E. P. Mathewson.....	1058
Chemicals Used in Ore Flotation. Oliver C. Ralston and L. D. Yundt.....	1058

CURRENT INDUSTRIAL NEWS:

.....	1063
-------	------

SCIENTIFIC SOCIETIES:

Tentative Standard Methods for the Sampling and Analysis of Commercial Fats and Oils, Other than Those of the Coconut, Butter and Lard Groups. American Electrochemical Society, and General Meeting, Fertilizer Division, American Chemical Society. Report of the Committee on Sampling and Report of the Committee on Research and Methods of Analysis.....	1066
---	------

NOTES AND CORRESPONDENCE.....	1072
-------------------------------	------

WASHINGTON LETTER.....	1074
------------------------	------

PERSONAL NOTES.....	1075
---------------------	------

INDUSTRIAL NOTES.....	1076
-----------------------	------

GOVERNMENT PUBLICATION.....	1077
-----------------------------	------

NEW PUBLICATIONS.....	1081
-----------------------	------

MARKET REPORT.....	1082
--------------------	------

EDITORIALS

WAR SERVICE FOR CHEMISTS

France and England freely acknowledge that they greatly decreased their efficiency by sending their scientific men to the trenches. Although they have since withdrawn most of those still alive and are now using them in special service, the dearth of technically trained men has been and is severely felt.

Secretary of War Baker, aware of this fact, is carrying out the full spirit of the *selective* draft, and specially trained men, so far as needed, are being assigned to the war service which they are trained to render.

More than others among scientific men, trained chemists have been needed for war purposes by both the Army and the Navy.

Fortunately, the American Chemical Society and the Bureau of Mines, acting cooperatively, foreseeing this need, took first a census of American chemists and later compiled from all data available a list of those enlisted. From this list of chemists actually in the Army and the Navy a large number have been selected for special fitness and have been already assigned. Many more, undoubtedly, will be so assigned, and if the present demand keeps up, it may later be necessary to ask for special enlistment for chemical work. That time has not yet arrived.

At present any chemist not required by law to enter chemical war service who enters voluntarily keeps one chemist in the ranks and deprives the chemical industries of his own service as well. A number of chemists have been commissioned, but these are picked men of special attainments and specific experience. The majority will serve as privates or non-commissioned officers until such time as they are found to deserve promotion.

DON'T ask to be assigned to chemical work until you are actually in the camp. Camp assignment must be made before your name will be submitted to the War Department.

DON'T send in your name, even for consideration for such service, if exemption is to be asked for or while exemption claims are pending. It leads to endless confusion.

DON'T try to deprive another chemist actually in the Army of his opportunity to render chemical service by yourself seeking such service, *until called*. The industries which supply the Army and Navy with the sinews of war need trained chemists and are being seriously handicapped by the depletion of their chemical personnel.

DON'T write to anyone in Washington to aid you in a claim for exemption. Even if they wished to do so, they are quite properly powerless for the law delegates exemption to the Local and District Boards.

DO send me your name, address, military and camp assignment when actually sworn in (not before). If you have not already filed details of your age, training, and experience, send this also at the same time.

CHARLES L. PARSONS, *Secretary*,
AMERICAN CHEMICAL SOCIETY

TOLUOL, TOLUOL, AND THEN TOLUOL!

There is work, urgent and vital work, immediately ahead for every member of the American Chemical Society. It is the arousal of this Nation to the imperative need of bringing into energetic cooperation the War Department, the gas companies and the people, as represented by their several Boards of Commissioners, so that the stripping of gas of its toluol content shall begin throughout the country at the very earliest possible moment.

Many of our troops are already near the French battle front, still more are in training camps in this country, impatient to get to France, and soon other drafted armies will be raised to augment this number until America's full force makes itself felt in bringing to a successful ending the greatest of all wars.

Press accounts have shown clearly the amazing development of artillery fire during the past two months. The quintuple barrage, the wavelike and weaving barrage fire of the British artillery during the recent drives east of Ypres, have successfully driven the Germans steadily back and at a sacrifice of man-power amounting to only ten per cent of the numbers estimated before the drives began.

When the Spring drives of 1918 begin, American soldiers will be participants in great numbers. If they are to prove equal in effectiveness to our British allies, if their casualty lists are to be held down to relative small numbers, we must provide them with the maximum possible amount of high explosives for barrage fire.

Of the several high explosives now in use, the War Department has pronounced tri-nitro-toluol (T. N. T.) as best. It is the easiest high explosive to make, and the safest to transport. For its manufacture toluol is required. At the present time we are producing annually approximately 11,000,000 gallons of toluol from the by-product retort coke ovens which have increased so rapidly in number since the war began. This quantity, however, is under contract for the supply of the Navy and our allies. At least a year is required for the construction of a large battery of by-product ovens. For the new army the only quickly available source of toluol is the gas plants. A statement to that effect was made to us recently by Brigadier-General Wm. H. Crozier, the chief of the Bureau of Ordnance of the War Department. Gas plants can be equipped within three to four months, some more quickly, to remove the toluol from gas.

General Crozier further stated that the mobile artillery alone would require by September, 1918, at least 22,000,000 gallons of toluol. Statistics show that during 1916 approximately 220,000,000,000 cubic feet of gas were produced in this country. Assuming an average recovery of 0.05 gallon of toluol per thousand cubic feet of gas, we should be producing from the gas plants within the next four months, if immediate steps are taken everywhere, at the rate of 11,000,000 gallons of toluol annually. Even at this, the recovery

of toluol would amount to only half of the requirement for an army of a million men. It is possible, however, by a more complete stripping of gas, to increase the yield beyond 0.05 gallon per thousand cubic feet, thus more nearly meeting the requirements.

With a situation so plain, with a duty so imperative confronting us, with the lives of so many of our men depending upon the promptness with which this work shall begin, the question naturally arises—What is responsible for the delay? The only answer we can find is—Democracy. In an autocracy a royal edict would have promptly demanded the recovery of all toluol from all gas, but under democracy, which we love and believe in, there must be the slower processes of congressional appropriations, of adjustments between government officials, gas companies and Public Service Boards and Commissions, and the arousal of the public to the necessities of the situation. The efficiency of democracy is severely on trial in this matter and for this reason we urge every chemist to do his part, not only as a chemist, but as an informed citizen from whom others have a right to expect advice on so grave a question. That the matter is urgent is shown by the fact that each day's delay means the sacrifice of T. N. T. sufficient for 150,000 three-inch shells.

Naturally the War Department has been compelled to wait until appropriations were made by Congress but this reason no longer exists.

The gas companies in turn have been in a quandary as to what to do. Did the government need their toluol? What would become of their investment if the war ended within the next year and the extreme demand for toluol suddenly ceased, as it surely would? We now know that more toluol is needed than all the gas companies can supply. Furthermore, General Crozier stated to us, and authorized public use of the statement, that the government is now in position to assume, in case of early ending of the war, the investment risks of gas companies through additions to their plants of the necessary equipment for recovery of toluol. Thus these two points are clear.

Finally there is the ever present conflict between gas companies and public officials representing the consumers, a conflict essentially financial in its character and evidencing itself continuously by questionings on the part of the one or the other as to the justness of rates, involving necessarily the question of standards for gas. Fortunately, the more general use of the gas mantle is rapidly eliminating the candle power standard, for the maintenance of which the burning of toluol is necessary. The term illuminating gas is now largely a misnomer. The great bulk of the gas, at least 60 per cent, is used as a heating agent and consequently the heating value, as expressed in terms of British thermal units, will soon be the prevailing standard.

Furthermore, we are confident that as soon as the people of the country understand the patriotic and vital call which is now made upon them, the former somewhat antagonistic attitude towards the gas companies will disappear and the way be promptly opened for recovery of all possible toluol. It would

be a shallow patriotism indeed if, understanding fully the situation, we should cheer our troops as they march away to training camps and then return to our homes insisting upon the retention of toluol in our gas or unwilling to sacrifice gas efficiency in order that a perfect barrage fire may precede those same troops going into action on the French front. To think otherwise would be to accuse our people of deliberate murder of their own. There may be matters of rates to be settled, matters of certain standards to be insisted upon; all such questions, however, can await adjustment until after the war.

The main question before the nation now is:

"*Shall we burn toluol or shoot it?*"

EXPLOSIVES AND DYESTUFFS—A FRENCH CONFIRMATION

A few weeks after the hearings on the Hill bill during the previous Congress, the late Hon. E. J. Hill of the Ways and Means Committee had printed in the *Congressional Record* a letter from General Hugh L. Scott, the then Chief of Staff of the Army. In this letter General Scott emphasized the direct relation between a well-rounded dyestuff industry and a national reserve for explosives manufacture. Some short-sighted congressmen, with rather marked pacifist leanings at the time, pooh-poohed the introduction of this letter by Mr. Hill as an effort to bolster up a protective tariff measure by sounding a war alarm and dragging in an argument which had no connection with the legislative matter under consideration. But the staunch old patriot was right, and gradually the country has learned to recognize so clearly the connection between dyestuffs and explosives that it is safe to say that no legislation inimical to the American dyestuff industry could now get the slightest favorable consideration by Congress.

An interesting confirmation of the soundness of this national viewpoint is furnished by recent developments in France, as recorded in the *Courier des États-Unis* of October 10, 1917, though the thought process is reversed. We argued from dyestuffs to explosives; the French on the other hand are preparing, with the strong aid of the government, to convert after the war a highly developed explosives industry into a dyestuff industry.

To this end a contract between the Minister of War and the Syndicat des Matières Colorantes has been submitted to the French Parliament for ratification. Under the terms of this contract the government, upon the cessation of the war, will turn over its explosives plants to the dyestuff syndicate, with the proviso that the plants and all equipment shall immediately pass to the government for explosive manufacture in case of a future general mobilization. The state reserves to itself the right of intervention and control and will receive one-third of the dividends distributed in excess of 4 per cent.

The expense, originally planned for twenty million, has been estimated to forty million francs. That the French public recognizes the national importance of the movement is shown by the fact that

the 60,000 shares of stock reserved for the public was oversubscribed eighty-three and a third per cent.

By this coöperation between the government and the people, France will at the close of the war treble gain—realizing upon its surplus explosives plants, creating a domestic dyestuff industry and retaining a potential explosives industry which can quickly be made available.

General Scott was a chemist as well as a soldier, and Mr. Hill a patriot rather than a partisan.

DR. ROEBER

In the stirring drama of the expansion of American chemical industries during the past three years, a unique figure stood out in the form of Dr. E. F. Roeber, whose death on October 17, 1917, was a shock to chemists in every section of this country.

Through the steady growth of his splendid journal, *Metallurgical and Chemical Engineering*, he exerted a wide influence. Filled with the spirit of the times, he labored unceasingly for the upbuilding of the chemical industries in the conviction that in this way he could best serve the country of his adoption. Indefatigable in multifarious committee duties, he gave of himself ungrudgingly.

Through such activities his name will live among us, and yet to those of us who knew him personally, there was another side which will always be remembered: the genial man, the jolly companion, and the sympathetic friend whose hearty handshake carried with it a constant message of good-will.

THE EXPOSITION

The Third National Exposition of Chemical Industries has now become a part of the history of the country. Still another floor of the Grand Central Palace was required to booth the additional exhibits. The marked increase in attendance was a just measure of the increasing popular regard for chemistry. The stimulation of that busy week is to-day being felt in every line of the chemical industries.

Some there were among the exhibitors who, becoming overconfident of success, failed to give due thought to the attractiveness and intelligence of their exhibits. They are to-day paying the price, and indulging in regrets. The exhibits as a whole, however, made a wonderfully attractive and inspiring display.

The addresses were well attended and appreciatively heard, in spite of a very badly ventilated auditorium. Plans have already been made for remedying that defect next year.

Again the managers of the Exposition have demonstrated their completely sympathetic coöperation with the Advisory Committee. It is a pleasure to bear witness to the fact that in no instance since the inception of the Exposition idea have the managers failed to comply with any suggestion of the Advisory Committee as to the proper policy for the legitimate and sound development of the Exposition. This attitude on the part of the managers has in turn resulted in the transformation of the Advisory Committee from an originally somewhat perfunctory body into an enthusiastic, thought-giving, working committee.

Again the press has done its full share in carrying the impress of the Exposition to the public. True, a special edition of one evening paper was abandoned because the exhibitors would not respond with sufficient alacrity and unanimity to the exhortations of its advertising manager, but this was lost sight of in the columns of space devoted to the Exposition in many papers which, in spite of the stirring character of world news at the time, recognized the national import of such a display and means of interchange of ideas.

Perhaps the most striking feature of the increased exhibits was the intelligent and carefully prepared displays of the natural resources of the South. In this work a number of the progressive railroads of the South were particularly engaged. The results should prove a well defined addition to the wealth of the nation.

The chief impression we received from the entire activities of the week was the conviction that the chemical industries are not isolated units seeking selfish advancement, but a coördinated group in our body politic seeking to serve the nation. With such a spirit, the limit of growth is far from sight.

A SPRING EXPOSITION AT CHICAGO

In response to invitations from the Chicago Association of Commerce, the Chicago Section of the American Chemical Society and Local Sections in adjoining states, there will be held next March, in the Chicago Coliseum, an Exposition of Chemical Industries under the same management which has so successfully conducted the three similar expositions in New York City.

The growth of chemical industries in the Middle West has kept full pace with the developments in other sections of the country, and, as in other sections, there is still room for greater and more coördinated growth. Bringing together under one roof the splendid accomplishments of the past will serve to inspire confidence in the future.

We predict for the Chicago Exposition the same phenomenal success which has characterized those already held.

THE SLACKER RING AGAIN

Far be it from us to add to the burden of work of any man or set of men in these busy days. Remembering, however, the resolution of the Jewelers' Vigilance Committee:

"RESOLVED, That we pledge ourselves to discontinue and strongly recommend to all manufacturing and retail jewelers of the United States that they in a truly patriotic spirit discourage the manufacture, sale and use of platinum in all bulky and heavy pieces of jewelry,"

and remembering also the activity of the Vigilance Committee in connection with this general subject, we record here for the information of the Committee the wording of a prominently placed advertisement card observed last week in a Detroit street car:

WE ARE SHOWING THE MOST EXTENSIVE STOCK OF
PLATINUM ENGAGEMENT RINGS
ALL SET WITH PERFECT DIAMONDS

SALLAN
WOODWARD AT GRATIOT

THIRD EXPOSITION OF CHEMICAL INDUSTRIES

The Third National Exposition of Chemical Industries was held in Grand Central Palace, New York City, September 24 to 29, 1917. The varied and attractive exhibits proved a veritable inspiration to the thousands who daily thronged the building and furnished concrete evidence of the tremendous strides forward of the chemical industries during the past year. Brilliant as the spectacle was, however, it is probable that the lasting impression of the Ex-

position will lie in the many thoughtful addresses given during the week, not only by men closely identified with these industries, but also by publicists, government officials, bankers and others, all of whom recognized the many fields of human endeavor touched by chemistry.

For the preservation of this thought record we reproduce here as given, or in abstracted form, these addresses. [EDITOR.]

OPENING ADDRESSES

September 24, 1917

THE BATTLE OF THE AMERICAN CHEMICAL INDUSTRIES

By CHAS. H. HERTY

Chairman Advisory Committee of the Chemical Exposition

The battle for national self-containedness, in that portion of the line held by the American chemist, is progressing favorably. It is not yet won, but many heights have been conquered, many formidable streams crossed, and the open plains of full national service are almost in sight. This Exposition, increasing in magnitude each year by one hundred per cent of its original size, constitutes the bulletin by which the nation is informed of the progress made.

In the center, the advance up the steep slopes of "capitalization" has been marked. In 1915 there was added to the chemical industries \$65,565,000; in 1916, \$99,244,000, and in 1917, up to September 1, \$65,861,000, a total gain of \$230,670,000.

On the extreme right the forces of "Empiricism" have steadily yielded ground to the advances of our research chemists. More and more called upon for utmost effort, they have never failed to respond.

On the left flank a steadily increasing force of the ablest American chemists is being gathered to capture the hill of "Obsolescence of Army Equipment" and is providing the great armies we are now raising with the most efficient forms of modern chemical means for both offensive and defensive warfare.

On the right center the terrain of "Congressional Apathy" has been partly won, as typified by favorable protective legislation for our dyestuff industry and by the guarding of the all-important electrochemical industries at Niagara Falls from power shortage, due to lapsing legislation.

On the left center, the quagmire plains of "Public Indifference" have been largely dried and made passable through the clearing skies of a sympathetic daily press, which has constantly emphasized the value to the independence of the nation of a full-rounded chemical industry.

Finally, the counter-attacks of subtle propaganda against the ability of American chemists and the worthiness of our products, such as American dyestuffs, have ingloriously failed.

The optimism engendered by such splendid progress will prove, however, a curse indeed if it leads us to overlook two features of the present situation.

In the first place, in order to man the present lines of this battle of the chemical industries, we have already drawn heavily upon our reserves in the universities throughout the country. Many professors, advanced students, and even only partly trained students, have been called into the industries. This, together with the losses by enlistment, has created a serious shortage of chemists whose replacement through all favoring means should be a constant charge upon the liberality of the lenders of our chemical industry, and the far-sightedness of those vested with the powers of national administration.

In the second place, this army has its camp followers—men who, under the guise of chemistry, seek to enlist capital in developments bearing all the earmarks of get-rich-quick schemes, the disastrous out-working of which may, perhaps, shake that confidence between capital and chemists which should grow daily stronger if this battle is to be fully won. And it must be won. Only patriotic motives underlie that conviction.

It is the nation's service to which we are called and to that service the good faith and untiring zeal of the American chemist is pledged.

AMERICAN CHEMICAL INDUSTRY AND THE AMERICAN CHEMICAL SOCIETY

By JULIUS STIEGLITZ

President American Chemical Society

Every cloud has its silver lining, and even the great black cloud of war, which has been oppressing the world these three years, has been penetrated, here and there, by bright rays of good accomplished. One of these brighter effects of the disaster, as far as this country is concerned, has been the influence of the war on our chemical industries.

Facing the necessity not only of very greatly expanding their output, but also of developing many new products and of making older products of a far higher grade in quality than ever before, our American industries, as evidenced by the three expositions held in this place, have met and conquered one great problem after the other. We may confidently expect, and, indeed, we must insist, that out of this period of forced effort we shall emerge independent of all foreign nations in regard to our ability to supply the basic chemical needs of our country, not only in quantity, but also in quality.

As a single instance of the progress these years have witnessed in a field we must continue to hold after the war, let me recall the dismay of our universities—and I am sure, also of our industrial laboratories—when, only in 1915, we saw the supplies of Jena glass and of other hard glass cut off. Yet to-day we are manufacturing in the United States glassware fully as good as, if not indeed superior to, the German brands we thought we never could do without.

When the war is over, no matter how fierce trade competition may be, we must see to it that our new industries survive, that we do not relapse into our old dependence on European sources for almost every article in which quality, not just quantity, is essential. In the heat of effort of these years only the most urgent and immediate of our needs have been met; some of these results will depend for their stability upon war conditions; they are still too fragile to collapse when the world returns to its normal life and trade freedom more. In this situation brought with magnificent possibilities for much greater chemical advancements, but also with great dangers for the permanency of some of the American chemical industries, the American Chemical Society, for which I am speaking, sees its opportunity of being of new and still greater service to the country.

COÖPERATIVE ACTIVITIES OF THE SOCIETY

Including in its membership of more than 10,000 the great majority of leading technical chemists, as well as practically all the foremost men of the chemistry staffs of our universities and colleges, the society is in a position to render service in any branch of chemistry, service that will be both expert and at the same time judicial and unbiased in its spirit.

Thus, the society, influenced by the conviction that our national welfare demands independence in dye manufacturing, was active in aiding the movement to secure a much-needed measure of protection by duties on dyes.

Then, at the invitation of the chairman of the United States Tariff Commission, the American Chemical Society, through its Advisory Committee, a few months ago recommended the name of an expert, Dr. Grinnell Jones, on chemical schedules, who is now working with the commission on the task of placing the tariff on a scientific, non-political basis.

The Society recently urged upon the Secretary of Commerce that standard chemicals and reagents are as essential for successful work, for the saving of wasted effort in chemical industries, as are standardized weights, measures and gauges in other industries. With the approval of Secretary Redfield, the Bureau of Standards, with the coöperation of a committee of the American Chemical Society, has now started this important work.

Then, our appeal in Kansas City to the women of the country to refrain from the purchase or acceptance of platinum jewelry had its immediate effect; within a few days thereafter the jewelers' representatives, in conference with the Secretary of Commerce, agreed not to use the precious metal for heavy articles, thus making a larger proportion of the valuable metal available for the industries. According to the latest information that has come to me, the price of platinum has at last begun to recede somewhat, instead of continuing the steady rise which its extravagant use in jewelry brought about and which put a burden equivalent to a duty of several hundred per cent on a vital necessity of our scientific and industrial laboratories. I have the fullest confidence that if the situation should remain intolerable, we shall have the support of the government in taking much more stringent measures to protect chemical industries and scientific work, so vital to our nation's life, against what is, after all, a mere luxury.

Further, at the instance of the American Chemical Society and in coöperation with a committee of the Society, the Bureau of Foreign and Domestic Commerce has started the compilation of as complete information as it can secure for the guidance of our industries in regard to the chemical needs of manufacturers, the sources of supply of crude and finished products, and the relation of the various products to one another and to specific industries. Thanks to the efforts of the able editor of our *Industrial Journal*, Dr. Herty, a large fund has been raised to make possible this coöperation of the Society with the government in this important work, and if the chairman of our committee, Dr. B. C. Hesse, has his strenuous way, the work will be a model of thoroughness and usefulness.

SOCIETY WELCOMES APPEALS FROM INDUSTRIES

I have mentioned these instances of the activities of the American Chemical Society in order to emphasize that the society would cordially welcome any appeals made to it by industries needing support of one kind or another. We are now organized for quick and effective action—in matters of legislation and policy, through our Advisory Committee to the President, in matters of research through our affiliation with the National Research Council, all of whose active members in chemical fields are also active members of our society.

When such appeals or suggestions are received, they will receive prompt and earnest consideration, and, if necessary, be looked into by a committee of experts, not only with that fair, judicial spirit which science develops in its devotees, but also with that

sympathy and consideration which the service of our country instills into her sons. Final action will then follow, with that fearlessness and energy which a good case always warrants, and which we trust will always be truly in the interest of American Chemical Industry.

GREETING FROM THE ELECTROCHEMISTS

By COLIN G. FINE

President American Electrochemical Society

It was certainly a very propitious moment when three years ago Mr. Roth and Mr. Nagelvoort suggested and planned the first chemical exposition. The American Electrochemical Society heartily welcomed the idea and felt fully confident that the enterprise would be popular and successful. An undertaking which is based on the promotion of the common welfare, an undertaking that affects the progress and prosperity not of a few individuals but of every member of the country, an undertaking that serves to teach and demonstrate in a very striking and lasting manner the diverse applications and activities of the most fundamental of all national industries—an undertaking of this kind cannot fail, it must succeed. At the first exposition the exhibits were confined to one floor; in the second year the booths extended over two floors and in this third year practically every square inch of space is occupied. Very soon Mr. Payne will have to build a bigger palace.

Never before in the history of electrochemistry has the vast importance of the various electrochemical products been so forcibly brought to the attention of our government and of our people as in the present year of the great war. Take from this country its electrochemical industry with its numerous and diversified manufactures and the martial strength of our country is hopelessly crippled. Think of the hundreds of machine shops that are utterly dependent on the electrochemical abrasives, carborundum and alundum; think of the thousands of rifles and guns turned out every month with the aid of high speed steel made from electric ferro-alloys; think of the millions of pounds of electrolytic copper that are absolutely essential for our electrical apparatus. There is the aeroplane whose light, strong stays are made from the electrochemical metals, aluminum and magnesium; there is liquid chlorine, a product of the electrolytic cell and the basis of the Carrel-Dakin method of treating the wounds of our heroes; there is electrolytic hydrogen used in all of our scout and observation balloons and there are the numberless electric alloys entering into the composition of nearly every item of the government's vast military equipment.

An interesting feature of the electrochemical industry is its American origin and its present international scope, international in so far as the industry is not restricted or confined to one or two countries or localities. Take, for example, the calcium carbide industry: this was founded by an American, Thomas Willson; within a brief generation it has grown in leaps and bounds; to-day there are large carbide factories in almost every civilized country of the world. Compare with this the sulfur industry confined to the United States and Russia. The natural saltpeter industry is confined to Chile, but the electrochemical saltpeter industry, founded by Bradley and Lovejoy, at Niagara Falls, has spread to every important civilized center.

Wherever low-priced waterpower or low-priced fuel is available in generous and steady amounts, there electrochemical industries have been and will be established. Our country has been foremost in the electrochemical industry ever since its inception, due to American genius on the one hand and to our vast natural resources on the other. May we continue to lead the world in the supply of the many electrochemical products, pure metals and alloys for the arts, gases for cutting and welding, chlorine and peroxides for our hospitals, chlorates and acetone for munitions, nitrates for the farm and defense, abrasives, electrodes, solvents and lubricants! May we continue to excel in the products of the electric furnace and the electrolytic cell!

THE PROGRESS OF AMERICAN CHEMICAL ENGINEERING

By C. W. THOMPSON

President American Institute of Chemical Engineers

This Exposition demonstrates the greatness of the progress which chemical industry in all its branches has made in the United States in recent years. When an industry is small, its requirements are small. As it becomes larger, its requirements become larger. The manufacture of chemical products on a small scale in a laboratory is a relatively simple operation, but when this manufacture is conducted on a large scale, involving the investment of considerable capital, then the problem is much more complicated and much more difficult to solve.

CHEMICAL MACHINERY

On this large scale the chemical engineer is the important factor; not so much, perhaps, in the development of the processes as he is in the devising of machinery that will carry out these processes. Most chemical processes have been developed upon a small scale in the laboratory. All of the reactions have been worked out in this way. When the process has become so developed, it is studied for the purpose of putting it into operation on a scale that will produce a relatively large quantity of chemical product. To do this, the knowledge of the mechanical engineer is needed, but in addition to the knowledge of the mechanical engineer, there must be supplied a knowledge of the resistance of materials to chemical reaction, which is provided primarily by the chemical engineer. This is particularly well illustrated in this Exposition, where apparatus for a great variety of uses in chemical manufacturing are displayed. In practically every chemical manufacturing operation a great part of the study leading up to its becoming a commercial success has been the finding of materials suitable for making the apparatus in which to conduct the chemical reactions involved.

In small scale manufacture, platinum, glass and porcelain have in most cases been satisfactory. The use of these materials, however, for large scale operations, has been prohibited by the high cost of the materials or their fragility. It has been found, however, that by the selection of certain alloys of iron, chemical apparatus can be manufactured in which certain chemicals have been made to react upon each other without reacting upon the apparatus. Such reactions could be conducted in porcelain or stoneware were it not for the difficulty of making large porcelain or stoneware vessels that would not be destroyed by the heat of reaction necessary to the reaction involved in the process. The discovery that silica could be made into chemical ware and that such ware had a very low coefficient of expansion, has made possible the use of such ware for many operations requiring the application of heat to liquids. With the demand made upon it, the manufacture of chemical stoneware of intricate shape and design has progressed to a remarkable degree, so that within the limits of its use there is practically nothing that can be asked for in this class of apparatus.

Our early knowledge of chemistry had to do almost exclusively with irreversible reactions. Modern chemistry has largely to do with the reversible reaction, a reaction which takes place according to fixed rule as determined by the temperature and pressure under which and at which the chemical reaction takes place. Every chemical manufacturer desires to get as high a yield of product as possible from every chemical reaction employed. To do this he must in many cases control the temperature or the pressure, or both, as the case may be, within certain relatively narrow limits. The need of chemical industries in this respect have been so great that accurate instruments for the measuring of temperature and pressure and for their automatic control, have become imperative needs. At this Exposition there are on view numerous pieces of apparatus designed

particularly for the purpose of controlling temperature and, to some extent, pressure.

ECONOMIES IN POWER PRODUCTION

Every chemical industry depends, to a certain extent, upon its operation being carried out economically. This economy must extend to all departments. One of the most important departments is that connected with the production of power. The importance of obtaining the highest efficiency possible from a steam boiler is self-evident, and this can only be done by having as complete as possible combustion of the fuel used. There is one sure way of doing this, and that is by having continuous readings made of the carbonic acid present in the stack gases. It would be too expensive to employ a chemist to take samples of these gases and analyze them frequently, but with modern CO₂ recording instruments, this is done automatically with great economy in steam production. Such apparatus has also been available in cases where the CO₂ is used in chemical processes. By a greater concentration of CO₂, the handling of excessive quantities of useless gases is avoided.

The designing of apparatus in which to conduct chemical reactions with the result that desirable chemical compounds are produced, is also peculiarly the work of the chemical engineer. The reactions themselves, as indicated above, have become known as the result of laboratory work, but to design apparatus so that these reactions will go on with the greatest practicable rapidity and to the highest degree of efficiency requires a man peculiarly trained in some way to apply on a large scale the law of mass action and the other laws of physical chemistry. The removal of an undesirable component rapidly and efficiently, thereby taking away the slowing-up effect due to its partial pressure, is often a difficult problem, but, with the modern methods illustrated in this exhibition, the problem becomes easier. Here we find apparatus designed for particular purposes, in which operations can be carried on in vacuum or with the assistance of efficient stirring appliances, or in the utilization of centrifugal force.

Much of our progress has been due to the utilization of electrical energy, and in this Exposition are shown the products of the electro-thermal reactions, also electrolytically prepared or refined metals and chemical products. Here also are seen illustrations of the removal of suspended matter from gases by terminals highly charged with static electricity, and means for separating minerals electrostatically or by the electro magnet.

These are only a few of the many illustrations which could be offered of what is seen in this Exposition, showing the mechanical genius of the American manufacturer and his ability to convert chemical reactions into profitable business enterprises. I believe it would be proper to extol this ability. The American cannot expect to excel in everything, and if he excels in this particular line it is a sufficient "crown of glory." That the manufacturer of chemical products has not accomplished everything that could be desired has not been due to his lack of ability or energy, but has been due to his inability to obtain those raw materials which nature has furnished to other countries more generously than she has to us.

With the progress of chemical industry the kinds and varieties of chemical products made are increasing from day to day. We see evidence of improvement in quality and the probable reduction in price as the competitive conditions become more nearly normal.

The Institute of Chemical Engineers is glad to join in this Exposition in an advisory capacity, or in any other way it can be useful, because it believes that the future commercial success of our country depends upon the continuance of the present efforts looking to the direction of the expansion of chemical production and the manufacture of chemical products.

NATIONAL RESEARCH COUNCIL AND U. S. TARIFF COMMISSION ADDRESSES

September 25 1917

INTRODUCTORY

By B. C. Hesse, of the General Chemical Company

The program of this evening is admirably adapted to illustrate and emphasize the relations that may and do exist between abstract scientific knowledge on the one hand and the realities of every-day life on the other. Not that abstract scientific chemical knowledge is alone so concerned, for there are many others that will occur to you, and I need merely remind you of Faraday's electromagnetic theory of light of 1845 together with the purely mathematical investigations of Maxwell in 1864 on the one side, and of the Hertzian waves of 1888 and Marconi's wireless telegraph in 1896 on the other side.

Some sixty years ago, an English youth, still in his 'teens, pursuing an abstract scientific problem, encountered an unexpected and astounding result and upon this he built an industry, which has since developed into gigantic proportions, but whose enormous influence and importance were not convincingly impressed upon the general public until the present World War. I refer, of course, to the present-day coal-tar chemical industry in all its ramifications into every-day life all over the world. This, however, was by no means the only case in which the peoples of the world were rudely awakened. Of the many results of that awakening, two will be discussed to-night.

Suddenly and even violently confronted with the actual reality of our dependence, both direct and indirect, upon foreign countries for a great many things in common and widespread use, the general public became most insistent in its demand, *first*, to know why such a condition had been permitted to grow up, and, *second*, to have that condition permanently abolished at the earliest moment.

Analysis of the situation disclosed that in the first of these two demands there were at least two general classes, the first class comprising those cases whose importance was recognized and for which all, or substantially all, needed raw and similar materials were available from domestic supplies, but whose utilization in such domestic manufactures was discouraged by domestic consumers of such manufactures, or by our Federal legislators or by both combined; in the second class were those cases whose real and interlacing importance did not sufficiently impress themselves. A first approach to an answer to the public demand as to why this condition was permitted is as to how it grew up; it grew up through our own acts of omission because as we built up our industries we did not, as a Nation, seriously, systematically and persistently study what effect sudden deprivation of the non-domestic materials employed in those industries would have on our Nation as a whole, and then act to prevent or minimize such effects; that applies to our citizens, to our Federal officials, and to our Federal legislators. Just why this condition existed is not easy of explanation but, no doubt, a large contributing factor was the general disbelief in a war of present-day proportions and effects.

If I am correct in my conclusion that this dependence grew out of this general disbelief in such a war then I am probably correct in deducing therefrom that the second public demand, permanently and immediately to abolish that dependence, is based upon a public belief in a possible recurrence of such a war and public determination not again to be so disadvantaged, in such an event.

In that view it becomes necessary constantly to determine what things not made in this country must be made here; then to determine the best way of making them; next to decide what measures, Federal or otherwise, are needed to make them permanent and, finally, to carry out the necessary program.

To help solve the first two sections of this program, namely—what to make and how, the National Research Council was

created; to aid in solving a part of the third section of this program, the United States Tariff Commission was created by Act of Congress in September, 1916. For products of and for our chemical industry the Chemistry Committee of the National Research Council has taken over the burden and the Tariff Commission has provided for expert chemical direction and execution in its technical staff. The National Research Council is largely a volunteer offering of our citizens; the Tariff Commission is the contribution of our Government. Since our citizens and our Government have so determinedly and so sagaciously joined forces we may confidently look forward to lasting results of untold value to our country; it is a sure way to make a democracy lastingly more efficient than an autocracy.

THE NATIONAL RESEARCH COUNCIL

While the immediate work of the National Research Council is necessarily directed towards helping to remove present defects in our means of national defense, yet it ultimately will be engaged in helping to determine the best course of development of the whole country and the best way to effect it. We may, therefore, expect that the influence of the National Research Council will ultimately penetrate and benefit every branch and division of our national activities. However, its work cannot last if the country does not continue to develop men and women who are capable of research work and, therefore, a collateral field of influence of the National Research Council will be to assist in keeping our technical schools, universities and colleges at the very forefront of educational efficiency. Finally, we may confidently expect that the National Research Council will be the very efficient "eyes of the Nation" by keeping close watch on all scientific and technical progress all over the world, discerning our own national advantages in developing selected portions for ourselves and in coordinating our efforts for such national development.

THE U. S. TARIFF COMMISSION

Among the Federal measures that influence our domestic development is the treatment we accord foreign products at our ports—that is, our tariff policy. The primary purpose of a tariff-levy is governmental funds; in normal times our customs receipts are almost one-half the total ordinary receipts of the U. S. Government; a subordinate purpose is to foster and enlarge domestic industry by wise and far-sighted adjustment of customs rates and at the same time not unfavorably to affect the cost of living.

Heretofore, such industries as employ much labor have by preference been fostered by our customs policy and in comparatively rare instances only has any other test of eligibility to tariff help been applied; the test of the measure of such protection has been from "difference in cost of production plus a fair profit" upward to all the traffic would bear.

In 1916, Congress created the third of our tariff commissions to help it solve the problem of customs rates fairly and equitably to all. At the same time, Congress greatly increased the difficulty of that problem by enacting what it intended and expected to be a set of customs rates on materials and products of the coal-tar chemical industry of such dimensions as to make importation unprofitable and domestic production profitable. Such rates had theretofore been consistently refused by Congress for more than 30 years because such an industry employed relatively little labor and its products were raw materials for so many domestic manufactures that not only would our cost of living be advanced but our competitive ability curtailed by such duties. This tariff of 1916 says in effect that, since the work of 2,000,000 of our people can be interfered with because 7000 other people are not here making things indispensable to the 2,000,000, we must have that industry here even if it employs only 7000 people; or, in other words, "key industry products" must be made in the United States.

The problem that now confronts the Tariff Commission is to get together all the material and facts so that Congress can enact a tariff that will provide half our ordinary government receipts, will not unfavorably affect the cost of living, will expand our domestic industry to its maximum and will prevent its being crippled because of failure of the usual channels of international trade.

THE "CHEMICAL SCHEDULE"

In order that the Tariff Commission may properly discharge its duties to Congress it is necessary for it to have comprehensive and complete detail information on a vast multitude of different subjects and items so arranged and so coordinated that it will lend itself to the treatment to which the Commission must submit it before a report to Congress can be made. For the purpose of so collecting and collating information the Commission has established a technical staff comprising specialists in the various technical branches involved. Among such specialists there is a chemist.

In reading our tariff enactments, the all-pervasiveness of things chemical is very striking; but only recently has that impressed the general public and obtained recognition from Congress. The chemists' interests do not end with Schedule "A," which deals largely with chemicals and with so much of the Free List as relates to things allied to those of Schedule "A," but they permeate almost each and every one of the fifteen schedules of the Act. Obviously, the chemist member of the Technical Staff of the Tariff Commission must examine a host of industries not ordinarily looked upon as chemical in addition to the very large number of industries that are acknowledged to be chemical in greater or smaller degree. His task is most difficult and its successful execution will require much farsighted, patient and diligent labor on his part and the frankest and fullest cooperation of our industries.

NATIONAL RESEARCH COUNCIL, CHEMISTRY COMMITTEE SECOND REPORT

By MARSTON TAYLOR ROGERT

Chairman Chemistry Committee, National Research Council

Being the subject matter of addresses delivered by the writer at the 55th Meeting of the American Chemical Society, Boston, September 11, 1917, and at the Third Exposition of Chemical Industries, New York, September 25, 1917

In the preliminary report of the Chemistry Committee of the National Research Council, the organization of the Council and of its Chemistry Committee was explained fully, and an attempt was made to point out some of the many ways in which such an organization could hope to be of service to the country in normal peace times. Before that article could be published, our country joined in the World War and it became necessary immediately for the Chemistry Committee to concentrate its attention upon matters relating to the security and defense of the nation. It seems desirable, therefore, after the past months of experience under these new conditions, to submit a second report, which shall epitomize what has been accomplished since the previous one, indicate the lines along which we are advancing, present some of the difficulties confronting us, and in general endeavor to depict the situation as we see it.

And so it may not be amiss at the outset to direct attention to certain matters which concern all loyal Americans vitally and the truth of which is borne in upon us daily, not because there is any new thought embodied in these statements, but because they appear to need constant iteration and emphasis.

IMPORTANT GENERAL CONSIDERATIONS

1.—The seriousness of the situation should not be underestimated. We are at war with one of the most efficient if not the most efficient nation in the world, a nation which has been preparing for the struggle for forty years and is concern-

trating every resource to the achievement of its purpose. Of the many mistakes already recorded in this war, none has proven more disastrous than that of underestimating the strength of the opponent.

2.—The duration of the war is a matter which no living being can forecast. The only safe plan is that adopted in England, where preparations are being made always for two years more of war. No matter how long the war may last, England's preparations will be always for two years beyond it, and we should not be one whit less forehanded.

3.—Speed in getting ready to do our share is of the utmost importance. France is admittedly at the maximum of her man-power and gaps in her ranks can be filled only with difficulty. It is not likely that England can increase her present fighting strength sufficiently to provide the necessary preponderance to secure a decision upon the western front. The only great increase in fighting strength for our Allies there must come from the addition of American armies, and until such troops arrive in sufficient numbers the outcome of the struggle still hangs in the balance. Not only men are needed, but supplies and equipment of all kinds as well, and meanwhile submarines are steadily reducing the number of vessels available as transports and freighters.

4.—The extent to which we are willing to work together and to make such sacrifices as are necessary for the common good will, in large measure, determine our success or failure. This applies not only to individuals, but also to corporations and to municipal, state and federal officials. Petiness and selfishness will, in the long run, defeat themselves, and, if sufficiently wide-spread, may defeat our country. As Benjamin Franklin said many years ago: "We shall either hang together or hang separately."

5.—Loyalty. The time has come when everyone must take his stand clearly and unequivocally in the ranks of loyal Americans or with the enemies of our country. There is no neutrality or "twilight zone" for those claiming United States citizenship. If it were necessary to emphasize the fact that spies are abroad in our land the Chemistry Committee has in its possession ample evidence of the work of such traitors. It is well to make clear also that what in normal peace times might be passed by as cavilling criticism may now be sedition, and what was formerly regarded as a wrong-headed opposition to our country's laws and administration may be treason to-day, and such expressions should be so recognized and promptly silenced.

6.—The brains of the country should not be squandered by permitting highly trained specialists, inventors and men of genius to enlist in the rank and file of the army for duties which could be satisfactorily discharged by men whose loss would not so seriously impair the offensive and defensive power of the country. Under the exigency of the moment, both England and France allowed men to go to the front at the outbreak of the war who should have been retained at home at all costs, such men as Mosely, for example, cannot be replaced, and both France and England are looking at the present time for the loss of the scientific experts who went to the front. As soon as the situation permitted both countries sent thousands of scientists and skilled artisans back from the front to the aid of the industries at home, rendering very valuable that assistance which depends almost entirely upon scientific preparation and efficiency. It has been stated (and creditably so) that England alone has recalled from the front, for war purposes, of such men. It takes time, however, to train the scientist and we should be careful to retain at home those who represent their country and our Allies more effectively here than in France. All that any loyal American can do that he be employed by his country in that capacity, for of such is the stuff of which the victory is made, and where he can help most. Skilled men of all kinds are needed in both the army and the navy, and in the case of the country

men it is hoped that those drafted can be detailed for service for which their scientific training especially fits them; this will avoid the further depleting of our industrial and research armies which would result from calling upon them for volunteers.

Turning now to matters which concern us primarily as scientists, everyone must appreciate by this time that wars are not fought as in the olden time, when individual physical prowess was the chief deciding factor, but that modern warfare is a highly complex problem in applied science and its outcome is decided largely in the laboratories and factories; or, to put it somewhat differently, military power is dependent upon scientific and industrial organization and efficiency. It is neither an impossibility nor even an improbability that a single chemical discovery might change totally the history of a nation. In fact, Germany would have been practically defenseless after the exhaustion of her accumulated stores of Chilean nitrate had it not been for the discovery of methods of fixing atmospheric nitrogen. The nation unfamiliar with aeroplanes, submarines, gas warfare, modern artillery, and all the engines of destruction of present-day warfare, would be more helpless before an army so equipped than was the American Indian with his bow and arrows against the firearms of the white man.

In a very real sense, therefore, American science is on trial in this struggle, and it is for us to demonstrate that American chemists are not inferior to those of other lands, and that our country can turn to them with confidence and assurance that they will play their part well. Never in the history of the world hitherto has the rôle of Chemistry in warfare approached anything like its present importance, and the opportunities and responsibilities of the chemist have increased concurrently.

MOBILIZATION OF AMERICAN CHEMISTS

Up to date, the mobilization of American chemists for the assistance of the nation has been effected mainly through three organizations which, in the order of their establishment, are:

I. NAVAL CONSULTING BOARD OF THE UNITED STATES—A Board which was called into being by Secretary Daniels for the study of scientific problems of interest to the Navy Department, and which recently has been acting also as a Board of Inventions for the Council of National Defense. Its chemical delegates, appointed by the American Chemical Society, are Drs. L. H. Baekeland and Willis R. Whitney.

II. NATIONAL RESEARCH COUNCIL—This Council was organized by the National Academy of Sciences at the request of the President of the United States, and its Chemistry Committee was established by concurrent action of the American Chemical Society, the National Research Council and the Association for the Advancement of Science, as explained already in our previous report. As the Department of Science and Research of the Council of National Defense, it is acting as a central clearing house for the chemical research work of the country.

III. COMMITTEE ON CHEMICALS OF THE ADVISORY COMMISSION TO THE COUNCIL OF NATIONAL DEFENSE—A Committee of which Dr. William H. Nichols is Chairman, organized under that branch of the Advisory Commission over which Mr. Baruch presides. It concerns itself with raw material and manufacturing problems and not with research, and is divided into various *Sub-Committees* for the more effective conduct of its business.

The close coöperation between the Chemistry Committee of the National Research Council and the other two organizations mentioned above is evident from the fact that the chemical members (Baekeland and Whitney) of the Naval Consulting Board are also members of our Chemistry Committee, and the Chairman of the latter is a member of the Committee on Chemicals, as well as of the Committee on Gases Used in Warfare and of the Board of Munitions.

Since its organization, the time of the Chemistry Committee has been occupied chiefly in the following directions:

1—The establishing of such additional *Sub-Committees* as

appeared to be expedient, keeping track of their various activities so as to avoid overlappings and duplication of work, and aiding wherever possible in bringing about more effective coordination between investigators interested in the same line of research.

2—In connection with the census of American chemists taken jointly by the American Chemical Society and the U. S. Bureau of Mines, the Committee has taken a census of all the research chemists of the country, and these returns, numbering many thousands, have been classified, carded and indexed, and are now on file in our Washington office. The Chairman of each *Sub-Committee* has been provided with an alphabetical list of the investigators in his own chosen field, showing the names and addresses of these men, the lines of research in which they have been or are interested, the amount of time they can contribute to such voluntary service, and supplying much additional collateral information.

3—In coöperation with Secretary Parsons of the American Chemical Society, the Committee has furnished to various officials of the War Department, and of other branches of the Government, lists of drafted chemists, requesting their detail to special duties where their chemical training will be of service to their country, and we have every reason to believe that the great majority of these requests will be granted and our chemists used for chemical work.

4—In extending and developing its function as a central clearing house for the chemical research work of the country for the purpose of bringing about a better coördination of such work and a closer rapprochement between individuals, corporations and state or federal officials; and its service as a general bureau of information in this field for the benefit of all.

5—The study of not far from 300 specific problems, correspondence with the investigators to whom the same have been referred, and the transmission of reports to the appropriate Government officials.

6—Moving the office of the Committee twice, first from Columbia University to the Woodward Building, Washington, D. C., and then from the latter to the Munsey Building, and the outfitting of these new offices.

7—Raising the funds, by solicitation among personal friends and public-spirited citizens, to pay the expenses of carrying on the above work. Among those whose generous financial assistance has enabled us to pay our way hitherto, we are indebted especially to Messrs. Charles Hayden, Frank A. Vanderlip, Thomas Leeming, Martin H. Ittner, and the American Chemical Society. As the National Research Council receives no appropriation whatever either from the Government or from the Council of National Defense, it was in no position to assume the expenses of any of its Committees.

8—Participating in conferences with visiting foreign scientists who have come over at the invitation of our Government or of our National Research Council, and assisting in the selection of chemists who have gone abroad to represent us there or to gather first-hand information for investigators at home. The data communicated by Drs. Grignard and Engel of France and the reports brought over by Drs. Dakin, Burgess and Hulett, have been of greatest assistance in our war preparations. In return, we are aiding our Allies by every means in our power, communicating to them freely whatever information we may possess which is of interest to them and supplying much needed raw material of all kinds. Drs. Grignard and Engel are still in this country studying our chemical industries and our natural resources.

FIELDS IN WHICH AMERICAN CHEMISTS ARE NOW NEEDED

I—FOR SERVICE AT HOME

1—AS TEACHERS. The maintenance of our training schools for chemists is of fundamental importance since upon them rests the responsibility for keeping up to full strength and efficiency

our army of chemists. They are the recruiting stations for our industries and for our research laboratories, and must see to it that a steady flow of new effectives is kept moving toward the industrial and military fronts. To disorganize our educational institutions by withdrawing so large a proportion of teachers that the chemical students cannot be trained properly would seriously jeopardize the future of our whole country. The chemistry teacher, therefore, who sticks to his task as a teacher is not in any sense a "slacker" but is rendering the most valuable kind of patriotic service, and it should be so recognized.

2—CONTROL AND DIRECTION OF INDUSTRIAL OPERATIONS, such as the manufacture of munitions, poison gases and gas masks, incendiary and smoke bombs, signalling devices and pyrotechnics, motor fuels, foods and drugs, dyestuffs and textiles, oils, paints, rubber, leather, metal goods, etc., etc.

In the opinion of the writer, it is desirable that all drafted chemists who have been exempted because of the value of the industrial service they are rendering, should be entitled to wear an emblem or insignia of some kind to indicate that fact and to show to the world that they are not "slackers" but are serving where they can help their country most. In France the industrial worker wears an arm-band or "brassard." As all male citizens there of military age are drafted, their assignment to industrial duty is regarded as a special privilege, and any industrial worker convicted of inexcusable stupidity or gross carelessness knows that he will be punished by being transferred immediately to the fighting front; whereas if suspected of any deliberately treasonable act he will be tried, not by a civil tribunal, but by a court martial, and, if convicted, will be shot.

3—INSPECTION, TESTING AND ANALYSIS OF MANUFACTURED PRODUCTS, especially those required for Government use, such as munitions and supplies of all kinds, the identification of new poison gases or shell fillers, the detection of poison in streams and wells, and the determination as to whether goods supplied are up to standard or not. This is where the engineering and testing laboratories, analytical laboratories, food and drug laboratories, of our educational and research institutions are already aiding existing Governmental agencies, and where they are quite certain to be increasingly called upon as our part in the war develops and expands, for this is what has happened in England.

4—DEVELOPMENT OF NEW PLANTS AND PROCESSES made necessary by the increased demands due to the war (as in the case with nitrates, toluene, glycerol, sulfuric acid, caustic soda, etc.), to the cutting off of our previous source of supply (potash, for example), or to wholly new war needs (such as poison gases, smoke and incendiary bombs, etc.).

5—SMALL SCALE MANUFACTURING OPERATIONS, to be conducted in our university and research laboratories, for the production of special drugs, differentiating biological and bacteriological stains, rare reagents, poison gases and research chemicals which, although of the utmost importance to the welfare and security of the country, yet are required only in such small amounts relatively as to make it very difficult to induce manufacturers to undertake their production.

6—RESEARCH. Chemists are needed to aid the Government in the solution of problems connected with the security and defense of the country, to protect our soldiers against enemy contrivances, and to increase our military offensive power. Sir J. F. Thomson and recently that "applied science can lead to reforms, research in pure science leads to revolutions."

7—ADVISERS. An adviser to our Government, bringing to it the best existing knowledge on any chemical subject and the best qualified experts, and then guiding researches to be undertaken in the most promising or most urgently needed directions. It is in the field that our Sub-Committee have already rendered splendid and most welcome service and when they can be of ever increasing value. With the exception of Prof. Bray,

whose residence on the Pacific Coast has made it impossible, every Sub-Committee Chairman has visited Washington at least once during the past summer, so as to get in closer touch with the situation there and thus be enabled to help more intelligently.

8—IN GOVERNMENT CHEMICAL LABORATORIES, to supplement the present working force, and to fill places made vacant by the drafts, by our army and by industry.

II—FOR SERVICE ABROAD

1—WITH OUR OWN FORCES IN FRANCE. Chemists are required for service with our troops in France, in the Sanitary Corps, the Poison Gas Service, the Ordnance Department, the Engineering Corps, the Quartermaster's Corps, and in many other positions. At the fighting front, they will be called upon probably to collect and make preliminary examination of poison gases, shell fillers of various kinds, fuses, bombs of different types, signalling devices, etc., sending the material so collected to the main laboratories back of the lines for more thorough investigation; the analysis of drinking waters, the detection of poison therein and their purification, the disposal of refuse and garbage, and the recovery of fats and other materials from the waste. In the laboratories back of the lines will be the headquarters for the major part of the chemical work of all kinds needed by our armies.

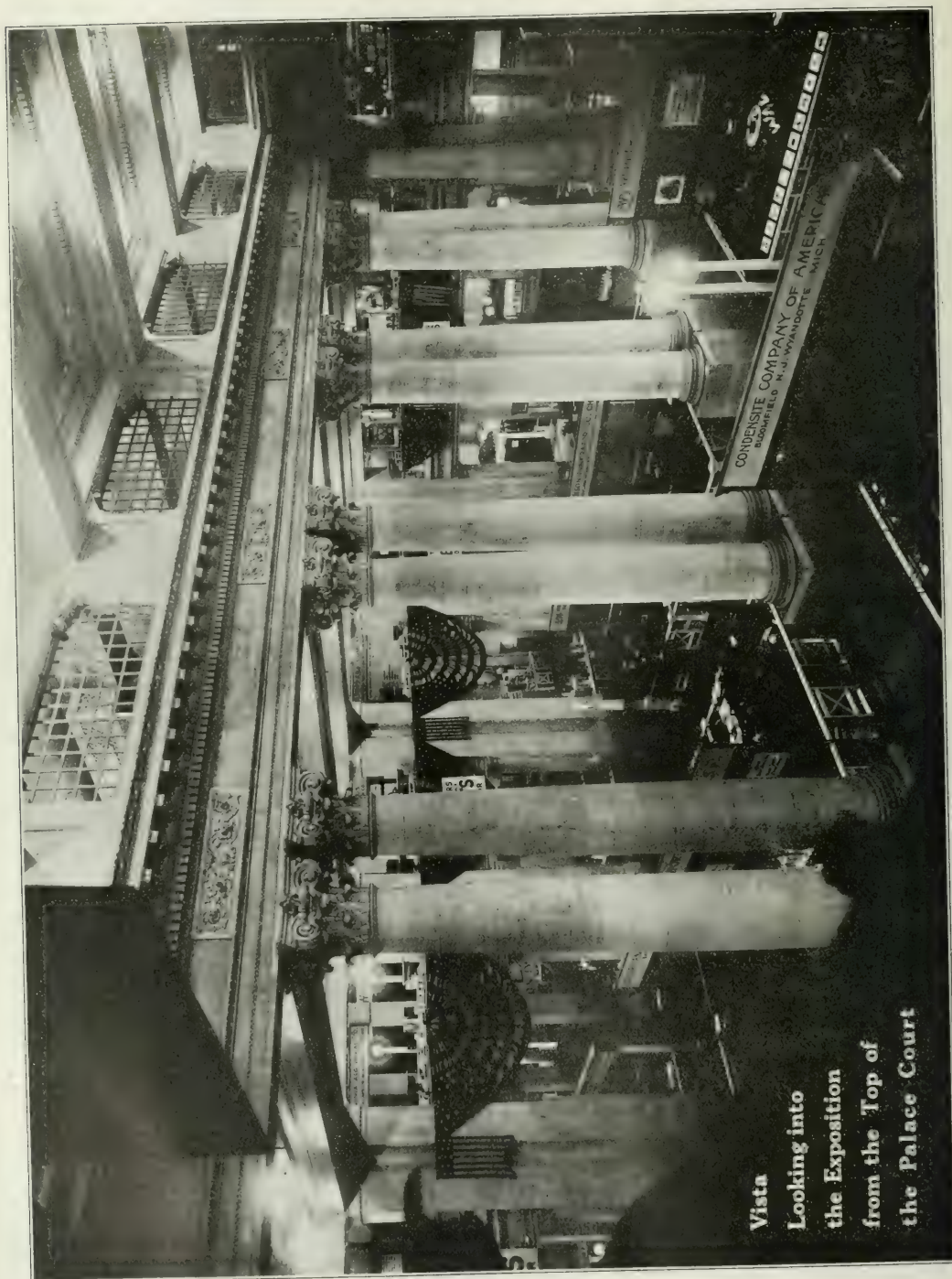
2—IN THE LABORATORIES AND CHEMICAL INDUSTRIES OF OUR ALLIES, THE FRENCH, where competent chemists are sorely needed to fill the ranks thinned by the war.

Attention should be called, in this connection, to the fact that the Chemistry Committee is not an employment agency and has nothing whatsoever to do with the finding of places for chemists out of a job. As already stated, it is assisting Secretary Parsons in securing appropriate detail for drafted chemists; but those who are seeking industrial positions should take the matter up with the Employment Bureau of the Chemists' Club, 50 East 41st Street, New York, which is the appropriate clearing house for all such matters and a most admirably conducted office. Those seeking Government employment as civilians should bear in mind the fact that Government Departments are required to select their employees from the Civil Service lists, and that to appear on these lists they must have passed the necessary examinations, further details concerning which can be obtained by direct application to the Civil Service Commission, Washington, D. C.

PROBLEMS

While we cannot discuss the details of the various problems submitted to the Committee, it is advisable to make a few general statements in this connection.

In the first place, many of our chemical investigators appear to overlook the fact that our organization is not the only agency for investigating the chemical problems of the Government and that, in addition to the Naval Consulting Board and the Committee on Chemicals already mentioned, the Government has various chemical laboratories of its own for the study of chemical questions of all kinds, such as the various laboratories of the Department of Agriculture, Division of Chemistry, Division of Plant Industry, Forestry and Animal Industry, Forest Service, Bureau of Soils, etc.; of the Department of the Interior, Bureau of Mines, Geological Survey, etc.; of the Department of Commerce, Bureau of Standards, etc.; of the Treasury Department, Internal Revenue Service, etc.; of the War Department, the Arsenal Laboratories, etc.; and of the Navy Department, the Chemistry Committee. It is the duty of a chemist, in considering his work, to determine whether or not the problem is one which is beyond or outside those existing agencies, or one of which it is unnecessary to express his opinion, his purpose being rather to supplement, rather than to duplicate, the assistance of those kind agencies. The Government laboratories are doing splendid work, and are doing



Vista
Looking into
the Exposition
from the Top of
the Palace Court

should be proud of the high standards maintained there. It is too often the case that the high-class work done by Government scientists is not assessed at its real value, nor are these investigators given the recognition which their distinguished attainments so richly merit. In the present emergency, the Government laboratories naturally are overwhelmed by demands made upon them from so many different directions, and our Chemistry Committee is in the position to mobilize the additional help required. When peace returns to our land, and aid of this kind is no longer needed, the Committee can then devote itself to those other activities described in its previous report.

In the second place, many of the problems referred to our Committee during the past few months immediately following our entrance into the war were not research problems at all, in the sense in which we understand the word "research," but related to the adequacy of our supplies of raw materials and chemical products. At the outset, and failing any other civilian organization to handle such questions, we did what we could to secure the desired information through our own men and by cooperation with the appropriate Government officials and with the Advisory Commission to the Council of National Defense. Since the organization of the Committee on Chemicals already noted, all such questions are referred to them.

Further, there is nothing strange about a Government accustomed only to peace conditions and up to within a few months apparently convinced of the impossibility of our ever becoming embroiled in a world-wide war, learning rather slowly the tremendous rôle of science in modern warfare and the many research problems which inevitably follow in its train and which must be studied in connection therewith.

It is to be hoped that these general remarks will furnish some explanation as to why there are now more volunteer investigators than can be supplied with problems whose study the Government has requested. The inability of the Committee to supply to all applicants important Government problems has been a cause of much disappointment and complaint on the part of our research men for the reason that they have not fully comprehended the situation. In fact, some university officers have specified that problems sent them should be of such a nature as to provide appropriate work for their full chemical staff, an order which would be an exceedingly difficult matter for the Committee to fill.

FINANCIAL NEEDS OF CHEMISTRY COMMITTEE

The greatest and most urgent single need of the Chemistry Committee at the present time is financial assistance to enable it to do properly and effectively the work for which it is organized and which it alone is in a position to accomplish for our Country. Without money, it can do but little. One way of meeting this situation would be for Congress to make an appropriation to the Academy of Sciences for the benefit of the National Research Council, since the Academy was created by the act of Congress as the advisory body to the Government in all scientific matters, and the establishment of the National Research Council by the Academy was at the request and with the approval of the President of the United States. The cost of a single day's warfare would be more than ample. Is it too much to expect that the combined intelligence of our investigators would bring the war to a close one day sooner? In such matters it is not the money which should be considered but the human lives sacrificed every twenty-four hours with all the accompanying train of sorrow and suffering. How much would it be worth in dollars, if such a strife could be shortened even a single hour?

In the absence of Governmental aid, the National Research Council has been enabled to conduct its work partly because certain of its active members are university officers, and the universities concerned have granted leaves of absence to these men and generously have carried them at part or full salary.

This, of course, the universities cannot continue to do for any length of time, as they themselves are facing serious financial straits due to rapidly diminishing revenues, nor is it fair that those endeavoring to serve the Government should have to do so at the expense of our universities.

When members of the Council, now partly or wholly supported by their universities, are cut off from this, one of two things must happen in the absence of Governmental aid:

- (1) The work of the Council will have to be abandoned.
- (2) The men concerned may accept officers' commissions in the Army or Navy or positions in some other Government Department. If the latter policy is followed by any considerable portion of the membership, the Council at once loses its civilian character and individuality by adsorption into the various Government Departments. While there is doubtless much to be said in favor of such a merger, it would be, from the writer's point of view, foreign to the original intent of the organization and a handicap to much of its work. As civilians, we enjoy a freedom of thought and action, and a privilege of conferring on a basis of equality with Government officials of all ranks which might not be accorded us as subordinate officials in a Government Department. Further, while all Government Departments have no objection to using a neutral civilian body as a central clearing house, they might not be so ready to do this where the Council Committee concerned was recognized as under the control of some rival Department.

This brings me to another matter, namely the great desirability of the Government making more extensive use of our organization, getting the habit of turning to it for the aid it is so well qualified to render, and recognizing it as the central clearing house for chemical research.

THE TARIFF COMMISSION AND OUR CHEMICAL INDUSTRIES

By WILLIAM S. CULBERTSON,

Member of the United States Tariff Commission

I am grateful to you for affording me this opportunity to discuss some of the broader aspects of our investigation of the chemical industries. It was clear from the time of the organization of our Commission in April that the chemical tariff presented complex problems of immediate importance which will become more important as the War progresses and as peace again comes. When we began work, we had before us the legislation Congress passed at the same time as the act creating our Commission which recognized the need of a new policy toward the coal-tar dye industry; we saw how vitally the chemical industries are related to the successful prosecution of the War; we saw that the very existence of many industries depends upon their maintenance; we saw the War revolutionizing these industries—financially, technically, and industrially; we foresaw some of the competitive difficulties which they will have to face when normal times return. And seeing these things we determined to make—as it has never been made before—not a partial and inadequate, but a comprehensive study of our chemical industries in their relation to the tariff.

We recognize frankly the difficulties of our task. The expert chemist and materials man no doubt realize more acutely than the layman the diversity of problems presented by the chemical schedule of the tariff law. Indeed, it is a curious fact in the tariff act, as like the practice of a house usually passed over by the average tariff student. It is a baffling statement, for here we are asked to look to the public, and to our own country, as being with your cooperation to make it financially self-sufficient. When we have employed some of the finest experts in the country and while neither time nor labor will be spared in seeking the needed sources of information, we must have brought these difficulties to a head with our chemical problems. We are looking for information from the chemical industry and from our institutions, from those experienced in the importance of chemical research, from those who are the

products of the chemical industry, and, above all, from the manufacturers actively engaged in developing our chemical industries. We, therefore, ask you, the progressive industrial leaders in this field, to give us your confidence and assistance in our work.

A GLANCE AT THE CHEMICAL SCHEDULE

Time does not permit even the mention of all the important questions raised by the chemical products enumerated in the tariff act. It may be of interest, however, to recall some of the difficulties which confront certain of our industries. War conditions have cut off the raw material of the sulfuric acid industry—iron pyrites—which in normal times is imported in large quantities from Spain. A new kelp industry has developed since the War and produces as a by-product iodine. The War has stimulated the mining of magnesite in California and the manufacture of metallic magnesium, tending to make this country independent of foreign supplies. The securing of an adequate supply of manganese is a serious war problem. Before the War monazite was shipped from Brazil to Germany where thorium nitrate and cerium nitrate were made from it: those two substances were then shipped to the United States where they were used in making gas mantles. Now the monazite comes direct to the United States and the entire process is performed here.

Because of the removal of the duty, the imports of wood alcohol have been greatly increased under the present tariff law. Acetone, also produced by the wood distillation industry, is used in making explosives and its production has increased rapidly under the war demand. Before the War oxalic acid came in large quantities from abroad, chiefly from Germany; the cutting off of this supply has stimulated domestic production.

Bleaching powder, ammonia and ammonia salts, the cyanides, sodium phosphate, the chromates, the nickel compounds, pigments—these and other products deserve more than enumeration, but I must pass on to several other problems in the chemical field.

ELECTROCHEMICAL INDUSTRIES

I am very deeply impressed with the progress made in the electrochemical industries of this country. The ferro-alloys, made possible by the electric furnace, have revolutionized the steel industry; ferro-silicon, for example, is indispensable in munition manufacture; the efficiency of metal cutting tools is due to tungsten, while the addition of chromium, nickel, vanadium or molybdenum confers special properties to steel, making it peculiarly suited to many special uses, including armor plate. The production of aluminum is one of the greatest achievements of the electrochemical industries. They have also produced carbundum and alundum, which have almost eliminated from the market such natural abrasives as emery. These new abrasives are important factors in the metal working industries, such as the shoe machinery industry, where mechanical perfection is necessary in the making of interchangeable parts. Calcium carbide and artificial graphite are also achievements of the electric furnace, and the separation of common salt by electrolysis into caustic soda and chlorine gas is marvelous enough to excite the admiration of the most indifferent. To visit these industries at Niagara Falls is to visit the frontier of industrial research. In America, we should be proud of them. A number of them are peculiarly American in origin. To-day, however, they are confronted with a serious problem of obtaining sufficient water power—so necessary for their operation. Unless this problem is handled in a statesmanlike way, our electrochemical industries will continue the migration already begun to Canada and Norway—both of which offer adequate, cheap water power.

We have in addition to the water power of Niagara great undeveloped powers in the south and west. According to recent statistics the maximum potential water horsepower in this country exceeds 60,000,000 and only 8.8 per cent of it is developed. We have here not merely a problem of statesmanship for members of Congress but a real task for the statesmen of business.

THE POTASH SITUATION

Before August, 1914, practically all the potash used in this country was purchased from the German Potash Syndicate. Geological conditions gave Germany a monopolistic control of this product. In 1910, the German Government by law limited the sales of the potash works up to the end of 1925 and fixed maximum domestic prices and minimum foreign prices.

After the outbreak of the War, Germany added to the restrictions on ocean trade by placing an embargo on the export of potash. In this country the need of potash is to-day acute. Many efforts have been made to discover new sources of supply which can be developed commercially and production has been greatly stimulated; but it is still far short of the demand. The most promising sources of supply are brine lakes in Utah, Nebraska, and California. High-grade potash is no longer available except in very limited amounts and the refining of low-grade potash presents many difficulties. When the German product again seeks a market in this country, the new domestic projects will face severe competition. The Geological Survey of the Government is keeping in close touch with this problem and it will also have our most careful consideration.

EXPLOSIVES AND NITRATES

The control which Germany had over potash has its parallels in other raw materials used not only by the chemical but by other industries. Platinum, for example, is a Russian monopoly. In our search for war materials we have had emphasized again our dependence on Chile for sodium nitrate, which has been the chief raw material in the production of nitric acid. The fear that this supply might be cut off and this country be left almost helpless in the production of explosives, has turned our attention to the fixation of atmospheric nitrogen. Congress appropriated \$20,000,000 for this new development. After an investigation, the committee recommended that nitric acid be obtained from the oxidation of ammonia and that a plant be erected.

This action is not only wise as a war measure but it is also a peace measure. As soon as the demand for explosives declines, nitrogenous fertilizer can be produced. We have here an example—there are many others in the field of industrial chemistry—of an industry whose development may be viewed either as a measure of military or economic preparedness.

COAL-TAR DYES

Such, in fact, is the way in which Germany views her coal-tar dye industry. This industry was regarded by the German Government as an important factor in national defense and when war broke out in 1914, it was almost without change transferred from the production of dyes to the production of munitions.

No problem connected with the chemical tariff is more complex and important than the problem of coal-tar dyes. Of the total consumption of artificial dyestuffs in the world in 1913, it is said that Germany produced 74 per cent and the remainder was produced only with Germany's permission, because she controlled the raw materials known as "intermediates." Under the shelter of war conditions a new industry has sprung up among us as if by magic and it is destined to contest and overthrow the monopoly which the Germans have had of the world trade in dyes.

As is well known, the organization of Cartels is encouraged in Germany and has been a leading factor in the advance of German industry. It has been particularly effective in the chemical industries. Because of the interrelation of products and the utilization of by-products, close organization has effected large economies. It has made the protection of patent rights easier; it has made it possible to purchase raw materials at a greater advantage; and it has enabled the industries to meet competition abroad more effectively.

In the dye industry organization has been important and powerful. Unquestionably a large part of its success was due

to the painstaking research of German chemists and the patents which they took out by the thousand. But financial control and business organization were also large factors in its supremacy. Before the War it was controlled by two communities of interests—the one known as the Badische group, the other as the Höchst-Cassella group. These two groups were closely coordinated and it was reported not long ago that a closer union had been entered into for the purpose of meeting effectively the conditions created by the War, which have led to the establishment of competing industries in other countries, particularly the United States.

The dividends of four of the large German dye concerns from 1902 to 1911 ranged, it is reported, from 196 to 300 per cent. This financial strength must be kept in mind when we are considering the competition which our industries will be called upon to face after the War.

When the War broke out in August, 1914, we were using some 60,000,000 lbs. of dyestuffs and 80 per cent of them were imported. Not only that, but 80 per cent of the "intermediates" used by the four or five domestic concerns making the remaining 20 per cent of dyes were imported. The country was practically dependent on Germany for color. The War brought almost a panic among the users of dyes. Prices mounted to unprecedented heights and dire prophecies were made.

The American business man and chemist, however, attacked the situation in a truly American fashion. Within three years after we were cut off from the German supply, we had invested huge sums in plants for making crudes, intermediates, and finished dyes. We were producing as large a quantity of dyes as were consumed here when the War started. We were receiving from abroad more money for exports of dyestuffs than we had normally paid out for dyestuffs imported. We still do not make a few such highly manufactured lines as the alizarines and indanthrenes and only a portion of our requirements of indigo, but in most lines of large consumption we are now able to meet all demands and we shall soon be producing the remaining lines of color. We have a right to be proud of our achievement in this field. When it is recalled that over 900 distinct chemical products are made from some 300 intermediates, which themselves have first to be chemically produced from 10 crude products distilled from coal tar, the vastness of the problem set before this youngest of our industries is apparent. The rapidity of its progress has amazed the world. The record of its achievement reads like a fairy tale and will prove an imperishable monument to American chemists and business men.

COMPETITION AFTER THE WAR

New conditions have been brought about by the War in industry as well as in all the other phases of our national life. Thoughtful students of industry are looking ahead to peace times and asking what competitive conditions will then prevail. What I have said makes it clear, I think, that this question is particularly pertinent in industrial chemistry. In the law of September 8, 1916, Congress has already said that the tariff is to be one of the means of preventing any attempt by a foreign competitor to destroy the new American dyestuffs industry. In revising the law of 1913, the plan was carried out, with a few exceptions, of raising the duty on intermediates from 10 per cent ad valorem to 15 per cent ad valorem plus a special duty of 2½¢ per lb. and on finished dyes from either the free list to 30 per cent ad valorem or from 30 per cent ad valorem to 30 per cent plus 30¢ per lb. The duty of 2½¢ per lb. on intermediates and the duty of 30¢ per lb. on dyes are referred to as "special duties" and after five years are either to be abolished or reduced gradually over a subsequent period of five years. The law provides for a census which may be taken by our Commission for the purpose of enabling the President to determine which of these alternatives shall govern. If the census shows that after five years from the passage of the act 60 per cent of the domestic consumption in intermediates and dyes is not produced in this

country, the law provides that the special duties shall be abolished by Presidential proclamation.

As you know, the Tariff Commission has no power to fix tariff rates or even to recommend them upon its own initiative. We are, however, vested with power to investigate all phases of the tariff problem and our report will be laid before Congress in ample time so that it may consider, in the light of our investigation, whether or not the new conditions created by the War require any further changes in our tariff laws.

PREVENTION OF "DUMPING"

Unfair competition was one of the methods employed by the German coal-tar dye industry to maintain its international supremacy. Unfair acts in this and other lines were no doubt in the minds of the members of Congress when they enacted the unfair competition section of the law of September 8, 1916. By this law it is a criminal act to import any article systematically into the United States at a price substantially less than the actual market value abroad plus certain charges with the intention of destroying, injuring, or preventing the establishment of an industry in the United States or of restraining or monopolizing the trade in the imported article.

In addition to this prohibition of unfair price cutting, the law makes provision against the practice known as "full line forcing." Articles will be assessed with a double duty which are imported into this country under an agreement that any person shall not use, purchase, or deal in or shall be restricted in his using, purchasing, or dealing in the articles of any other person. If, for example, after the War, the German dye industry controls by patent a color needed in this country, it cannot use the necessity of the American consumer as a means of forcing him to purchase his full line of dyes from abroad when all the colors except the one controlled by the patent can be purchased in this country.

On account of the present abnormal conditions in international trade, neither the Department of Justice nor the Treasury Department have been called upon to act upon any cases under these provisions of the law, but they will become valued means of protecting the American chemical industries, particularly the dye industry, from the determined trade aggressions of foreign competitors. They might be made more effective by giving the Tariff Commission power to issue an order against persons who after investigation are found violating the law, requiring them to cease and desist from the unfair acts. In other words, the Tariff Commission, which now is vested by law with the duty of investigating "dumping" cases, could be given in addition a jurisdiction over these cases such as the Federal Trade Commission has today over unfair methods of competition. Many cases could be reached in this way in which the evidence would not be sufficient to warrant criminal prosecution.

ORGANIZATION AND REGULATION

Tariff laws and "dumping" legislation will not alone protect our chemical industries. The German industry attained success by years of research, by a numerous hierarchy, and by international coordination. In American industry there is no need for protection in this respect.

The chemical industry is one of the industries in which export cooperation might be expected to prove highly successful. While tariff and unfair competition laws will afford some protection in the domestic market, they afford no protection in foreign trade. It is our duty to secure the services of the Federal Government, by the passage of laws of protection and promotion, and to extend cooperation and support to the United States industry on foreign markets. The Federal Government has the duty and capacity to protect and promote our industry.

Many important services because of our chemical industry are our chemical industries. Their products are at least as important as they are indispensable to the production and products of other industries. The metal working industries are dependent on the

products of the electric furnace. The textiles must have dyes. We must have chemicals for the refining of sugar and petroleum, for the manufacture of glass, pottery, paper, paints, and varnishes, rubber, and cement. The tanning industry leans heavily on the chemical industries. Agriculture gets from these industries its fertilizers. Medicinal and pharmaceutical products, toilet preparations, photographic materials, motion picture films, cleaning compounds, baking powder—to mention these among the many which suggest themselves reveals how close chemistry comes to our daily life. In the problem of national defense it is a controlling factor. The factories that produce nitrogenous fertilizer in time of peace will yield us nitric acid in time of war; those producing intermediates and dyes can turn their machinery and workers to making explosives. Hard steels for shells and armor-plate are achievements of the electrochemists. *I might go on enumerating cases illustrating the close relationship which exists between our chemical industries and our national interests. I have said enough, however, to indicate my feeling. The healthy development of our chemical industries is a matter of national concern. It is the duty of the Government to study its needs sympathetically. In turn, it is not only your duty but your privilege to be business statesmen in solving your problems of production and distribution—to plan not merely for profits but also for a national industrial system serviceable to the capitalist who invests, the worker who toils and the public that consumes.*

WAR AND THE FUTURE OF INDUSTRY

I have spoken of some things this evening which, at first glance, seem to have no bearing on the tariff problem. But our tariff problems, in so far as they touch production, are also industrial problems. They must be considered as a part of the more comprehensive task of the progressive development of our national life. The War in which we are now engaged will inevitably affect radically American industry. More than ever before conditions demand a constructive program, not merely for war but for peace. Modern war is in methods an economic as well as a military struggle. It is teaching us the value of coöperation. Society is learning its obligations to industry; industry is learning its obligations to society. We are relearning the old lesson that we can not under modern social conditions live to ourselves. Things which once were private matters are now admitted by all to be matters of public concern. It is not strange that many men are now wondering whether or not social coöperation, if it is good for national defense, is not equally good for the progressive development of our economic life after the War. Let us face these new problems with an open mind. Let us look forward not backward. Let us coöperate together in bringing from the fire of sacrifice, through which the world is passing to-day, more efficient methods of production, juster means of distribution, and a nation rededicated to righteousness and international fair dealing.

THE TARIFF COMMISSION AND ITS OPERATION WITH REFERENCE TO THE CHEMICAL SCHEDULE

By GRINNELL JONES

Technical Expert, U. S. Tariff Commission

The structure of the Tariff Act as we have it to-day goes back to the Act of 1883, when the dutiable articles were for the first time divided into Schedules. Schedule A was assigned to Chemical Products, Schedule B to earthenware and glassware, Schedule C to metals; while wood, sugar, tobacco, foods, liquors, cotton, flax, hemp, and jute, wool, silk, paper and books, and sundries were classified under Schedules D to N. This same order is found in all the later Tariff Acts. The Schedules of dutiable articles are followed by the Free List, in which the articles admitted free of duty are arranged alphabetically with entire disregard of the classification by Schedules.

In the Act of 1890 we find for the first time the Schedule subdivided into numbered paragraphs, which proved such a great

convenience that it has persisted to the present time. There have been, however, frequent changes in the paragraph number assigned to any given article.

In subsequent Acts there have been considerable additions to the number of substances mentioned by name, but these additional substances have not always been added to the Schedule and paragraphs to which they would seem properly to belong. For example, articles made of carbon have been added to the Glassware Schedule; thorium nitrate has been added to the Metal Schedule; and saccharin has been classified with sugar rather than with coal-tar products; and we now find dried egg albumen in Schedule A, and liquid egg albumen in Schedule G. Schedule A, in 1883, was made to include not only chemicals proper but oils, drugs, pigments, dyes and extracts for tanning and dyeing, explosives and alcoholic preparations. This same grouping and a great deal of the phraseology has persisted to the present time in spite of the numerous revisions, and many of the things which seem strange in the present Act can be traced back to the Act of 1883. For example, we find sponges included in Schedule A in the present Act instead of among the sundries in Schedule N. This classification appeared in the Act of 1883 and has been copied in all later Acts.

The arrangement by paragraphs also leaves much to be desired, since the same paragraph includes such dissimilar articles as amber, dutiable at \$1.00 per lb., and dextrose, dutiable at $\frac{3}{4}$ ¢ per lb. On the other hand different barium compounds are dutiable under five separate paragraphs. Asafetida quite properly gets a paragraph by itself, but "gunpowder and all explosive substances" are compressed into one paragraph, although further search discloses fulminates in a separate paragraph. Paragraph 5 reads, "Alkalies, alkaloids and all chemical and medicinal compounds, preparations, mixtures and salts, and combinations thereof, not specially provided for in this section, 15 per centum ad valorem." However, this close juxtaposition of alkalies and alkaloids is not quite so bad as it sounds because nearly all of the alkalies are elsewhere provided for by name and therefore not included here. Paragraph 5 is the basket clause which levies a duty on any chemical which may have been overlooked in drawing the Act or on any newly discovered substance which is not covered by any of the general descriptive or class names in other paragraphs.

The rates in the Act of 1883 were high, but the general tendency in the revision since has been downward. Chloroform was dutiable at 50¢ per lb. in 1883 and has been gradually reduced to 2¢ per lb. Refined glycerine which was dutiable at 5¢ per lb. in 1883 is now 2¢ per lb. Castor oil has come down from 80¢ to 12¢ per gal. and linseed oil from 25¢ to 10¢ per gal. Bicarbonate of soda has been reduced in the same time from $1\frac{1}{4}$ ¢ to $\frac{1}{4}$ ¢ per lb. and soda ash from $\frac{1}{4}$ ¢ to nothing. Perhaps the most extreme case is the alkaloid strychnine which has come down from 50¢ per oz. to nothing. On the other hand cases where articles on the Free List in 1883 have been removed from it are rare, the most conspicuous examples being alizarine, indigo, the essential oils and balsams.

There has been a marked tendency to alternate from ad valorem to specific duties and back again, especially in the earlier tariffs under consideration.

The continual increase in the number of items mentioned by name has resulted in a corresponding increase in the detail of the import statistics published by the Government. If a substance is specified by name in the Tariff Act, all shipments of the article which came into the United States must necessarily be so described and invoiced and can, therefore, be entered in the published import statistics. In many cases, however, a substance not mentioned by name in the Act will be dutiable under some general class name and in such cases it is usually entered on the customs house records under that general class name, thus

making the ascertainment of more detailed statistics impracticable. For instance, the tariff act names six barium compounds and as a result these are all brought out individually in the import statistics published by the Bureau of Foreign and Domestic Commerce. All other barium compounds are dutiable under Paragraph 5, which reads, "Alkalies, alkaloids and all chemical and medicinal compounds, preparations, mixtures and salts and combinations thereof, not specially provided for in this section, 15 per cent ad valorem," and the imports of all other barium compounds except those mentioned by name are buried in the import statistics under this general grouping.

In a few cases the attempt is made to bring out in detail in the import statistics substances not mentioned by name in the act. For example, we have import statistics on stearic acid, which is not mentioned by name in the act. It is possible, however, that this is a case of incomplete record, since shipments of stearic acid may be entered on the customs records as an "acid not specially provided for, 15 per cent ad valorem" and so recorded in the import statistics.

Recently there has been a movement within the American Chemical Society to secure more detail in the statistics on the Imports of Chemicals. It is evident that the best way to do this is to enlarge the list of substances mentioned by name in the tariff act. About a year ago, Congress passed a special Tariff Act on the Coal-Tar Products, in which the number of intermediates mentioned by name was greatly increased. As a result we now have detailed import statistics on each of these intermediates. Nevertheless, during the first three months of 1917, over 100,000 lbs. of material were imported which are described in the import statistics as, "All similar products, obtained, derived, or manufactured in whole or in part from the products provided for in Group I." Group I includes the coal-tar crudes and this description, therefore, is equivalent to "Other intermediates not mentioned by name."

It is evident from this brief survey of the tariff history that Congress acted wisely in creating a permanent non-partisan commission to gather, in a systematic and comprehensive way, the information needed by Congress in revising the tariff in the future.

The United States Tariff Commission was created by an Act of Congress signed by the President on September 8, 1916. The Commission was organized on April 1, 1917, and immediately made comprehensive plans to carry out the varied and important duties assigned to it by the law and appointed a staff of Special Experts to assist in the work. The duties of the Commission will be primarily the collection and editing of the facts necessary to apply, intelligently and consistently, to the endless detail of the tariff act itself, the general tariff policy, adopted by the people and Congress.

THE TARIFF INFORMATION CATALOGUE

The part of the work of the Commission which will be of most interest to this audience is the preparation of a Tariff Information Catalogue. The purpose of this Catalogue is to have on file ready for immediate use pertinent information in regard to each commodity now mentioned in the Act, whether dutiable or on the free list, as well as all other commodities not specially mentioned but included in the comprehensive general or basket clause. The Catalogue will contain a full and true description of each commodity, including an explanation of the recognized commercial grades or varieties. All exonyms will be noted and cross-indexed. This will be followed by a brief description of the process of manufacture with special emphasis on the raw material needed and on any general economic characteristics of the industry, such as a need for abundant and cheap power or special skill and highly skilled labor, etc. The causal root of the commodity will be ascertained in order to learn the industry likely to be adversely affected by the imposition of any tax which would result in a rise in price. Consideration will also be given

to any possible rival commodities which might be used as substitutes. The statistics of production in the United States and in the principal foreign countries will be included, together with the statistics on exports from and imports into the United States and the amount of revenue collected on each article. The geographical distribution of the industry within the United States will be noted. A statement of the treatment under previous tariff acts and any decisions of the Treasury and of the Courts affecting it will be compiled. In many cases a compilation of market prices over a series of years will be made. Whenever reliable data in regard to the cost of production are available, they will be included and in many cases a special effort will be made to secure such data, although it is recognized that at the present time costs are so abnormal as to have little value as a basis for determining future policy.

It is intended that this Tariff Information Catalogue shall be a living, growing thing, kept continually up to date by additions and corrections. The information thus collected is to be available for the use of Congress and its Committees or Members, on request, at short notice, and will also be used as a basis of reports by the Commission to Congress.

Such portions of this work as are of general interest will be published. For example, a classified synopsis and index to all the Court and Treasury Decisions affecting the tariff on chemicals is now being compiled by a lawyer experienced in tariff practice in cooperation with the chemical expert of the Commission and it is expected that this compilation will be published.

Care will be taken to keep separate and distinct from this Catalog all confidential information, especially in regard to the operations of individual manufacturers—such information to be available only to the Commissioners and its confidential staff.

For this work a staff of special experts and clerks has been organized under the direction of Mr. William M. Steuart, formerly Chief Statistician of the Manufactures Division of the Census, and the work is now actively in progress.

Since the primary object of Congress in creating the Tariff Commission was to have on hand exact and reliable information to be used in framing future tariff acts, the Commission earnestly desires the full coöperation of American business men in its task. It is hoped that they will volunteer information in regard to any notable changes which are occurring in American industries or in the conditions of international competition, and that all requests from the Commission or members of its staff for information and advice will be given careful attention and frank and full answers. They are invited to submit to the Commission any suggestions which seem to them desirable in regard to administrative features, the classification or nomenclature of articles or the rates of duty to be imposed. Such suggestions, to be of value, should be as detailed and specific as possible and accompanied by the reasons for the change proposed. They will be filed and indexed in such a way as to be readily available. It is especially important that information should be sent to the Commission in regard to articles formerly imported exclusively but now made in the United States.

The full consequences of the American economic crisis and importation of a rapidly expanding, big, modern, big chemical industry, because of the great abundance and highly technical character and because of the new economy, changes that have occurred in many branches of the economic life, since the outbreak of the European War.

American Chemical Society, that the ammonia complexes created by such a containing existing physis crystalline materials and by themselves and themselves have been examined by thermal gravimetric analysis in a vacuum furnace equipped with a thermogravimetric analysis (TGA) system. The results are very close to results of 100% yield. A study of the thermal stability of the complexed materials and the thermal stability of the complexed materials is also being conducted and will be reported in the near future.

ascertain what have been the consequences of existing legislation and to forecast those of proposed legislation.

The units of the Tariff Information Catalogue on sulfur, barium compounds, and abrasives have already been prepared and the work on potash compounds and dyes and other coal-tar products is well advanced. Much of the statistical information on many other classes has already been assembled.

I have been seeking what may be the limits, of the territory that I have to explore, but with little success. I have found, however, that it includes Abrasives and Lubricants; Bleaching Powder and Dyes; Explosives and Fertilizers; Olive Oil and Cyanides; the Salts of Potash and Radium, Bromine and Balm of Gilead; Aconite and Zaffer. It is evident that the Commission directly or through its staff must appeal to specialists in many lines for information and advice, and that only through this coöperation can a true statement of the recent achievements and present position of the American chemical industries be prepared in proper form for the consideration of the Commission and of Congress. Your aid is earnestly desired in this undertaking.

THE DEVELOPMENT OF OUR EXPORT TRADE

EXTRACTS FROM ADDRESS BY W. S. KIES

Vice-President of the National City Bank of New York and American International Corporation

September 26, 1917

The chemical industry of the United States has shown greater efficiency and greater powers of quick response to business demands than almost any other of the great industries of the country, as illustrated by the fact that exports of chemicals in 1917 (\$185,000,000) were practically seven times as great in value as in 1914 (\$27,000,000), while exports of all industries, as a whole, were only three times as great.

But this does not tell the full story because the list of exports does not include the great group called "explosives," which is so closely allied to the chemical industry as to be in fact a part of it. In explosives the value of our exports grew from \$6,000,000 in 1914 to \$820,000,000 in 1917. Under this class were listed cartridges, dynamite and gunpowder. Under the heading "other explosives," the value of our exports grew from \$1,000,000 in 1914 to \$420,000,000 in 1917, showing that in the industries closely allied with chemicals the growth has been quite as striking as in chemicals proper.

In the articles which may be considered as strictly chemicals, we exported, for example, in 1914 acids valued at \$500,000; in 1916, \$24,000,000; and in 1917 approximately \$55,000,000. Our dyestuffs exports have grown from one-third of a million dollars in value in 1914 to \$12,000,000 in 1917, and these latter figures do not include any foreign dyes reexported. A few other illustrations may be of interest. Our exports of soda salts and preparations grew from practically nothing in 1914 to \$18,000,000 in 1917. In the tabulations issued by the Government, under the heading "other chemicals," the exports grew from \$9,000,000 in 1914 to \$75,000,000 in 1917.

The importance of the chemical industry is evidenced by comparison of the amount of capital and value of products turned out with that of other leading industries. According to the census of 1915, the value of capital of the group known as "chemicals and allied industries" was \$723,000,000 in 1914. In the great woolen, worsted and felt goods manufacturing industry, the total capital in the same year was but \$413,000,000, and in the silk goods industry \$210,000,000. The capital of the automobile industry in 1914 was \$408,000,000, and the capital of the flouring mill industry was \$380,000,000. The amount of capital invested in the group distinctly classed as "chemicals" was, in 1914, \$224,000,000, which represents an increase of nearly eight times since 1880.

A study of the statistics of your industry reveals a further interesting fact, that the industry as a whole shows a decreasing

value of product per dollar of capital invested—in other words, that yours is an industry where the cost of experimentation and the development of new processes make constantly increasing demands upon capital. In 1880 there was invested in the general chemical industry in this country \$29,000,000. The value of products was \$38,000,000 annually, or \$1.33 per dollar of capital. In 1915 the capital invested strictly in the chemical industry was \$224,000,000, the value of products \$158,000,000, or \$0.70 per dollar of capital invested. The capital, from 1880 to 1915, increased about eight times. The number of employees in the industry during that period increased but a trifle over three times, and the wages and salaries paid increased about five times, from \$6,000,000 to \$31,000,000. This indicates that as an industry you are more dependent upon capital and brains than upon labor; that the success of the industry depends upon the development of improved and cheaper processes and the intensive use of the capital employed.

During the last three years, the chemical industry has received a great impetus. Large amounts of money have been spent in its development. When the war demand for your product shall have ceased, your great problem will be to find markets that will absorb your production. In many lines, before the war, Germany was supreme and competition with her was impossible. She held, to a very large extent, the South American markets. In 1914 we sent to all of South America only \$3,000,000 worth of chemicals. In 1917 the value of our exports to South America will amount to nearly \$15,000,000. But even this latter figure does not indicate an export trade of very substantial proportions. Germany, prior to the war, as we all know, had a grip upon the chemical markets of the world, and in South America it was perhaps stronger than in other parts of the world.

In considering the subject of the development of trade in South America, or in any other foreign country, the basic problems are the same. These are: (1) the cost at which the article can be produced and sold in a foreign market; (2) distribution, which includes salesmanship, advertising and transportation; (3) financing, which comprehends the always difficult problem of credits.

Fundamentally the South American market is not much different than any other. It must be studied to be understood. Consumers in South America will purchase goods on the same principles that consumers elsewhere do—on the basis of price, adaptability and quality. Where the price is out of line with that of a foreign competitor, quality may sell the article as a result of genius in salesmanship. Where the quality of two articles is practically the same, the cheaper will be moved. We come right back home, therefore, to the most important problem—the cost of production. Shall we be able to produce in this country after the war on a basis which will enable us to compete with the products of other countries of the world? All industry is intensely interested in the answer to this question.

So far as German figures are available, the production in the chemical industries, per dollar of capital invested, is much greater than in this country. The reason probably lies in the more intensive application of science and the use of men of science in the industry. In fact, a German author, writing on the industries in 1897, said, "It is generally recognized that the German chemical industry owes it preponderating position solely to the highly scientific preparation of its collaborators." With the cost of production at or near the costs of our leading competitors, the development of any given foreign market is an assured possibility if enough thought and attention be given to the task.

The outbreak of the war in 1914 had a paralyzing effect, during the first few months, upon American industry. As a matter of fact, in the months immediately prior to the war, business had been declining. It was at this period of contraction of our domestic market that American manufacturers turned

with one mind toward foreign trade. The seeking of new markets and the subject of the development of our foreign trade assumed a prominent position in the discussions of chambers of commerce and manufacturers' organizations and associations everywhere.

Particular attention was directed toward South America. The interest aroused in South America bordered on hysteria. But after attending meetings, passing resolutions and hearing many speeches on the subject, the substantial manufacturer realized that no permanent progress could be made in a foreign market without credit and banking facilities. The need for the establishment of banking facilities abroad to aid in the building up of our export trade had been impressed upon the bankers of the country, and, in response to the demand, the National City Bank opened in Buenos Aires on November 10, 1914, the first branch of an American bank to be established in a foreign country. Since that time branches have been established in Brazil, Uruguay, Chile, Colombia and Panama, and branches will soon be opened in Peru and Venezuela. By the expiration of this year ten branches will be in operation in South America. During the war period banking facilities have been provided pretty well covering all the important parts of South America. It may be well to add that during this period the National City Bank has established branches in Russia and in Italy, and, through the International Banking Corporation, which it has acquired, has provided banking facilities in India, China, Japan, the Philippines and the Dutch East Indies.

During the war period substantial progress has been made by the United States in the development of its South American trade. Unquestionably this has been largely due to the fact that we have had the market pretty much to ourselves. Will we be able to keep the business which we have built up during the last three years? The same question is asked, with just as deep interest, of our export trade elsewhere. To appreciate the development of this country's export business in the last three years, let me recall the figures to you.

Fiscal year ending June 30	IMPORTS	EXPORTS
1914.....	\$1,893,935,657	\$2,364,579,148
1915.....	\$1,674,169,740	\$2,768,589,340
1916.....	\$3,197,885,510	\$4,333,658,865
1917.....	\$2,659,355,185	\$6,293,806,490

It is unreasonable to expect that this volume of business can be maintained, particularly our exports of manufactured articles. A very large proportion has been munitions, food products and war supplies to our allies. To South America and neutral markets, we have exported vast quantities of goods heretofore purchased in Europe. When the war shall have ended, our business in war supplies will be at an end. We may, of course, look to the exportation of huge quantities of raw materials, for Europe is bare of them. Our machinery, machine tools, construction materials and steel products will be needed for rehabilitation purposes. But the rehabilitation work will proceed much more rapidly than we think, and it will be only a short time after the cessation of hostilities when European exporters will seek to regain their footing in the markets we have temporarily possessed. We can, therefore, assume a great decline in our exports and a sharp decrease in our favorable balance of trade.

That portion of our present South American business which rests on the merit of our product and its ability to meet competitive prices will remain ours if our manufacturers exert themselves to keep it. A part of our present South American business will unquestionably revert to its old channels.

Germany's commercial representatives throughout the world, and particularly in South America, are active. The German banks continue their business, and numbers of German houses, at least until recently, have been able to keep their customers through supplying them with American goods and English goods and taking orders for German goods for after-the-war delivery.

It is reported that large quantities of wool have been purchased in South America and held in storage for shipment to Germany as soon as the war shall have ended. So thorough was the economic penetration of Germany into the life of almost any country whose market presented any attractions that we may safely assume the work will be taken up where it was left off, as soon as the war shall end.

The present conditions afford an opportunity for the getting together of labor and capital, the development of a better understanding, and mutual study and consideration of the problems of the future, and it is the manufacturer's duty to take advantage of this opportunity to the fullest degree. We may possibly question the proposed price fixing activities of the Government as they affect industry in general, as in violation of fundamental economic principles, but every patriotic manufacturer should accept his tax burdens in the real American spirit. We are at war, sacrifices must be made by everyone, and the money to win the war must come from those who have it. The future of the nation and of democracy is at stake. While everything at Washington may not be progressing as the critic on the side line would have it, nevertheless, appreciating the magnitude of the task, it is our duty to support the Administration loyally and wholeheartedly in its every effort and in truth, gentlemen, our progress toward preparing for our part in this world conflict has been truly remarkable, and compares most favorably with the really marvelous accomplishments of England.

Realizing the stupendous task before our Government in the waging of the war to a successful conclusion, the manufacturers must rely upon themselves in the task of insuring the future of their export business. There is much that they can do independent of the Government assistance. Foreign markets must be studied. The characteristics and habits of the peoples with whom they would trade must be understood. Young men must be trained for the service. The demand of various markets must be ascertained, and their needs must be conformed to. Well-thought-out sales campaigns will succeed in foreign countries as well as in the United States, and these can be now planned with an eye to the future. Business acquaintances which have been made during the last three years should be developed into business friendships which will last. The credit systems of foreign competitors should be studied and plans made for meeting competition along this line. Every effort should be made now to accommodate in every possible way the new foreign customer that has been put on your books during the last three years. Foreign markets should be visited by trained salesmen, or, better, by representative officials of the firm. All the information, statistics and data bearing upon market possibilities should be availed of.

Finally, the success of the American manufacturer in maintaining his hold upon export business will depend upon the development of a broader spirit of cooperation and of nationalistic American banks and American facilities for doing business should be made wherever available. The interest of every American should be the interest of all in a foreign market. American business standards and American business methods in foreign countries should be such as to warrant the respect and approval of all. Through organization of Americans in the various foreign markets, our business should can be advanced, and this can be accomplished when our manufacturers come thoroughly realize the importance and necessity of co-operative effort in foreign fields.

Now is the time to plan intelligently for the future and to build a firm foundation for a permanent export business, for while at the moment the United States may be successful and clearly and the possibility of the coming storm may disturb us, yet with the dawn of another day we may awake to find the storm clouds gathered and the sun still shining upon a world redeemed forever from the hate, fury and murder of war.

THE FUTURE OF CHEMICAL INDUSTRY IN THE UNITED STATES

BY J. H. BAEKELAND

Member of the Naval Consulting Board of the United States

September 26, 1917

Judging from the scarcity of aniline dyes at the beginning of the war, most people made the erroneous deduction that we had no chemical industry to speak of. This is a gross error. As far as the mineral chemical industries are concerned, this country, even before the war, could stand excellent comparison with Germany or any other country. In fact, when it comes to the production of acids and heavy chemicals, the United States, in several of these branches, was decidedly ahead of Germany. This is particularly the case in her important electrochemical industries, which were developed far ahead of those of any other country.

There is no doubt, however, that we were behind in the manufacture of synthetic organic chemicals, which include the coal-tar dyes. But there was nothing strange or abnormal in this situation. The importation of these products in the United States before the war did not exceed \$10,000,000 a year, this covering more than 1000 different kinds of products, all of which require special processes of manufacture, and some having to be worked in very small units. Their manufacture mainly requires not only good chemists, but also inexpensive skilled labor which it takes a long time to train. As a business proposition, there was little to attract shrewd American business men.

Even the chewing-gum industry of the United States exceeded by several million dollars the value of all the synthetic chemicals imported every year in the United States. One single chain of Five and Ten Cent Stores, in 1913, exceeded the total export business of the whole German coal-tar industry throughout the world by \$11,000,000. One single mail order house, in the same year, did more business than all the German color plants together, and the total dividend payment in 1913 of all the dyestuff manufacturers in Germany was only half of a special dividend of one single mail order house in the United States. In 1913, the entire German color industry paid \$11,000,000 in dividends while the Ford Motor Car Company, with one single standardized product, did a greater annual business than all the German coal-tar dye plants together, with their 1200 different products, and earned four times their combined dividend while paying three times their wages and in the meantime, distributed throughout the world, comfort and happiness, and made our country bigger by making it more accessible to the man with the small bank account.

If Germany has specialized in this branch of chemical industry, it was merely because she did not have the same opportunities for enlisting in other fields of enterprise. Here in this country we had new mines to exploit, new fields to cultivate, new railroads to construct, and many more industries of immediate importance claimed the full attention of our men of enterprise or scientific training. No wonder, then, that a little paltry industry of this kind was neglected.

Nevertheless, as far back as the early seventies a few enthusiasts started the manufacture of aniline dyes in the United States. They were making quite some headway, but in 1883 they had to perish through unfavorable tariff legislation. At that time German agents were already at work in this country and were leading our textile manufacturers by the nose, and they helped them in their lobbying for the lowest tariff on dyestuffs, claiming that Germany would serve them, furnishing them with what they called their "raw material." This situation acted as a boomerang and paralyzed our textile industries at the beginning of the war.

Since then this country has realized that we must not estimate the value of the color industry in dollars and cents, but by the direct bearing it has as a key to all other industries. A few cents' worth of the right kind of dyes decides whether a hundred dollars' worth of textiles can be sold or not in the open market. What is most extraordinary, almost a wonder, and bears witness to the flexibility and adaptability of American enterprise, is that in less than three years we should have made ourselves independent of Germany in the line where she had the start on us since half a century.

This awakening of the chemical industry has carried us along in other chemical lines also. Attention has been given to problems which formerly were outside of our natural field of action. We have carried the mass-production of synthetic explosives to a point never dreamed of. With truth it can be said that if it were not for one of our largest chemical manufacturing companies which promptly rushed to the rescue of the Allies at the beginning of the war and furnished them with explosives of which they were so short, the war might have been ended a year ago in favor of Germany. Since then the chemists of France and England have also shown abundantly what they can do if conditions require it, and everything points out that after this war is over the supremacy of Germany in some of the chemical industries in which she heretofore was a leader will be a thing of the past.

Years before this war started, long before our soldiers were called in, we were raising right here in the United States an army of chemists. Our technical schools, engineering schools and universities were graduating them year by year—a modest set of men who attended to their own business and who were scarcely noticed in the din of shrieking publicity of business and trade. They were holding their meetings, comparing their work and living among themselves, and when the great problem arose to face the new conditions, we heard the cry of the ignorant public: "Have we any chemists in America?"

It was little known then, even at the beginning of the war, that we had an American Chemical Society of which the membership was larger than the total membership of the chemical societies of Germany, France and England combined. These were the men who took up the call for chemists and who helped our engineers to face the new situation which has arisen by the war. To-day this Society counts over 10,000 members. Its publications on industrial chemistry are second to none in existence and are read the whole world over. It lives without any subsidy, gift or contribution and is self-supporting enough to spend yearly over \$100,000 on its publications alone.

FUTURE PERMANENCE OF AMERICAN CHEMICAL INDUSTRY

If anybody asks what have the chemists been doing, let them visit this Exposition and be convinced that our chemists have not been asleep. But you will ask: "Is all this going to last? Are not most of these industries simply war-babies, bound to vanish as soon as peace is declared and conditions again become normal?" Some of these industries undoubtedly will disappear as soon as the war is over, particularly some ill-conceived projects, badly managed and badly financed. Others will have to shift the bulk of their production to other articles; others again may have to reduce their capacity. Then almost all of them will have to be satisfied with smaller profits. The latter effect will not be so much of a detriment as some people may imagine. The apparently high profits of to-day are considerably offset by the uncertainty of obtaining the raw materials and other feverish conditions which make manufacturing more of a gamble than it ever was heretofore. Smaller but steadier profits are more conducive to the sound development of an industry.

As stated before, we already had made a splendid record even before the war in the development of our industries of heavy chemicals, in the mineral or inorganic line. The steady development of these industries will very probably proceed as

in the past. Our greatest development will consist in the further extension of industries in the organic field. When the present crisis came, we had no trouble in finding chemists and chemical engineers in the field of acids and heavy chemicals. Our lack of experience was mostly evident in the newer problems of coal-tar dyes and other organic industries. Here, as in other fields of chemical industry, it is not enough to know a chemical reaction on a laboratory scale. It makes an enormous difference whether you are manufacturing by the ounce or by the ton. In a laboratory, operations can be performed in little glass vessels, or in porcelain or expensive platinum. On a manufacturing scale, all this becomes totally different and the difficulty is no longer the chemical reaction itself, but the vessels and the methods of carrying it out. Acids and other substances which attack iron and other metals have to be handled in machinery which can withstand their action and insure not only the highest yields but great purity, and exclude the possibility of accidents. An entirely new industry had to be created for this purpose—the industry of chemical machinery and chemical equipment. But this was not all; the best chemists and best engineers are powerless if they do not have carefully trained and experienced foremen and workmen. Labor in the chemical industries does not count so much by number as by quality and reliability. One careless act of one single workman can blow up a whole plant or stop manufacturing for several weeks. These have been the great impediments during the first months when we had to tackle entirely new industries. Now that we have familiarized ourselves with the conditions, and that we have every right to feel confident in our further efforts, there is every good reason and every good opportunity why we should turn our abilities to other lines of organic industry besides that of the coal-tar industry.

It is said, with right, that one of the reasons why we had no coal-tar industry in the United States was that there was no available coal tar because our methods of making coke and gas were such as to exclude this raw material as a by-product. Conditions have changed since then, and now we are abundant producers of coal tar, and the quantity of this raw material, from which so many chemicals are made, will undoubtedly keep on increasing for many years to come.

But there are other raw materials in the organic line which hitherto have not been utilized to the proper extent. For instance, our petroleum and natural gas have thus far been used for little else than as a fuel. It only requires research and enterprise to make it a raw material and a starting point of as many valuable products as coal tar has supplied until now. The same can be said of our agricultural products. In fact, every agricultural product is a starting raw material from a chemical point of view. Starch, sugar or wool may be a starting point of alcohol, one of the most useful chemicals ever introduced to mankind, and for which the future industrial uses are almost limitless as soon as it can be manufactured and distributed at a sufficiently low price. Nevertheless, our chemical engineers have been thinking along inorganic or mineral lines. From now on they have learned to tackle problems in organic chemistry. If they succeed half as well in this new line as they have done in the old, there is very little doubt that this country, with its limitless resources of organic products, will find ample opportunity of building up new chemical industries for products hitherto of little use or newly known, but for which a market can be found as soon as they can be supplied at a sufficiently low price and at a cost as we become aware of the new possibilities. It will be the story of so many chemical substances which at first found no market and of which some time afterwards the demand exceeded the supply.

NEW ATTITUDE NECESSARY TOWARD CHEMICAL INDUSTRY

I mention this particularly because some foreign-born men are inclined to believe that the chemical industry will be con-

stricted by the present market and by the world competition of other chemical-producing countries. There is no doubt that at first a strong commercial struggle between competing manufacturers will set in. This will be the critical period, and I fear that during this period this country will be at a disadvantage unless we change radically our present attitude. Those who framed the Sherman Law did not consider that if a certain amount of competition is good, too much competition may be killing for all competitors concerned. In reckless commercial competition, the healthy technical efficiency, which is the basis of every sound industry, is frequently overlooked. Several manufacturers in this country, underbidding each other and in the meantime leading to over-production, can hardly compete with those of other countries supported by a paternal government which encourages the formation of trusts or Cartels, and favors exportation by subsidies or bounties, as done frequently in the past. These remarks apply specially to Germany. We know that not only had she her political agents distributed in all foreign countries, but she maintained a staff of agents who were always on the watch to detect a weakness in our situation and who never missed an opportunity to mix in our attempts of tariff legislation. The influences which in 1883 killed our dyestuff industry are still at work to-day, when they surreptitiously introduce words of double meaning which jeopardize the intent and purpose of our latest tariff laws. To what extreme measures Germany is ready to go in order to maintain her supremacy in certain industries can easily be guessed by what we have learned of late. In her political machinations in all countries, some glimpses of her intentions can be gained, now and then, by incidents such as the following. On Feb. 1, 1916, in the *Faber-Zeitung* of Berlin appeared the following paragraphs:

"The German coal-tar dyestuff industry ought, after the conclusion of peace, to be permitted to sell dyestuffs only in Germany and Austria, in Turkey and Bulgaria, until the German textile factories are again fully occupied and all warehouses and stores and all consumers are again supplied with good white, dyed and printed goods. Only then should it be permissible to furnish German coal-tar dyestuffs to neutral or hostile countries."

"If foreign countries begin again soon to receive good German coal-tar dyestuffs, they might easily ruin the business of the German export trade in finished products."

For the German coal-tar dyestuff industry there are probably two other points to be considered; first, this industry and the German industry in coal-tar products would for the present have no right to sell raw material and by-products to foreign countries, in order not to create unnecessary competition; and, besides, it would be permissible to furnish dyestuffs to America only if the American government should promise to bury for a long time the unjustifiable so-called anti-trust question in connection with aniline-dye interests."

Are our textile manufacturers sufficiently awake to the danger of dependence upon foreign competitors for their essential supply of dyestuffs to make some slight sacrifices in behalf of American dye manufacturers who, with their cooperation, can forever assure them an adequate home supply of dye?

These and many other attempts will be made at first to strangle our new industries. It will depend almost on our common sense of our homeland as to the kind and volume of our chemical and engineering whether what we have gained as benefits by splendid country-raw materials be lost again through political bumbling and terrorism. Presently, we have seen what we should have regarded long since as a tariff commission, and the quality of the men who have been named for this body guarantees that they will be able to do nothing to their industrial competitors, present and future. (1917 Commerce Commission on Tariffs and Customs Duties, 4th Annual Report, 1917.) They would be made their names by names mentioned, there is no money in the matter.

OTHER MANUFACTURING INDUSTRY

There is no question about industries which will back us in our commercial and political battle, (some of our present industries)

I refer to the power problem. In a country blessed beyond comparison with all the necessary natural resources for a large chemical industry, with a home consumption greater than that of any other country, with an enterprising population, with immense deposits of coal and other sources of fuel, navigable streams, railroads, and ever-increasing methods of land and water transportation, we, nevertheless, are very short of cheap water powers. Our great development of the electrochemical industries in the United States was due to the fact that for the first time we placed at the disposal of our industries abundant electrical current at lower rates than had been obtainable in the past by means of steam. We became the leaders in those industries. Niagara Falls and its industries became a by-word of electrochemical supremacy throughout the world. Some of the most epoch-making inventions in this branch of chemical industry were encouraged by this condition. Since then other countries have gone us one better in the production of cheap water power. Unless we change our present condition it looks as if our electrochemical industries, our leading chemical industries, were going to be wrested from us to find a more inviting home in Canada and in Norway. Unfortunately, here again the condition is one of "dog-in-the-manger" politics.

For purposes like electric lighting or traction, or most chemical industries, a few dollars more or less a year expressed in kilowatt-hours amounts to a mere trifle. But when it comes to making chemicals or metals at the very lowest possible cost, then every dollar counts, and here we are unfortunately face to face with the distressing fact that, with our present methods of financing, the fixed charges of our water powers amount to about 90 cents financing and 10 cents engineering. If engineers succeeded in increasing their efficiency of operation 10 per cent, it would only amount to 1 per cent in the total cost. So, if any improvements have to be made, it must be in the financial side of the problem. Meanwhile everyone advances his own arguments why it should be this way, and everyone is more or less right—from his personal standpoint. Capitalists say: "Some of our Government laws about the utilization of our water powers are so uncertain and threatening that we prefer to invest in less risky enterprises." Then our rates of interest in this country are considerably higher than they are in Europe. Some other persons have proposed that the United States Government should use its own excellent credit and thus be able to issue bonds for water powers at low interest, in the same way as the Panama Canal has been constructed. With our wasteful methods of financing and banking, and the many middlemen, it costs usually about 9 per cent to accomplish this result by the time the bonds are floated and put in the hands of the hesitating investor. This puts the annual cost of some of our cheapest water powers at \$10 a horsepower-year, of which \$9 is for interest and bonded charges and \$1 for general operation and maintenance expenses, to which has to be added profit for dividends. But with interest at 4 per cent the cost per horsepower would suddenly be reduced to \$5 to \$7 per horsepower-year, which brings it closer to that of some of the water-power developments in Norway. Then, again, others say that the Government has no right to participate in any such enterprise, or that it is unprepared and unfit for any such business operation. To this others retort that the erection and operation of a hydroelectric plant is much easier and less expensive for the Government than for private companies, because the Government has already in its power the question of extending the navigability of streams, which, by the way, has always been a never-ending source of "pork-barrel" appropriations. Streams are made navigable by the erection of dams. By the proper selection of stream and location the cost of the dam can be made to furnish the most important part of the total outlay for a hydroelectric plant; all that is necessary is to add the turbines and the electric equipment for obtaining at somewhat increased cost a first-class hydro-

electric plant, furnishing forever electric current for any purposes. A hydroelectric plant as a Government enterprise would not involve much of a new departure as compared with that splendid example of good engineering, the Panama Canal, which is a national monument of efficiency, and which, similar to the present problem, is an asset for national defense in time of war, while in the meantime it is an aid to private shipping enterprises. The methods of hydroelectric plants are, by this time, well established and well known, and leave little scope for further improvement except the enormous cheapening which is possible for such plants in the reduction of fixed charges by very economical financing.

These are some of the dark points on the horizon of our chemical industries. What will happen depends very much on whether in the future our legislators will look at everything from a political or a one-sided standpoint, or whether they shall have learned in earnest to utilize the advice of competent men, and put the welfare of the United States before sectionalism and personal political ambition.

RUSSIA AND ITS RELATIONS TO THE UNITED STATES

ABSTRACT OF ADDRESS BY C. H. BOYNTON
President American-Russian Chamber of Commerce
September 26, 1917

The speaker emphasized the unusual political conditions now in Russia and expressed the belief that the Russians would be able to straighten out the tangle themselves. He strongly emphasized the necessity for America forming its opinion of Russia from information and data furnished by Americans, especially the men in the American Diplomatic and Consular Service, and American business men in direct contact with Russian affairs.

Mr. Boynton enumerated many of the natural resources of Russia, whose territory covers two and a half times that of the United States, with a population of 180,000,000, and a birth rate higher than that of any civilized nation: in the ten years between the Russo-Japanese and the present war, Russia had in many instances doubled the output of her raw materials and her natural wealth.

Russian Commissions are now studying manufacturing, mining, railroads, textiles and every branch of industry, and the methods and laws under which other countries have developed their resources. It is intended to re-draft entirely legal procedure, corporation law, mining law and almost every law which enters into economic development.

Mr. Boynton stated that he had yet to meet an American with sound business judgment, who had made a visit to Russia and personally investigated Russian affairs, who did not return enthusiastic over the future possibilities of Russia.

Russia offers an unlimited field for chemical development in all classes, in the beginning as an importer of American chemicals and later as a chemical producer.

Mr. Boynton gave numbers of instances showing our political indebtedness to Russia, and the sentimental and practical reasons why we should assist her in maintaining her democracy and aid her in developing her resources.

NATURAL RESOURCES SYMPOSIUM

September 27, 1917

AHOPPA AWAN TEWA (THE DEAD THEIR DAY)

EXTRACTS FROM ADDRESS BY C. H. CRAWFORD
Assistant to President, Nashville, Chattanooga and St. Louis Railway

It might be wondered why a concern with but one product to sell, which, strictly speaking, is not competitive but is an essential—the absolute basis—of all industrial products, Transportation, should take the trouble, expend the money and use

up the time of part of its personnel to attend an exposition of this kind, but if you will look over the exhibit you will find that several railroads have done this. What is the reason?

All railroads have at least two kinds of industries—those that "just grow" and those that are planted. There seems to me to be a middle ground, largely uninhabited, in matters of this kind which is much better for all concerned.

I do not believe that there is any business organization that realizes Preparedness more clearly than do we, with all that it connotes of internal readiness. It is only within the last few years that the old-time industrial departments of railroads, which were great in the same manner as are balloons, have been modernized by the addition of serious-minded scientists equipped with the indispensable industrial research laboratories, as the sciences upon which success must be based are so interdependent that a specialist in one of them is not of much value unless he has at least enough knowledge of the others to know when he is getting beyond his depth in them. But the immediate and crying need of our chemical industries is research of the business order and they have such limitless possibilities that it is clear beyond any one to venture prophecy as to what they may become.

So far in our endeavors we realize that we have but "scratched the surface." The underlying idea is that particular idea upon which most of our great industries have been based—that of service; and, adapting our views and wishes of what should be done to our abilities to perform it, we have made up our minds and have told a few people who have already come to us for advice and assistance, that if there was anything in America at which we could get there was no trip too long for us to send a properly qualified man to get the information that might be at the end of the road to put at the disposal of our client.

There was a time in our history when if you went to a banker for a loan for which you wished to hypothecate securities, he seemed to figure as to how he would get your securities for the least possible percentage of their value, but no legitimate banker does such things as that now.

By the same token there may have been times in the past when the railroads did business on some such piratical hypothesis, but that day is over and most of us who represent the younger generation of railroad men are inclined to deny rather vehemently the existence of these old-time rules of the "biggest gun" because we have only a little hearsay but no knowledge of how they were worked.

At the first chemical exposition, held within a year after the war began, in 1915, and attended by over 60,000 people, there were no railroads; at the second, which more than doubled the first in most ways and was attended by nearly 80,000, there was one; this year if you look around you will find five; and while we all have recognized within the last few years the utter futility of prophecy it would not surprise me greatly if the geometrical ratio between these numbers be carried into the progression which will be shown by the number of those you will see in 1918, because few things, if indeed any, have done more toward broadening and quickening the advancement of industrial chemistry or to bring to all of the different industries that go to make up our business life greater realization of the benefits accruing from properly directed chemical-industrial engineering and research.

There isn't a productive industry shown in this great exhibit, of whose internal value for publicity, education and business acquaintance every live manufacturer should avail himself, that is not absolutely dependent upon some kind of original raw material coming from the earth and very few of them are of any value until they have been assembled with others—transported in some way to a central point where they went through the various processes we call "manufacturing" to some useful form.

New discoveries which industrial chemistry is continually performing are the basis of the increasing tendency to develop low grade properties. Many places in the country are working over their old dumps and making more money than did the origi-

nal property. It does not take much of a mathematician to see the effect of this because the freight on a car of 45 per cent ore is about the same as the freight on a car of 75 per cent ore; hence it is inevitable that such plants will go to the source of their raw material and it is apparent that the railroad which knows the most about the mineral deposits in its territory is going to be the strongest contender when it comes to locating them.

After the lesson of the last three years no real American disputes the importance of making ourselves independent of all other countries. I think I am safe in making the assertion that twenty-five years ago the whole railroad industry in America did not have ten chemists in its regular employ; nowadays a railroad that does not have a sufficient number of well-trained chemists to do its work is a "back number," whether it knows it or not, and the field of the chemists on railroads has just begun to open as railroading is also becoming a science whose operation uses more than half the known elements. The chemist's first efforts seem to have been destructive although he did not so intend, but in the future, while his critical field will continue to expand, his greatest use will be in the way of aiding the industries to do better instead of sitting by to tell them how bad their products really are.

The South that was practically left for dead something over a generation since is coming into a life of which few of its citizens in the past even dreamed and we are expecting to be among those present at the profit-taking. The resurrection of the South is a real thing. The value of our cotton crop this year will just about equal the value of all of the gold that the State of California has produced in the best fifty years of its history.

A few years ago there were only a few Southern textile mills; a few years earlier than that there weren't any. But they took approximately 55 per cent of the 1915 crop; they took about 60 per cent of the 1916 crop. The percentage they require of the present crop will be still higher.

The number of industrial and developmental projects that were inaugurated in the South during the first half of this year is simply astonishing. The statement in the *Manufacturers Record* shortly after the close of the first six months lists more than twenty-seven thousand (27,167) and, strange to say, this number does not exceed that of the corresponding period of 1916 but it does represent a great deal more money as these ventures involved sums of money all the way from a few thousand up to, in one case, fifty million, and when I tell you that the projector of the fifty-million-dollar enterprise was the Bethlehem Steel Company you are at liberty to decide for yourselves as to whether or not it will be put through. These great industries are being established in the South as permanent ones and the communities which are successful in securing chemical industries in the beginning are the ones that are going to become their great centers.

BUILDING A COMPLETE CYCLE OF CHEMICAL INDUSTRIES ON THE CLINCHFIELD

EXTRACTS FROM A REPORT BY A. V. KILPATRICK,
Chemist Industrial Agent, Carolina, Clinchfield and Ohio Railway

The Carolina, Clinchfield and Ohio Railway, frequently spoken of as "The Clinchfield," traverses a portion of Southeastern Kentucky, Southwestern Virginia, Eastern Tennessee, Western North Carolina and South Carolina. The source, manufacture and distribution of many of the raw materials, the chemical industry a central and growing business enterprise in the domestic trade of the more important sections of the United States. The Clinchfield territory produces significant amounts back from the necessity of assembling raw materials and the distribution of finished products.

One of the principal considerations that led to the construction of the Clinchfield was the necessity of insuring the economic production of power, other minerals and the virgin timber. The coal fields made available by the Clinchfield are

among the largest and most important in America—comprising hundreds of thousands of acres of high grade bituminous coal situated in the Cumberland Mountains of Southeastern Kentucky and Southwestern Virginia.

The Clinchfield is a leader in the fostering of certain industrial developments new to the entire South. As an example the first pottery designed for the manufacture of decorated tableware has been built on the line.

The fact that the Clinchfield was the first railroad to exhibit at the Chemical Show is representative of the pioneer character of its entire development.

The examinations of our natural resources have been and are now being carried out under the direction of experts, thus reducing to a minimum the element of chance in the establishment of industries. This policy further prevents any mistakes in locating plants that are not likely to succeed. This has characterized the industrial development in a chemical way, which for completeness and success has but few parallels in America.

The economic and successful operation of chemical industries, in fact any industry, is due quite largely to cheap power and raw materials. The superior quality of the coals from the fields of Eastern Kentucky and Southwestern Virginia, served by the Clinchfield, is indicated by calorimetric tests, showing upwards of 14,000 B. t. u., with low ash, sulfur and phosphorus.

The undeveloped water powers tributary to the Clinchfield are potentialities of much importance to the chemical manufacturer. The magnitudes of these powers vary from a few hundred horse power up to several thousand, and these can be developed at reasonable costs, well below \$100 per horse power.

The building of a large Portland cement mill on the line was undertaken only after it had been established beyond reasonable doubt that the necessary raw materials of the proper character as regards quality and quantity were available and that the territory to be served would supply a market for the finished products. This industry has been increased 300 per cent since 1911.

The construction of a plant for the manufacture of hollow tile, terra cotta and brick was begun only after it was fully proven that the raw materials were suitable in every way. The output has been increased 260 per cent since 1911. The brick plant is typical of the chemical plants on the Clinchfield, forming another link in the cycle, and fitting in nicely with the cement plant, inasmuch as it adds additional materials of construction.

In addition to the cement and brick and the development of other building materials along the Clinchfield there followed in rapid succession plants for the manufacture of other materials of construction, including quick and hydrated lime, sand, crushed stone, gravel, limestone, sandstone, marble, granite, timber and lumber.

Several tannic acid extract plants were located along the Clinchfield, because of the natural advantages offered in the way of cheap fuel, cheap power and an unlimited supply of chestnut wood and tan bark, all of which can be assembled at convenient points at very low rates.

The spent chips from the acid plants represented a waste, whose fuel value is low and, therefore, practically worthless, but the chips become of value when used for the production of cardboard and low-grade paper. As a consequence of this a large soda pulp mill was erected. This plant will use in part the spent acid chips, but will draw its main supply of raw material from the practically inexhaustible supply of pulp woods in the forests of the Clinchfield. Before the pulp mill was completed its capacity was doubled. The pulp plant needs hydrated lime to causticize the soda liquors. To care for its needs a large lime and hydrating plant was built. The lime plant draws its limestone from nearby local deposits, and is now supplying the pulp mill with hydrate, and a tannery with lime to be used as a depilatory. The calcium carbonate resulting after the causticizing of the soda liquors is now finding a market.

Tannic acid is a commodity that will permit of long shipment, but instead of sending all the material off the line, a large tannery was built to consume a portion, and to provide a market for local hides. This same industry uses lime and sodium sulfide as a depilatory. These chemicals are now being manufactured in large quantities.

A factory for the production of shoes is now under consideration, which will utilize the unfinished leather from the tannery in the production of a finished article.

The pulp mills need a bleaching agent. A large chemical plant was built, and is now supplying the pulp plant with large quantities of bleach of a very high grade, making the pulp plant a self-contained unit, and adding another link to the cycle.

A large dye plant was built on the Clinchfield and it needed sodium sulfide for the manufacture of sulfur black. Another chemical plant on the line in a neighboring town promptly supplied the sulfide of the proper quality and without delay.

The same dye plant consumes large quantities of coal-tar by-products, and to take care of its needs, plans are now under way to provide the requirements locally. The residue from the coal-tar by-products will not be used in the usual way, but will find another outlet which will permit of producing power at a cost that will rival the cost of power at Niagara Falls. When this is completed, this industry will form a complete cycle, when it is considered that the dyes are used by the textile mills on the line, and, furthermore, the textile mills are getting their raw cotton from the fields tributary to the Clinchfield.

The only possible link lacking in this cycle is that there is not at present being manufactured a full line of fertilizers necessary for increasing the cotton and other crops. This phase of the chemical industrial development is being seriously considered, and we have hopes that such an industry will soon be founded. The necessary raw materials are either on or nearby the line of the Clinchfield, and when coupled with the cheap power available in connection with a ready market, the proposition becomes most interesting.

A large pottery was built to utilize the naturally occurring raw materials on the line, and to further the chemical cycle, a large number of modern homes were built for the employees.

To provide the pottery with the necessary raw materials of the proper quality, large kaolin refining plants were built as well as feldspar and silica grinding plants.

The vast quantity of hard woods standing in the forests along the Clinchfield represent a potentiality of much importance to the charcoal and wood alcohol producers. The saw mills along the line are wasting a thousand cords of hard woods every day, that are suitable for the production of charcoal, wood alcohol and acetate of lime. If a plant is built on the line to utilize this enormous waste we have assurances that a charcoal iron furnace will be built thus completing the cycle for this particular industry. There is now a limited market locally for the alcohol and acetate of lime, but these commodities will stand long shipments; therefore, there is at all times a good market for these chemicals, and this is particularly true of the present time.

The above sums up briefly but somewhat comprehensively the building and operation of a complete cycle of chemical industries on the Clinchfield. Other chemical plants, for which the Clinchfield is particularly well adapted, and which with the vast amount of natural resources available, would do well to locate along the line are: a plant for the production of artificial abrasives; for the production of nitrogen compounds; for the production of calcium carbide, carbon electrodes, bleaching agents; caustic soda; pharmaceutical compounds; organic compounds and dyes; water glass; glass products; ultramarine blue; ferro- and non-ferrous alloys, etc.

DEVELOPMENT OF CHEMICAL INDUSTRIES ALONG THE NORFOLK AND WESTERN RAILWAY

NATURAL RESOURCES DEVELOPED AND UNDEVELOPED

EXTRACTS FROM ADDRESS BY E. A. SCHUBERT
Mineralogist, Norfolk and Western Railway

With the advent of hostilities in Europe, when the source of supply for many of the chemicals essential to industry in the United States was cut off—our scientists immediately arose to the occasion with the result that the chemical industry has developed and now occupies a high position. This is evidenced by the large amount of capital invested in chemical companies and organizations, and the great number of chemical plants that now are in operation or are building in different sections of our country. In fact, so rapid has been this development that chemists, engineers, and geologists have been in demand far above the supply. The condition applicable to chemistry throughout the United States is equally applicable to the development of industry in the territory traversed by the Norfolk and Western Railway. This system, some 2000 miles in length, is the main artery for transportation to one-half of the State of Virginia, large portions of North Carolina, West Virginia and Ohio, as well as certain points in Maryland and Kentucky.

The industrial development along the Norfolk & Western Railway had a very humble origin; starting with the old flour mills, the Catalan forge, spinning wheel and other minor industries, gradually the possibilities for industrial supremacy impressed themselves upon the artisan and capitalist, until now in practically every village and city, smokestacks are seen sending forth evidences of manufacturing activity. Thus the chemical industry has risen out of the development of the simpler minerals and elements found in economic quantity, until now there are large fertilizer plants, chemical works, gypsum factories, brick plants, paint mills, lime grinding mills, lime kilns, acid plants, by-product ovens; soap factories, zinc works, aluminum works, carbide plants, textile mills, furnaces and numerous other institutions of a similar character operating and securing their source of raw minerals from the several deposits that in the past have been looked upon as sources of samples rather than the basis for large industrial plants.

COAL—The first shipment of coal took place in 1887. During that year less than 100,000 tons were transported. This tonnage rapidly increased until 1917, from present indications, will see about 40,000,000 tons of coal mined and transported. In addition, at least 5,000,000 tons of bechive coke are converted in the territory. This vast tonnage represents the output from about 300 mines.

ANTHRACITE Comparatively little development has been done on these measures except in Pulaski and Montgomery Counties where three or four mines now are in operation. This coal is not as hard as the Pennsylvania anthracite but carries from 76 to 78 per cent fixed carbon.

Based on this bountiful coal development, there are three by-product coking plants either in operation or now building and several chemical and dye plants are projected in connection with these operations.

SHALE Throughout the Valley of Virginia, in Piedmont, North Carolina, in West Virginia and Southern Ohio are some of the largest deposits of shale so far discovered.

CLAYS The clays of our territory have been exploited, primarily for brick making only. However, throughout the Valley of Virginia and in Piedmont, North Carolina, large deposits of clay, kaolin and spess are found adaptable to all branches of ceramics, chemical pottery and paper purposes.

LIMESTONE The limestone industry has been quite highly developed. A large number of lime kilns, a central lime grinding plant, chemical works, blast furnaces and steel mill draw their supply from these deposits. At Kenova, West Virginia, a very large plant is converting a dolomite marl from Ohio into magnesium oxide for steel furnace lining. This plant

now is turning out about 1,000 tons of finished product per day and has demands far beyond its capacity. Based on high-grade limestone and other requisites, there recently has been organized and now is building at Ivanhoe, Virginia, a calcium carbide plant that will have an initial capacity of 15,000 tons of carbide per year.

SILICA—The silica deposits of our territory are confined to the Oriskany measures found high on the Alleghany and other mountains. The silica is quite hard. It now is being prepared for the market by two different plants; one near Roanoke, which supplies the requirements of a glass factory and sells on the open market; another in Bristol that is engaged in the manufacture of cleansing powder, using silica as a basis. It ranges from 98.8 to 99.5 per cent pure silica. The tonnage is very large and gives promise for the development of other industries requiring this element as the base.

PHYRROTITE OR MUNDIC

Inasmuch as the present new industrial development requires for its base primarily sulfuric acid, therefore, the question of sulfur ore is of great importance. For a number of years the deposits locally called Mundic ore, which are found in Floyd, Carroll and Grayson Counties, Virginia, Ashe, Alleghany and Watauga Counties, North Carolina, have been known, but comparatively little work was done on them except to remove the gossan for blast furnace consumption. On a few miles of the lead, the Pulaski Mineral Company began experimenting with these ores for the manufacture of sulfuric acid. This company spent large sums of money, finally succeeded in perfecting a process and about ten years ago installed its first acid-producing unit. This industry has been so successful that up to the present time it has increased its capacity about 400 per cent, and manufactures fuming sulfuric acid and sintered iron ore for use in the blast furnace.

It is not possible to convey to this audience the full magnitude of these leads, which are three and perhaps four in number, paralleling each other. All development has been confined to the lower lead and practically to the one point. The General Chemical Company is recovering its ore from open pits, showing the vein to be about 165 feet in width and recovery has taken place to a depth of nearly 200 feet. The vein has been drilled at this point about 300 feet more.

About 15 miles to the Northeast, at Sylvatus, a large amount of work has been done on this same lead; many diamond drill holes were put down, cutting the ore at depths ranging from 500 to 900 feet below the surface, showing it to vary in thickness from 10 to more than 200 feet. This lower lead is from 50 to 60 miles in length. The second lead is practically the same length and varies in width from 10 to 70 feet. The third lead is practically unknown. All of this ore carries a small percentage of copper; the sulfur content varies from 28 to 36 per cent, while the iron content ranges from 30 to 35 per cent. With a large number of chemical and fertilizer plants of various descriptions requiring sulfur ore for a base, this vast undeveloped area gives promise for a source of supply extending far into the future.

STICKLE Paralleling the pyrrhotite lead in Floyd and Carroll Counties, a Berton Company has spent a great deal of money on the development of the ochelotite pyrrhotite. The indications are that this vein is about 14 feet in thickness and carries 1 to 2 per cent nickel with other values. The lead has been traced for at least 10 miles.

TRAVERTINE and **TRIPOLI**—A large great bulk of the travertine from one found in the Shenandoah Valley, in North Carolina as well as in many counties in Southwest Virginia. I have given a great deal of consideration to these deposits, which by nearly every measure are of the highest quality and could be used to have them for the better part of the way used in the production of a pig iron and steel, and in the manufacture of various goods, besides strength and purity are essential. We have in our territory many miles of these leads ranging in thickness from 10 to

20 feet, carrying 45 to 50 per cent metallic iron and from 3 to 25 per cent titanium.

MANGANESE—Until very recently all manganese recovered in America came from Virginia. At one time at least 90 per cent of it was recovered from one mine. From the Potomac River down into Tennessee large sums of money have been expended in exploring manganese deposits; some of these with success; others have been a failure. The manganese of our Valley region is embedded in a very stiff, tenacious clay which makes it rather expensive to handle, but the total tonnage available within this territory (and most of it is along the Norfolk and Western Railway) is very large.

Other regions of great promise are to the east of Lynchburg and south of the James River, where in the past nearly all development has centered on the property known as the Piedmont or Myers.

Manganese is found in nearly every county of Southwest Virginia; some of the deposits are very promising; others have little value, but I am certain that under careful management many millions of tons of ore are available for the iron and chemical industry in this State of Virginia and that if the proper equipment is installed it can be prepared for market at a price that will return a profit in competition with our foreign ores. Already a number of large manganese plants are in operation, others are developing as a result of the high price of this mineral and I believe that even after the close of hostilities the possibilities for these mines to continue operation are flattering.

BARITES—At one time Virginia produced a very large percentage of barites required by the trade, but some 8 years ago all mills were compelled to shut down and the mines abandoned. There still are available in Tazewell and Russell Counties, Virginia, large lenses of barium sulfide averaging over 98 per cent.

ARSENIC—In Floyd County, Virginia, is the only exclusive producing arsenic mine in America, known as the Brinton Arsenic Mines. Development started on these deposits about 12 years ago; about \$500,000 has been spent; the mine developed to a depth of about 300 feet on the slope, and up to the present time about 2,000 tons of arsenious oxide have been refined. A tunnel driven into the mountain cuts five veins of arsenic ore ranging in thickness from 14 in. to 7 ft. Vein No. 3 is the only one being worked at the present time. The ore recovered carries about 35 per cent metallic arsenic. This lead has been traced for about 30 miles.

ALLOY METALS, PRODUCTION AND USES, ESPECIALLY IN RELATION TO THE WAR

NOTES ON OBSERVATION MADE ABROAD

Address at Special Joint Session of the New York Sections of the American Institute of Mining Engineers and the American Electrochemical Society, September 27, 1917

By GEO. K. BURGESS

Chief of Division of Metallurgy, U. S. Bureau of Standards

Problems involving the use of metals were given particular attention during a recent visit to France and England, and although a considerable part of the information thus obtained concerning metals is of a confidential nature, a few general impressions may be recorded here which may have a bearing on the rôle and participation of the United States in the war.

First, as to production and distribution of metals and other metallurgical supplies and products, there is a rigid governmental control exercised through the Ministries of Munitions in both France and England. This control extends even to orienting the nature and scope of metallurgical manufacture and includes not only the original distribution but may be exercised to force repartition of stocks already assigned, as the exigencies and emergencies require.

The practical advantages of this single control without confusion or ambiguity, of metal and other stocks, appear to work for the greatest possible efficiency and economy in production, manufacture and distribution.

Second, there have occurred at various times either momentary or prolonged shortages of certain metallurgical materials, and this has served as a stimulus for the production of substitutes.

The scarcity of copper threatened at one time to become very acute and was sufficiently so in England and France to start a series of investigations on copper substitutes for its various uses as a metal and in alloys, and some of these substitutes have been found so satisfactory they will undoubtedly stay. Thus the metal zinc, particularly when alloyed with other metals, was in this way made to play a more important rôle than hitherto; and pure iron—such as that produced electrolytically—came into prominence.

In this development of substitutes, as well as improvements in the realm of alloys for various purposes, America has by no means been lacking, and this field is everywhere being very actively worked. It includes many domains which are being constantly extended both here and abroad, such as high speed steels, light alloys for aviation construction, non-corrosive alloys, and many others.

Another illustration of a much-needed substitute will occur to everyone. There is one ingredient in steel which is considered essential and which reached relatively fabulous prices—I refer of course to manganese. The production and working of steel with low manganese and the possibility of using less costly substitutes, should be intensively investigated—the problem is being attacked in several laboratories and works and appears to have been partly solved for certain classes of steel.

One of the most striking cases of efficient substitution is illustrated in the French semi-steel shell replacing steel; it has even been claimed that "semi-steel" saved France. In any event, it was characteristic of the French genius in meeting spontaneously an emergency, that, with a sudden shortage of steel and the greater part of their blast furnaces in enemy hands, little iron foundries were established pretty much everywhere, almost literally over night, and the necessary output of shells thus maintained.

Another phase of the question of limited supplies is illustrated in the renewed scrutiny of specifications with a view to eliminating all items concerning quality that are not absolutely essential. This is particularly true, for instance, for certain of the chemical requirements previously insisted upon with great severity for certain steels used in the manufacture of shells and numerous other products. For example, the British had for a time a drastic limitation for the copper content in shell steel, which, if enforced, would eliminate practically all steel made from ores originating in the eastern United States and other areas, as the copper therein present is not removed in any of the furnace operations.

Metal supplies are used in such tremendous quantities that in a specification every proposed item which may act to limit or complicate production or manufacture should be scrutinized with the greatest care to determine whether it is really essential for the end sought. Elaborate investigations concerning such matters, about which there may be doubt or conflicting opinions, will repay their cost many-fold and also, what is in many cases even more important, save time.

On the other hand, there are cases where no pains, trouble or cost should be considered too great in order to secure the quality desired. It may even be necessary to revolutionize a whole industry to obtain the end sought; such, for instance, may be the case for certain munitions—high explosive shells, for example, the premature exploding of which works deadly havoc with lives and morals.

It may thus be found advisable for American steel manufacturers—or at least some of them making certain grades of munitions such as H. E. shells—to consider seriously improving their ingot casting practice to conform more closely to methods which have been demonstrated to give without ambiguity "sound steel." Some of the methods of ingot casting in current use in this coun-

try—small end up, fast pouring, no hot top, no tun dishing—are conducive to anything but "sound steel."

In the several French and English plants I was privileged to visit—of which Hadfields, Ltd., and Creusot are typical—the ingot practice appeared to be as perfect for shell steel as could be devised and, incidentally, such practice appears to be both economical and rapid.

There is another aspect of the specification question which should not be forgotten and which makes for reduction in cost and simplification generally; namely, the number of different specifications of similar materials should be cut down to the lowest possible. There should be not only national but international effort in this direction especially when supplies for several nations may be drawn in part at least from a single country. Perhaps the latest example of this kind of coöperation working to secure as few standards as compatible with the common needs, is given in the work of the International Aircraft Standards Board, on which Canada, France, Great Britain, Italy and the United States are represented; they find they can get along with 39 steels, 2 brasses, etc., and have a single, general, metal specification. I believe there is room for a great deal more simplification and reduction in number of metal specifications in the United States.

Finally, although I have no intention of entering into a discussion of the question, I should like nevertheless to state the belief that a further simplification leading toward international uniformity should be effected and the present is not an inopportune time—I refer to the introduction of the metric system of weights and measures. This would make for interchangeability of munitions and parts of numerous war appliances on the front in France and at the rear as well; and, in fact, one may pertinently ask if the securing uniformity of measures, which goes hand in hand with standardization of parts, may not become an imperative necessity?

SYMPOSIUM—THE CHEMIST AND THE BANKER

Addresses at the Special Meeting of the New York Section of the American Chemical Society, September 28, 1917.

THE CHEMIST

By ARTHUR D. LITTLE

Most chemists know perfectly well what a bank is. It is an institution for minimizing the wear on paper money and is generally located in the best looking building in town. It works this way. You take your salary check to the bank before two o'clock and give it to a man in a cage whom you don't know. He writes \$1,000, or, maybe, only \$65, in the little book you bring and you can then, without losing a dollar of real money, spend your salary by simply writing other checks. Once in a great while, to hold your custom, this man writes in "interest 18 cents" in the little book and you spend Sunday in trying to find the error. Then the bank lends part of your salary to the United States Government for which it gets 2 per cent gold bonds against which it issues bank notes to enable it to pay rent and salaries, and it lends the rest of your check to railroads and manufacturing corporations and to farmers to move the crops. Its profit is the difference between the interest they pay and the 18 cents the bank pays you, as pointed out by Stanley Jevons in "Money and the Mechanism of Exchange."

Now the chemist goes at least once a month to the banker's bank whereas the banker seldom or never comes to the chemist's laboratory. It is not surprising, therefore, that the banker rarely acquires an equally clear-cut understanding of the relation of chemistry to the salary check he draws. To-night, with this great Exposition for our background, it is our privilege to enlighten him and I will ask the bankers present kindly to move into the front seats, without crowding.

Chemistry deals with the properties of matter and the changes which they undergo. Banking deals with the properties of money and the changes which they undergo. Money is merely

a special form of matter set apart by agreement to facilitate the exchange of other forms of matter. The conclusion seems inevitable that banking is merely a department of chemistry like metallurgy or paper making.

The authenticity and fineness of the gold coin which constitutes the monetary basis is determined by chemistry. The mint is a chemical plant. Southern chemists get the best results from it.

It is chemistry rather than mining which is ultimately responsible for the amount of gold produced. The chlorination process and the cyanide process, by rendering profitable the treatment of vast quantities of low-grade ores, profoundly affected the value of every ounce of gold in Christendom and the exchange value of all securities and commodities. But gold and the currency based thereon are only the exponents of individual and national wealth. The commanding influence of chemistry becomes most apparent as we consider the true wealth of nations: the things which money and securities merely represent.

WIDE RANGE OF CHEMISTRY

There is an unfortunate tendency among financial men to regard as chemical only those activities which have to do with the production of alkali and acids, dyes, explosives, synthetic drugs, and analogous materials within a narrowly limited field, whereas there is hardly any industrial activity which does not from some point of view present a clearly defined chemical aspect. Agriculture thus becomes a department of photo-chemistry and the production of indigo by the plant under the influence of sunlight is no less a chemical process than its synthesis in a factory. When, however, that synthesis was accomplished in the laboratory, wise bankers began to scrutinize the credit of indigo planters.

Our national wealth is largely founded upon agriculture. Bankers annually bestir themselves to move the crops. There would be far less to move were it not for chemical fertilizers, chemical sprays to keep down the ravages of insects, and bisulfide of carbon which saved the wine industry of France and to which the American farmer is scarcely less indebted. By its utilization of the cottonseed chemistry had added before the war at least \$200,000,000 annually to the value of the cotton crop and the war itself is being fought with explosives made with cotton lint. Cotton is no longer merely a textile fiber. It is the raw material for great chemical industries, for the production of moving picture films, artificial leather, artificial silk, the endless varieties of celluloid, lacquers, aeroplane varnishes, dopes for patent leather and reinforced glass. Corn is still primarily a food crop but it has become much more. Chemistry has made it yield oil, dextrine, glucose, starches, and adhesives in great variety, thus bringing new grist to the banker's mill.

In every state and most conspicuously in Washington, chemical laboratories supported by the public funds attest the dependence of agriculture upon chemistry, which science thus becomes the fountain head of this great source of national wealth.

The securities based on steel production loom large before the banker but are rarely credited by him to chemistry. Yet making steel or aluminum, or extracting and refining, copper and nickel, are as definitely chemical operations as making coal tar dyes, so also with manufactures of the most diverse sorts: the tanning of leather, making bread, bricks, cement, lime, paper, coke, carbide, glass.

But wealth to be available for exchange must for the most part be transported and to facilitate such transportation great financial structures have been built up by bankers. Of these structures or the properties they represent chemistry is again the corner stone. Who would build railroads or big canals without Portland cement and dynamite, steel rails and bridge members? The Bessemer process alone, and chiefly because of its influence on transportation, was claimed by Abram S. Hewitt to add \$500,000,000 yearly to the world's wealth.

A volume of fascinating interest could be written on the influence of chemistry upon the wealth of nations. The discovery of sulfuric acid caused wealth to flow in a broad stream to Sicily

and the substitution of pyrites for sulfur threatened the island with bankruptcy. Not gold, but the cyanide process for extracting gold, established the prosperity of South Africa. The nitrate beds of Chile and the potash mines of Germany constitute national assets of the first importance because chemistry synthesized their values as it now in nitrogen fixation plants synthesizes wealth from air.

FINANCIERS BEGINNING TO APPRECIATE CHEMISTS

Although the chemist is still often made to feel that he is speaking a foreign language when talking to a banker the events of the last three years have stimulated a rapidly growing appreciation in the minds of men of affairs and financiers of the fundamental importance of chemistry as a factor in national development and the basis of prosperity.

The time has come for chemists and bankers to find a common language and to establish a mutual understanding. The bankers need not prove that they can help the chemists; we admit it. We are not sure that they realize the extent to which we can help them.

Some bankers are finding it worth while to study Spanish because it leads them into a new financial world. It is in the power of chemistry to open up a new universe of finance.

Dewar has said that the whole object of the training of a chemist is to produce an attitude of mind. For what do men in hundreds daily risk their lives in aeroplanes over the battlefronts of Europe? They do it simply to get a new point of view from which the enterprise of armies may be directed by their commanders. Is it not then wise for the financiers who are the generals of industry to utilize to the utmost the scientific imagination, which is only logic in flight.

With due mental reservation for a few conspicuous exceptions, it may be said without much fear of contradiction, that bankers generally seem to chemists to lack imagination and to experience a surprising difficulty in visualizing an unfamiliar situation. For instance, it hurts a chemist to see great quantities of raw material going to waste. It doesn't seem to hurt a banker very much. A chemist views with his mind's eye the vast potential wealth awaiting development by chemical methods, in the gas, oil, salt, sulfur and wood waste focussed in Louisiana. Frequent reference to it fails to arouse the enthusiasm of the banker, and very little happens. Evidently the chemist has not learned the proper formula for presentation of such large affairs.

In financing a cotton mill it is, I am told, possible to estimate the cost within a few cents per spindle. No such accuracy can be expected in case of a chemical plant, and particularly generous allowances must always be made where new processes are involved. Chemical investments in their early stages are undoubtedly speculative, and often highly so in character, but the speculative feature stands commonly in an inverse ratio to the amount of capital available for development. Important chemical enterprises should be initiated only by men with large reserves of capital and who wear thick woolen socks. Widows and orphans and small investors should keep away from them. Unless you can stay in it to the finish it is dangerous to get into a good thing too soon. By way of example, the first three companies organized by Count du Chardonnet for the manufacture of artificial silk failed; stock in the fourth sold at \$2280. One can, on the other hand, point to highly successful chemical enterprises which have been established on an initial capital of \$50,000 or less. What is particularly needed is a more direct approach to capital by chemists, through chemists.

THE CHEMICAL ENGINEER VS. MORTGAGE FORECLOSURE

In their contact with existing industries, banks are beginning to recognize that it is sometimes better policy to call upon a chemical engineer to set a business straight than it is to foreclose a mortgage. They do not always seem to appreciate, however, the extent to which the adequacy or the lack of chemical control of material and processes may affect the desirability of credit lines. A balance sheet does not always show where the dollars go in business. Many of them may be going up the

chimney or down the stream, or into the slag pile. Many may disappear in low yields or products classed as seconds. A chemical audit of a plant is sometimes more informing than a balance sheet. Bankers all the world over are straining their energies to aid their Governments in placing gigantic war loans. How shall these staggering burdens be carried and the obligations ultimately paid? The chemists' answer is: By conserving the values we already possess; by converting into actual wealth the vast potential values in raw materials now wasted; and by developing the estate.

If New England farmers cannot raise sheep because of vagrant dogs, let us intern those dogs. Since labor is scarce let us stop the nonsense I have just seen perpetrated by digging one trench instead of four to connect public services with a new building. Let us see if the simple expedient of making it difficult to insure flimsy construction and bad risks will not cut something substantial from our annual fire loss of \$200,000,000. Through long years of peace and plenty dwellers in American cities have carried a heavy burden of municipal extravagance and inefficiency. Now is the time for us to realize that every dollar so wasted is a dollar filched from the fund for national defense. Equally serious to the nation and closer to the individual are the losses from preventable ill health. There are the yearly losses, amounting into billions from bad agriculture, bad packing, bad distributing systems, and the absence of dehydrating plants.

NATIONAL WASTES

The suppression of these especially discreditable forms of national extravagance concerns banker and chemist and all good citizens. There are other colossal wastes which more directly concern the chemist in his professional capacity and the banker as a financial agent—wastes of coal and natural gas and yellow pine and cereal straw in amounts running into figures which sound like stellar distances and which seem to make about the same impression on the average mind. Suppose Niagara Falls ran coal instead of water, how long would we burn the coal at the base of the Falls to make a spectacle and remain easy in our consciences?

The losses due to inefficient manufacturing, though indeterminate, are far greater than either bankers or manufacturers realize. They are in large measure subject to chemical control and when thus minimized have often spelled the difference between disaster and dividends.

Suppression of the waste thus far enumerated would pay our war expenditures within five years and thereafter make our country the financial reservoir of the world.

It is finally the mutual duty and opportunity of the banker and the chemist to cooperate in the development of the estate which is our country. To a similar end England has mobilized her scientists and made grants of over a million Pounds to promote industrial research. Her manufacturers are organizing Research Associations to cooperate with the Government and divide the financial burden Pound for Pound. While the resources of our own country offer literally boundless opportunity for profitable research, we have still to utilize many research results of large importance which are immediately available.

To this extent, the chemist, with his proofs in hand, now waits upon the banker.

THE BANKER

By G. A. O'REILLY

Foreign Trade Representative, Irving National Bank, New York City

Under ordinary conditions and in normal times the spectacle of a banker presuming to address a body of chemists upon their exclusive and somewhat mysterious specialty, or indeed upon any other subject closely related to this specialty, would be rather unusual, perhaps a bit amusing, and certainly would suggest a quality of nerve which quite consistently and even profitably might be applied to some more heroic, although probably not more difficult task.

Just where the theories of banking and the practice of chemistry come together is a subject which, it is feared, in the past has not claimed the attention of banking circles to the extent to which its merit would appear to entitle it—and just why bankers and chemists have not yet succeeded in breaking through the wall of indifference, or worse, which separates them, is a matter which properly may be made the subject of considerable discussion and explanation.

However, the conditions under which we meet are not ordinary conditions, and the times in which we live are not in the least normal times. Conditions are far from ordinary when throughout the world men may look out upon a situation strewn with the wrecks of institutions upon which men had learned to depend for safety and security and guidance, and where, as affecting the relations between men—race, and creed, and kin, have lost their meaning; and times are far from normal, when, after a thousand years and more of Christian teaching and thought and inspiration, Christian men consistently may speak of saving the spirit of the world from the savage ferocity of Christian nations, and when into each thought there creeps the shadow of a fear that never again will the peoples of the world be able to get together in the delightful old-time relationships, which now seem so far away.

And so, the task which, under other conditions, would be so difficult of treatment, becomes easy and live and tangible because in it is found the possibility of treating some of the wonderful big things which have come into this new war-inspired field of national thought in which institutions of the future must be created to take the place of those we have seen so ruthlessly destroyed.

These are wonderful days in which we live. Upon every hand are striking and unmistakable object lessons to point the way for us and to guide national thought and impulse. Doubts and uncertainties which for years have clouded our horizon, in a day have been cleared away. Recently it was my privilege to attend the deliberations of three of the country's great business conventions: the National Petroleum Association, the War Congress of American Business, under the auspices of the Chamber of Commerce of the United States, and the American Bankers Association—all at Atlantic City and all held in rapid succession.

Under any conditions these would have been unusual gatherings. Held as they were, at this time, and under the stress of war, their normal importance was vastly increased. Many interesting subjects were discussed and in masterly manner. Widely separated points of view and almost every possible shade of national business interest were represented.

Understand, they were not war conventions, nor were they characterized by any of the fervid war utterances with which the country was filled only a few weeks ago, and still, whatever the subject and however its treatment was begun, the discussion inevitably found itself moving along war channels, and the conclusions reached invariably were based upon war considerations. War was in the air and would not be denied.

Another striking characteristic of these conventions was found in the highly constructive quality of their deliberations. No time was wasted upon appeals to the patriotism of our people, or to their fighting spirit. The spectacular aspect of war nowhere was in evidence. The atrocities which the enemy is perpetrating under the guise of war received hardly a passing glance. No attempt was made to explain our presence or motives in the war, and above all, there was no note of doubt or uncertainty as to either the seriousness of the war or its intimate relation to our national life.

It was as though the diverse and conflicting business interests of the nation at large and in obedience to some unexpressed impulse which dominated the entire situation, had found a motive so big and so truly national that in its presence the sectional and personal quibbling of times of peace and security were unable to live. A new American national spirit seemed to be in the atmosphere and in it, the newly discovered power of a great nation spoke eloquently.

It was altogether splendid, and the lesson it taught was full of inspiration. If such a spirit can be applied to a purpose like ours here to-night, the solution of our rather unusual problem should be easy and the determination of a proper relationship between even so divergent elements as chemistry and banking, should present no serious difficulties—otherwise, our time will be wasted, our effort fruitless, and discussion instead of bringing our respective specialties and view-points more closely together will only intensify the difference between them, and hence drive them farther apart. It is so easy to talk about getting together and so popular, and we feel so virtuous when we indulge in talk of this sort almost as though the idea involved upon our part some unusually commendable attitude of charity toward our fellow-men. We are so disposed to stress the intention to get together and leave entirely out of consideration other elements of at least equal importance.

As a matter of fact, the big thing in the proper getting together of men of naturally divergent view-points is to discover or provide a proper medium in which they may get together and which will concede sufficiently to each of the different view-points concerned, so that all may feel upon familiar ground and reasonably comfortable.

The true relation of banking to chemistry is to be found in most tangible form in the very simple, easily understood, and well-known theory of practical business. The situation is not difficult unless we are unreasonably disposed to make it so. If the banker can relieve his function of the oppressive weight of self-constituted and unjustified importance under which it has struggled in the past, and bring it out into the open, and give it the sort of contact with other business institutions which it needs and deserves—and if the chemist can emerge from the somewhat mysterious atmosphere in which unfortunately, through his fault or otherwise, he and his function have been enshrouded, and give the average business man and the banker a chance to realize how tangible and how intensely practical a business institution chemistry really is, the solution of the problem which forms the basis of discussion here to-night will be found in understandable form in the practical working out of the business transactions of every day.

Of course, to the banker or to any other layman, chemistry is a bit difficult and mysterious and, until he is properly informed, rather apart from the business things of every day. But a little broadening of our general attitude toward the other fellow's specialty, a little fuller development of our powers of observation as we move through the business walks of life, and a little greater effort on our part to discover true relationships between apparently unrelated things, will do wonders toward creating in the world of business and finance a thorough respect for the intensely practical business possibilities which exist in the subject of chemistry.

CO-OPERATIVE METHODS IN DENMARK

In this direction Europe has gone much farther than we. A few years ago, I had occasion to make a rather thorough study of the cooperative institutions of Europe. Those of Denmark were found to be particularly interesting because of their high condition of development, and because of the extent to which the practical spirit of co-operation dominated the entire situation. The people of the country did not do much talking about getting together; they got together or at least were together.

This wonderful little population of less than 3,500,000 people, able in normal times to sell annually in London alone more than \$100,000,000 worth of goods, butter, pork, and cod, succeeded in demonstrating that they could trade in those commodities, too, and failed to give the slightest recognition to the entire co-operative plan, nor have they asked for either the government's aid nor even officially recognized the *SMITHS* scheme because it was a bad day.

So there, the chemical industry, as in most countries, is supposed to be with my assistance, raising its head and making

to only when normal methods of treatment fail to work, but rather an institution which is fundamental in even their simplest processes and in which the most modest farmer possesses vested rights.

As a result of intelligent investigation and analysis, the farmer knows his different soils as he knows his friends, and treats them with what impressed me as rather greater consideration. If one of his crops is not performing up to the rather arbitrary standard decided upon by the cooperative agricultural society of which he is a member, his attention is directed to that fact by the Society and the situation immediately is made the subject of investigation and treatment by the scientific establishment which is a serious part of the equipment of every well-regulated Danish organization of this class.

If the milk product which he delivers to his cooperative dairy is deficient in some important element, the matter comes to his attention at once. The formula upon which he has been feeding his cows is inspected and, if necessary, a change is made to suit the requirements of the particular case.

If the eggs which he delivers to his cooperative egg export society are not up to a proper standard, his hens, their housing, diet and treatment immediately are made the subject of investigation and again the remedy applied in whatever form is deemed most desirable, not by the farmer himself but by the scientific institution which speaks for the larger united interest of which the farmer is a part.

It is interesting, too, to learn that this service comes to the farmer not in a special or unusual way, but as one of the commonest details in the management of his farm, and practically without extra expense to him.

THE BAMBOO HAT OF THE PHILIPPINES

In the Philippine Islands a few years ago, an effort was made, and with only modified success, to manufacture and introduce into the United States a lady's summer hat made of the bamboo fibre. This is one of the most beautiful hard fibres in existence. It possesses every quality which reasonably could be demanded by the millinery trade for a reasonably cheap, light, wide-brimmed hat of fine finish and pleasing appearance. The bamboo is found in unlimited quantities in the Philippines, and the people are so expert in its treatment that a reasonably high-grade hat could be produced for not to exceed fifty or sixty cents. Such a hat, if it happened to be agreeable to the requirements of the American trade, should retail in the United States for from \$3 or \$4 upward.

At just about the time when this bamboo hat was beginning to promise commercial success in the United States, there was developed a demand for hats in colors. The Philippine hat situation, because it lacked facilities for the proper treatment of bamboo fibre with color, was entirely unable to respond. It happened that there was not in the Islands a color chemist. Experiments performed in the Government Bureau of Science and by private concerns were not satisfactory in their results. It was easy enough to color the fibre, but to treat it with fast colors without dulling the very desirable bamboo surface was found to be entirely beyond the equipment of the local situation.

As a result, this hat, basically probably the best in the world of its general class, is practically unknown in the United States, and the Philippine Islands have lost a commercial product which, if properly developed, would represent at least half a million dollars per year.

It would be possible to spend the entire evening in describing a layman's impressions concerning the importance of application of the powers of chemistry to needs of situations which have come under my somewhat casual observation in different parts of the world. The Philippines, China, Manchuria, Japan, India, Korea, Formosa, the countries of Europe, and even our own country, furnish countless illustrations upon either the

striking success with which chemistry has been applied to material problems, or the equally striking need for such application.

However, I shall assume that this feature of the situation is understood or, at least, is well outside my proper function, or, as described by a Chinese cook who practiced his peculiar brand of chemistry upon me for a number of years, it "no b'long my pigdin." Therefore, I shall proceed with my own subject—the banker.

BANKING NOT PARASITIC

The other day I heard a man, a banker, say that banking was unfortunate in that it was parasitic—that it lived upon the lives of others and created nothing of its own. Of course, he was wrong—altogether wrong—but, unfortunately, his remark only reflected an all too common estimate of the profession and an estimate for the existence of which bankers themselves are not a little to blame.

There is nothing in the nature of the bank, unless perhaps it be the banker, which should conduce to the creation of such an impression. If logically founded, properly equipped and intelligently directed, it can perform a business function in which the creative element figures as prominently as in production or manufacture or distribution.

The producer creates by transforming the riches of the earth into tangible and usable value, which he disposes of to his advantage. The manufacturer creates by changing the form and increasing the usefulness, and incidentally, the value of the product which he, in turn, disposes of, and to his advantage. The wholesaler and the retailer, without any essential change in the form of what comes from the manufacturer or the producer, sells the product, probably to a greater personal advantage than either of the others.

The banker, in a spirit differing in no essential from that which actuates the producer, the manufacturer, the wholesaler, and the retailer, comes into these processes of production, treatment and distribution even more frequently and certainly not less importantly than any of the others. Indeed, we might say that his is the most important function of all in the carrying on of these processes.

The bank makes it possible for the farmer—the miner—the lumberman—so to conduct their producing activities that if they proceed intelligently and consistently they always can find the financial means whereby operations may be continued and properly extended. In even a greater degree, the manufacturer, the wholesaler and the retailer have learned to depend upon the bank for assistance. The treatment of commercial paper whereby the immense commercial credit of the country may be utilized, transactions in connection with foreign trade, the conservation and investment of funds, the treatment of stocks, bonds and securities—all are functions performed by the bank and recognized by business men of all classes as vitally important in the nation's commercial life.

I have said that the true relation of banking to chemistry is found in the theory of practical every-day business. This theory must be taken seriously and literally by both banker and chemist if they are to derive the greatest benefit from each other and from business. Regardless of tradition and of possible personal inclination, they must descend from their respective pinnacles, whether of financial exclusiveness or scientific preoccupation, and get together in the intensely practical and really very comfortable atmosphere which the thoroughly up-to-date business man of to-day has created and prepared for them. If in doing this it becomes necessary to disturb an occasional delightful fiction, or to smash an occasional professional idol, it is believed that both may be done to the entire benefit of all concerned.

CHEMICAL PUBLICITY NECESSARY

Just how much of a transformation in the chemist and in chemical industries must take place in order to produce the de-

sired result, the chemist knows better than I. In any event, a substantial movement in the right direction has been made. A few more national Chemical Exposition meetings throughout the country—a considerably increased extension of chemical activities into the fields of business and finance—the dropping of the few unhelpful traditions with which the profession still is encumbered—and the position of chemistry in the industrial life of the nation will be established effectively and unmistakably.

If, in the interest of such an end, a suggestion from the financial viewpoint might be offered, it would be this—do not be so exclusive—do not allow your excellent arguments upon the business and financial merits of industrial chemistry to be wasted upon yourselves and each other. Concerning these merits, undoubtedly, you are fully informed and thoroughly convinced.

Hold your own Chemical Conventions and meetings and discussions, but do not stop with these. Get outside the chemical field into the conventions and meetings and discussions of business—of industry—of finance—and tell to them your story of the wonders of chemistry and prove its just claims upon their interest. Do not allow the consciousness of the merit of your proposition to blind you to the fact that to others who have not enjoyed such close contact with it as you have, it is not so clear. Realize, as you must, if the purpose you have in mind is to be accomplished, that the chemist as far as the business world is concerned, occupies the position of the business man who has something to sell, and in common with that business man, is expected to make the first move. Study the selling methods of the business man, and discover the importance which he attaches to the theory of following the line of least, instead of greatest, resistance, to results. Try to meet the business man and banker upon their grounds instead of upon yours, or at least, upon some pleasant, neutral ground in which their present indifference toward your interests will not exist. Try to get the banker's point of view—to see how natural it is for him to follow the line of least resistance in his investments—to give first consideration to the definite, tangible, well-developed, and thoroughly explained propositions which come to him through recognized channels rather than to the perhaps wholly meritorious investment, opportunity to which industrial chemistry rather casually calls his attention. If you direct a portion of your efforts into these channels, it is almost certain that before long, you will find that the present objectionable features in the attitude of the banker toward chemistry will have disappeared.

At this point, it may be stated, and it is hoped, with becoming modesty, that the case of the banker at least in this chemical connection, is not entirely without hope. After all, he is rather an intelligent sort, possesses a reasonable amount of nerve, is able to appreciate a good thing when he sees it and, in general, should constitute excellent raw material upon which to work.

He has no quarrel with the chemist, or with industrial chemistry. Indeed, he does not know either of them well enough for anything like that. We might say that he has not the pleasure of a quarreling acquaintance with them. He has not even been distinguished by being selected as the victim of the designs of the fortunately infrequent non-chemist, who with a promoting tendency, an elastic conscience, a vivid imagination, and a glib tongue, sometimes takes advantage of the credulity of the business man. He is virgin soil but, like most soil of that kind, requires considerable cultivation.

The tendencies of modern banking are well suited to the future development of a more active financial interest in the possibilities of industrial chemistry than has existed in the past. The most advanced school of banking thought, which has secured a large and rapidly increasing representation throughout the country, inclines strongly toward the theory of logical intimacy in the relationships of the banking function to business activities.

THE BANKER A BUSINESS MAN

The banker of to-day—or rather of to-morrow—because it is with him that we are concerned, as the world does move, must be, first of all, a business man. He must be able to get away from the fictions of former years, in which the banker, because of his intimate association with money, became obsessed with the idea that he and money were of the very essence of each other and that they mutually reflected each other's virtues for the general edification of mankind—he must be able to speak the language of business—to meet the business man upon business grounds—to discuss with him business problems, and, by his ability to provide the remedy frequently required, must even prove himself to be the better business man of the two.

He must realize that in the larger sense, the bank must depend upon business and not business upon the bank—that in the great mass of institutions indispensably connected with business activities, the bank is only one, and not by any means the most important one.

This banker of the future must enter into the business life of the community more extensively and more actively than in the past. He must so equip himself and his institution as to be fully prepared to perform whatever function may be submitted to him by the business of the situation of which he is a part. Upon business questions which come to him for treatment, his function must be that of a specialist—a sort of physician for the treatment of ills which affect the natural life of business.

It may seem that this is an unreasonably high standard of business excellence to be required of a man already deeply immersed in the purely financial details of his institution, but the developments of modern business leave no doubt as to the nature of its requirements upon him. The pace which he must observe is being set for him without any particular reference to his inclinations or to the habits which he may have formed. The developments of modern business demand certain classes of banking service, and also demand that in providing this service, the bank should perform up to a certain standard of excellence.

Naturally, a discussion at the present time upon two such nationally important subjects as chemistry and banking, particularly in relation with business, would include consideration of the greatest business enterprise in which this or any other nation ever has taken part—the war.

The theory that the true relation between chemistry and banking is found in business, finds considerable justification even in conditions existing before the war. When viewed in the light of the big, wonderful new things which war has brought into the world, the conclusion becomes irresistible. The indifference with which in former years private interest viewed national problems and difficulties finds but slight resemblance in the magnificent response which everywhere has been made to the nation's call.

And so, while in considering the business relationship between chemistry and banking, we should concede sufficiently to the advantages which will result to both from a proper getting-together, we must not lose sight of the fact that the big thing in this relationship will be the national interest. For us, there are just two worth while things in the world to-day—one, to win the war, the other, to protect American interests afterward. Naturally, winning the war comes first, but nevertheless, to that end should be determined, and upon the understanding that wars are to be won principally that nations may live in greater peace and security and in prosperity afterward.

We must realize that the financial and industrial life of war must not control the international relations of the future. We must not forget that the business strength of commercial countries of the world is based upon a constitution which will endure to the end of time—and that this struggle will be taken as soon as the day when peace is declared, and long afterwards, than before—and that if it is not so, we must be prepared to protect our own interests in peace no less strenuously than we now protect them in war.

ORIGINAL PAPERS

THE DEPOSITION OF SILVER FILMS ON GLASS¹

BY ALEXANDER SILVERMAN AND RAYMOND M. HOWE

The purpose of the investigation was threefold: to produce the best mirrors possible, with the highest possible percentage deposition, and at room temperature, if possible. The work naturally divides itself into two parts. In the first part mirrors were studied from a qualitative standpoint. In the second part the most satisfactory processes were studied quantitatively.

PART I—QUALITATIVE

At first the qualitative results obtained in a previous investigation² were duplicated and the most promising methods studied more thoroughly. Methods involving the use of sugars, tartrates and formaldehyde as reducing agents were included. Accordingly, molar solutions were made of potassium tartrate, tartaric acid, milk sugar and cane sugar. A 0.2 molar solution of silver was made by nearly dissolving the ammonia precipitate in AgNO_3 solution, by the addition of more ammonium hydroxide, and diluting with water to the required volume. The formaldehyde used was a 40 per cent solution.

The volumes given in the tables were used and in each case enough water was added to make a total volume of 20 cc. This made a convenient total for test-tube mirrors.

SERIES I (Nos. 1-12) involved the use of potassium tartrate as a reducing agent. It shows very clearly

Assumptions regarding the influence of concentration were verified. The silver nitrate concentration which gave the best results was at least 0.15 molar.

When the concentration of the tartaric acid was as high as 0.2 molar no mirrors resulted. When of 0.1 molar concentration no mirrors resulted with silver solutions which were of less than 0.15 molar concentration. The stronger solutions of tartaric acid gave white precipitates which sometimes redissolved. With tartaric acid solution of 0.025 molar concentration and the silver nitrate 0.15 to 0.2 molar concentration the best mirrors resulted. More silver nitrate than this was unnecessary—less tartaric acid was insufficient for a satisfactory reaction.

In general, the silver nitrate concentrations which gave the best results were greater than 0.15 molar. The concentration of the reducing agent had to be less than 0.1 molar under the conditions of experiment.

SERIES III (Nos. 25-36)—The series in which milk sugar was used as the reducing agent was extremely gratifying. The solution when heated to about 80°-85° C. turned black and then the mirror began to form. This formation was uniform and gradual and did not tend to deposit in spots as did many of the other mirrors. The mirrors formed whether the silver solution was 0.2 molar or only 0.015 molar concentration. The 0.2 molar solution was stronger than necessary but gave good results. The 0.015 molar solution was not strong enough to produce a mirror of desirable thickness. All intermediate concentrations gave good

RESULTS WITH VARIOUS REDUCING AGENTS

SERIES I—TEMP. 70° C. Reducing Agent: Potassium Tartrate(a)					SERIES II—TEMP. 70° C. Reducing Agent: Tartaric Acid (a)					SERIES III—TEMP. 70° C. Reducing Agent: Milk Sugar (a)					SERIES IV—TEMP. 80 to 85° C. Reducing Agent: Cane Sugar (a)					SERIES V Reducing Agent: 40% Formaldehyde				
No.	AgNO ₃ Red. Sol. (b)	AgNO ₃ Red. Cc.	MIRROR FORMED		No.	AgNO ₃ Red. Sol. (b)	AgNO ₃ Red. Cc.	MIRROR FORMED		No.	AgNO ₃ Red. Sol. (b)	AgNO ₃ Red. Cc.	MIRROR FORMED		No.	AgNO ₃ Red. Sol. (b)	AgNO ₃ Red. Cc.	MIRROR FORMED		No.	AgNO ₃ Red. Sol. (b)	AgNO ₃ Red. Cc.	MIRROR FORMED	
1	5	2	Fair		13	5	2	None		25	5	2	Fine		37	2.5	2	Fine		52	22	5	4	Poor
2	10	2	Fair		14	10	2	None		26	10	2	Fine		38	5.0	2	Fine		53	22	3	4	Poor
3	15	2	Fair		15	15	2	Good		27	15	2	Fine		39	10.0	2	Fine		54	22	20	4	Better
4	5	4	Poor		16	5	4	None		28	5	4	Fine		40	15.0	2	Fine		55	22	5	2	Poor
5	10	4	Poor		17	10	4	None		29	10	4	Fine		41	2.5	1	Fine						
6	15	4	Poor		18	15	4	None		30	15	4	Fine		42	5.0	1	Fine		56	10	10	2	Poor
7	5	6	Poor		19	5	6	None		31	5	6	Fine		43	10.0	1	Fine		57	10	20	2	Better
8	10	6	Poor		20	10	6	None		32	10	6	Fine		44	15.0	1	Fine		58	10	5	1	Poor
9	15	6	Poor		21	15	6	None		33	10	6	Fine		45	2.5	3	Fine		59	10	10	1	Poor
10	5	1	Fair		22	19	1	Fine		34	15	6	Fine		46	5.0	3	Fine		60	10	20	1	Better
11	10	1	Fair		23	19	5	0.5	Fine	35	15	6	Fine		47	10.0	3	Fine		61	0	5	1	Poor
12	15	1	Good		24	20	1	drop	incomplete	36	2.5	4	Fine		48	15.0	3	Fine		62	0	10	1	Good
											2.5	2	Fine		49	1.5	1	Fine		63	0	20	1	Good
											3.5	2	Fine		50	1.5	2	Fine						
											4	Fine		51	1.5	3	Fine							

(a) Molar Solution. (b) M/5 Solution

the influence of concentration. The mirrors at the best were only fair.

The concentration of the potassium tartrate must be less than 0.1 molar. This concentration gives only fair mirrors. Where the concentration of the potassium tartrate is 0.05 molar better results are obtained.

The silver solution giving the best result had a concentration of 0.15 mole per liter. The temperature was 70° C.

SERIES II (Nos. 13-24)—Mirrors produced by means of tartaric acid were much better than those produced by potassium tartrate.

results. The sugar varied from 0.05 molar to 0.3 molar concentration and in each case the results were good.

The process was superior to that involving the use of tartrates as reducing agents. With tartrates the concentration of both the silver nitrate and the reducing agent had to be controlled carefully. With the milk sugar mirrors the only limit from a qualitative standpoint was that the concentration had to be sufficient to produce the mirror. Qualitatively there was danger of using too much of either ingredient: 0.025 molar concentration for the silver nitrate and the same for the milk sugar was sufficient in most cases.

SERIES IV (Nos. 37-51)—What was said of the milk sugar series was also true for cane sugar. Since

¹ Presented at the 55th Meeting of the American Chemical Society, September 10 to 13, 1917.

² Silverman and Neckerman, *Trans. Am. Chem. Soc.*, **37** (1915), 505.

this was cheaper and more easily obtained in the pure state, it was deemed advisable to use it rather than some more expensive material such as fruit sugar, milk sugar, honey, etc.

SERIES V (Nos. 52-63)—During the qualitative study described in an earlier paper, already referred to, some promising mirrors were obtained by using formaldehyde as a reducing agent. The authors realized that this method had never been successful. Liebig and others had used it for a while but were forced to abandon it because of the appearance of brown spots in the finished mirror. The same difficulties were encountered in this laboratory since the presentation of the earlier paper. The mirror would begin to form in spots which would grow until the surface was coated. These were undoubtedly responsible for the brown spots observed by Liebig. The resulting mirrors were of doubtful quality.

The tendency to form spots was greater in the summer than in the winter, so cold solutions were used in order to determine the influence, if any, of temperature. When ice-cold solutions were used the mirror formed was very good. The reaction proceeded much more slowly at the lower temperature and no difficulty was encountered with "crinkling." The silver in a simple silver-formaldehyde solution had to be of at least 0.1 molar concentration. At 0° C. the 0.1 molar silver solution gave good results. At room temperature a 0.2 molar solution was necessary. This also worked better at the lower temperature.

SERIES VI (Nos. 64-72)—It was evident from the action at 0° C. that the formaldehyde method only needed control. This had been secured to a certain

SERIES VI—EFFECT OF METHYL ALCOHOL
Reducing Agent 40% Formaldehyde

No.	M 5 AgNO ₃ Cc.	Reducing Agent Cc.	Methyl Alcohol Cc.	Mirror Formed
64	20	0.5	1	Fair
65	10	0.5	1	Fair
66	5	0.5	1	Fair
67	20	1.5	2	Good
68	20	1.0	2	Good
69	20	0.5	2	Poor
70	20	1.5	0.5	Poor
71	20	1.0	0.5	Fair
72	20	0.5	0.5	Very good

extent by means of lowering the temperature, an undesirable procedure. The alternative lay in controlling the action by chemical means.

Alcohol was found to be of value as a control agent. After several trials it was noted that a batch such as No. 72 would produce an excellent mirror in 30 seconds. Quantitative work showed that this method was too wasteful as it deposited only 3 to 5 per cent of the silver. Because of the short period of reaction, it was also concluded that this reaction was far from being controlled. However, this batch promised to be of value for small scale work, such as patching, or in cases where economy was not essential. The alcohol and silver solution were mixed thoroughly and then the formaldehyde was added, the whole being mixed by shaking as quickly as possible.

In this work the importance of concentration has been shown, as with the tartrates. The possibility of control is evident when alcohol is used with formalde-

hyde. For this reason very dilute solutions were employed in hope of being able to control them.

PART II—QUANTITATIVE

The solutions used in this part were of the following concentrations: 0.2 molar silver, 1.0 molar cane sugar, 0.8 per cent formaldehyde.

In each case, as before, enough water was added to make the total batch up to 20 cc.

SERIES VII (101-104)—The action of very dilute formaldehyde was tried on a silver solution corresponding to 0.05 molar¹ concentration. The action was allowed to proceed until the mirror "fogged" or

SERIES VII—PER CENT SILVER DEPOSITED
5 Cc. M 5 AgNO₃ Solution Used in Each Experiment

No.	Formaldehyde Cc. 0.8%	PER CENT SILVER DEPOSITED	Time Min.	MIRROR FORMED
101	4	15.6	16	Poor
102	3	18.2	18	Poor
103	2	21.1	20	Poor
104	1	34.2	120	Poor

"crinkled." This showed very clearly that the formaldehyde should be kept as dilute as possible. In the first place, dilution allowed the reaction to extend over a longer period of time. This was shown to be favorable to the formation of good mirrors when cold solutions were used. With ice-cold solutions, if other conditions were the same, the reaction took place more slowly than at room temperature and better mirrors resulted. By using dilute formaldehyde solutions not only better mirrors resulted but also a larger proportion of the silver was deposited as a mirror.

Unfortunately, the concentration of the formaldehyde is not the only controlling factor. Even mirror No. 104, which was produced under favorable concentration conditions, still had the brown spots and was poor qualitatively.

SERIES VIII (Nos. 105-126)—In marked contrast to the formation of the formaldehyde mirrors were those produced by the hot sugar processes. Under uniform temperature conditions no one place could be considered the starting point for the development of these mirrors; they seemed to form simultaneously over the entire area. Because of this marked regularity it was decided to study the effect of sugar on the production of formaldehyde mirrors.

From a qualitative standpoint its influence was the same as when used in the hot processes. The silversing solution colored somewhat and then the entire mirror began to form. When sufficient sugar was used there was no sign of spots. With these sugar-formaldehyde mirrors it seemed desirable to have at least 5 cc. of the sugar solution present in order to secure silversing solution in order to secure the desired amount. Smaller amounts than this did not result in sufficient increase of deposition so as to warrant the risk of losing homogeneity.

With at least 5 cc. of sugar solution present there was a wide possible range of variation of the formaldehyde concentration. As much as 4 cc. of the dilute formaldehyde gave good results in the presence of 1 cc. of sugar solution. Without sugar the quantity of formaldehyde required for silversing and only a small

¹ Concentration based on total quantity of liquid in test tube.

SERIES VIII (All Mirrors Fair)										SERIES IX (All Mirrors of Very Poor Quality)										SERIES X 5 Cc. M/5 AgNO ₃ Solution in Each Experiment 2 Cc. 0.8% Formaldehyde in Each Experiment																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																										
0.8%					SILVER					80% 0.8%					SILVER					5 Cc. M/5 AgNO ₃ Solution in Each Experiment					2 Cc. 0.8% Formaldehyde in Each Experiment																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																					
No.	Sol.	Sugar	Formaldehyde	Weight	Per cent	Time in Min.	No.	Sol.	Sugar	Formaldehyde	Weight	Per cent	Time in Min.	No.	Sol.	Sugar	Formaldehyde	Weight	Per cent	Time in Min.	No.	Sol.	Sugar	Formaldehyde	Weight	Per cent	Time in Min.	No.	Sol.	Sugar	Formaldehyde	Weight	Per cent	Time in Min.																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																												
100	5	3	2	0.0059	5.5	40	127	5	3	2	0.0175	16.2	8.5	2	0.0150	13.9	100	152	3	3	0.0175	16.2	8.5	2	0.0150	13.9	100	157	3	2	0.0111	10.3	150																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																																													
101	5	3	2	0.0073	6.8	40	128	5	3	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2	0.0212	19.6	6.8	2

fraction of the silver was deposited as mirror. There appeared to be a limit to the silver which could be deposited in the presence of sugar. As the sugar content decreased, the silver deposit increased until a certain concentration of the sugar was approached (0.05 molar). Further dilution resulted in but slight increase in deposition.

The effect of temperature changes up to 30° C., which was taken as the limit for room temperature, was not material.

With respect to the presence of sugar in the formation of mirrors by the use of formaldehyde the following conclusions were drawn:

- (1) A small amount of sugar reduced the deposition efficiency of the process.
- (2) It made the deposition of uniform formaldehyde mirrors possible.
- (3) The effect of temperature changes, previously so serious, was overcome.
- (4) Wider variations of the formaldehyde content were permissible.

These mirrors were all fair.

SERIES IX (Nos. 127-151)—In spite of the fact that deposition had been controlled to some extent the work was not considered complete. The process was still too inefficient. Since alcohol had been used to control the action of formaldehyde it was again tried with dilute solutions. The resulting mirrors were of very poor quality but the deposition efficiency was high.

The following facts were deduced from the results of this series:

- (1) The importance of the silver concentration was pronounced. In the presence of sugar, decreasing concentrations of silver give slightly higher deposition percentages. This is true of mirrors in which alcohol is used instead of sugar, but to a higher degree.
- (2) Alcohol is not as good a retarding agent as sugar. This is shown by the action of the formaldehyde: 4 cc. of formaldehyde solution in the presence of a small amount of sugar gave good results. Here the same amount yields undesirable results, both from the qualitative and quantitative standpoint.
- (3) More silver is deposited in the presence of alcohol than in the presence of sugar.

SERIES X (Nos. 152-167)—This series was run in hopes of securing a good mirror through the presence of sugar, and a high percentage of deposition by addition of alcohol. The mirrors secured were excellent. The percentage of silver deposited was higher than in the case of alcohol alone. The sugar lowered the rate of reduction and gave the mirror a much longer time to form.

Except in the case of very small amounts of sugar no "fogging" resulted at all. The mirrors were thicker than necessary.

LOWER CONCENTRATION OF SILVER: FORMALDEHYDE VARIED 3 Cc. M/5 AgNO₃ Solution Used in Each Experiment

SERIES XI (2 Cc. 0.8% HCHO)										SERIES XII (3 Cc. 0.8% HCHO)													
Sol.		Sugar		Formaldehyde		SILVER		Time		Sol.		Sugar		Formaldehyde		SILVER		Time					
Cc.		Cc.		Cc.		Gram		Min.		Cc.		Cc.		Cc.		Gram		Min.					
168	1.5	1.5	0.0089	13.7	50	187	1.5	1.5	0.0103	15.9	40	169	1.5	1.0	0.0113	17.4	50	188	1.5	1.0	0.0114	17.6	40
170	1.5	0.5	0.0148	22.8	50	189	1.5	0.5	0.0130	20.1	40	171	1.0	1.5	0.0112	17.3	50	190	1.0	1.5	0.0114	17.6	40
172	1.0	1.0	0.0130	20.1	50	191	1.0	1.0	0.0120	18.3	40	173	1.0	0.5	0.0134	20.7	50	192	1.0	0.5	0.0158	24.4	40
174	0.5	1.5	0.0100	15.4	50	193	0.5	1.5	0.0121	18.7	40	175	0.5	1.0	0.0104	16.0	50	194	0.5	1.0	0.0128	19.8	40
176	0.5	0.5	0.0125	19.3	50	195	0.5	0.5	0.0161	24.8	40	177	1.5	1.5	0.0098	15.1	45	196	1.5	1.5	0.0133	20.6	40
178	1.5	1.0	0.0102	15.7	45	197	1.5	1.0	0.0125	19.3	40	179	1.5	0.5	0.0130	20.1	45	198	1.5	0.5	0.0126	19.5	35
180	1.0	1.5	0.0114	17.6	45	199	1.0	1.5	0.0095	14.6	40	181	1.0	1.0	0.0112	17.3	45	200	1.0	1.0	0.0114	17.6	40
182	1.0	0.5	0.0124	19.1	45	201	1.0	0.5	0.0144	22.2	35	183	0.5	1.5	0.0115	17.45	40	202	0.5	1.5	0.0138	12.8	40
184	0.5	1.5	0.0126	19.5	45	203	0.5	1.5	0.0141	22.5	35	185	0.5	0.5	0.0136	21.0	45	204	0.5	0.5	0.0130	20.1	35

SERIES XIII (Nos. 105-107)—Here 4 cc. of formaldehyde were used with large amounts of sugar. The mirrors were good but not sufficient advantage was gained to warrant the use of more formaldehyde.

EXPERIMENTS WITH DIFFERENT ALCOHOLS
3 Cc. M/5 AgNO₃ Solution Used in Each Experiment

Series and No.	ALCOHOL	Molar 0.8% Cane Sugar			SILVER DEPOSITED		Time in min.
		Used Cc.	Formaldehyde Cc.	Weight Cc.	Gram	Per cent	
XIII 105	Methyl. 80%.....	1.5	1.5	4	0.0087	13.6	40
106	1.0	1.5	4	0.0094	14.5	40
107	0.5	1.5	4	0.0100	15.4	40
XIV 108	Ethyl.....	1.0	0.0	2	0.0189	17.5	40
109	1.0	1.0	2	0.0218	20.2	120
110	Propyl.....	1.0	0.0	2	0.0194	17.9	35
111	1.0	1.0	2	0.0211	19.5	120
112	Amyl.....	1.0	0.0	2	0.0157	14.5	33
113	1.0	1.0	2	0.0194	17.9	104
114	Ethylene Glycol...	1.0	0.0	2	0.0176	16.3	30
115	1.0	1.0	2	0.0207	19.1	94

SERIES XIV (Nos. 108-115)—Other alcohols were introduced in the place of methyl alcohol. Apparently they all work the same. It is of interest to note that here there was also an increase in deposit where sugar was used in connection with the various alcohols. The time of reaction was increased so much that a higher deposit resulted, with a mixture of sugar and alcohol, than with either when used alone with formaldehyde.

GENERAL CONCLUSIONS

In hot processes cane sugar is the most satisfactory reducing agent. Other sugars give good results but no better than cane sugar. The tartrates are not as satisfactory as the sugars.

A rapid cold process was developed. It requires a batch of the following proportions—used as indicated: 20 cc. of 0.2 molar silver nitrate solution are mixed with 0.5 cc. of 80 per cent methyl alcohol; to this 0.5 cc. of 40 per cent formaldehyde is added and the whole mixed thoroughly.

A slow cold process was developed which is based upon the following principles:

(1) Low concentration of the reducing agent (formaldehyde) gives the best results. This helps lengthen the time of reaction.

(2) Low concentration of silver nitrate gives high deposition percentages.

(3) Sugar added to the solution in sufficient amounts controls the action of the formaldehyde in such a way as to produce even mirrors. It also lengthens the time of action.

(4) Alcohol added to the solution results in a high deposition efficiency.

By grouping these principles the following batch results:

- 16.5 cc. of 0.037 molar silver solution
- 1.0 cc. of 1.000 molar cane sugar solution
- 0.5 cc. of 80 per cent methyl alcohol
- 2.0 cc. of 0.8 per cent formaldehyde solution.
- Total, 20 cc.

After 40 minutes, over 20 per cent of the total silver deposits as mirror in each case, and if left longer a heavier mirror results. The cost of materials is not over one cent per square foot, or eleven cents per square meter of surface silvered. The mirror is very firmly attached to the glass for two reasons:

(1) The temperature of the glass and solution is the

same: as a result deposition is more uniform than that which occurs at higher, more difficultly controllable temperatures.

(2) Since deposition takes place at room temperature, differences in coefficient of expansion do not cause the newly formed mirror to be loosened from the glass as may be the case where hot processes are employed.

UNIVERSITY OF PITTSBURGH
PITTSBURGH, PENNSYLVANIA

THE RECOVERY OF WATER-SOLUBLE POTASH AS A BY-PRODUCT IN THE CEMENT INDUSTRY¹

By WILLIAM H. ROSS AND ALBERT R. MERZ

When a potash silicate like feldspar is ignited at a sufficiently high temperature, sintering and finally fusion take place without any change in the chemical composition of the mineral. With the addition of lime, however, an entirely different result is obtained. A calcium aluminium silicate is then formed and the potash is set free or volatilized in amount depending on the proportion of lime taken, on the temperature and the time of ignition. In the case of small scale experiments it has been shown that at a temperature and with a proportion of lime corresponding to that used in Portland cement manufacture complete volatilization of the potash may be brought about on igniting for about one hour.

Since potash silicates occur in the raw materials used in cement manufacture it is to be expected from these observations that loss of potash will take place in the burning of cement. That some potash is lost has long been known, but there seems to have been no quantitative data on the subject previous to the results obtained by R. K. Meade in 1905 from analyses of the raw material fed into the kiln, the clinkers coming out and the coal used as fuel. The results of three separate tests with the material from one plant showed that the potash volatilized varied from 46 to 52 per cent of the total present.

PRELIMINARY EXPERIMENTS

With a view to securing more definite information in this direction, an investigation was undertaken over five years ago to ascertain the percentage of potash occurring in the raw materials used in the different cement plants of this country and also the percentage of the total potash that is volatilized in each case. Representative samples of raw mix and ground clinker were collected from the different cement plants in the United States and in Canada with a view to analyzing each sample for potash. With the data thus obtained and knowing the ratio between the raw mix and the cement produced, and the output of the latter, it was thought possible to calculate for each plant the approximate quantity of potash that escapes from the kilns. After partly completing this work it had to be abandoned for a time. A few months ago the problem was again taken up and entirely new samples were collected. The work has now been completed and the results obtained form the subject-matter of this paper.

¹ Presented before the Portland Cement Division at the Fifth Meeting of the American Chemical Society, Boston, September 26 to 28, 1916.

ANALYSES OF SAMPLES

The total number of cement mills from which samples were received number 113, of which 104 are in this country and 9 in Canada. The number of plants in this country which supplied samples is only four less than the total number which operated in 1915, or nine less than the total number said to be in operation in 1916.

The results obtained in the analyses of the samples show that the potash occurring in the raw mix used by the different plants from which samples were received varies from 0.20 to 1.16 per cent. The raw materials used in the mills of the Universal Portland Cement Company, and consisting of blast furnace slag and a high-grade limestone, contain considerably less potash than the average for the other cement plants of the country.

In a communication received from the manager of one of the large cement plants in the Lehigh Valley district, the statement was made that the raw cement material used in this district contains less than 0.3 per cent. We find, however, that in no case does the raw mix used in the plants of this district run as low as 0.3 per cent, but that some of these plants make use of cement material almost as rich in potash as may be found in any cement plant in the country. In general, it may be stated, however, that high potash-bearing raw material is not characteristic of any particular part of the country.

Knowing the percentage of potash in the raw mix for each individual plant the total potash in the daily run of raw mix is readily calculated. In a corresponding way is obtained the potash in the daily production of cement. The difference between the two values gives the amount of potash volatilized. This is found to vary in different plants from 0.35 to 5.34 lbs. of K_2O per barrel of cement produced. The average for all the plants, when consideration is taken of the variation in output of cement of the different plants, amounts to 1.94 lbs. per barrel of cement.

Omitting the plants of the Universal Portland Cement Company, the corresponding average for the remainder of the 99 plants of this country from which samples were received amounts to 2.09 lbs. The average for the nine Canadian plants is 1.95 lbs.

POTASH ESCAPING FROM CEMENT PLANTS

If the average annual production of Portland cement in this country be now taken in round numbers as 90,000,000 bbls., and if the same average conditions be assumed to prevail in the few plants from which no samples were received as was found on an average for all other plants, then the total potash (K_2O) escaping from all the cement plants in the United States as at present operated will amount to about 87,000 tons annually.

The process which at present is most generally considered in connection with the recovery of the potash that escapes from cement kilns is that of electrical precipitation. With present installations a recovery of approximately 99 per cent of the dust has been secured. It happens, however, that the finest portion of the dust escaping from any cement plant

contains relatively the highest percentage of potash and a 99 per cent recovery of the dust therefore represents a somewhat less efficient recovery of the potash.

In the plant of the Security Cement and Lime Company, where the Cottrell process has been installed for collecting the dust, it is estimated that the potash recovered amounts to 90 per cent of the total volatilized. If this value be accepted as the efficiency of recovery of the potash in the most economic installations, then the total recoverable potash in the cement plants of this country under present working conditions amounts to about 78,000 tons annually.

The potassium compounds occurring in cement dust may be divided into three groups as follows: (1) Those which are readily soluble in water; (2) those which are slowly soluble; and (3) those which are insoluble.

The insoluble potash represents the combinations occurring in the original silicates of the raw mix which is carried over mechanically in the dust before being subjected to a sufficiently high temperature to bring about decomposition. The form of combination which is slowly soluble in water is supposed to be due to a recombination of the volatilized potash with the silicates in the dust. In some plants where coal is used for burning, the extent to which the potash occurs in this "recombined" form may be considerable, while in certain other plants where oil is used for fuel this combination of the potash is present in comparatively small amount. Thus, in an analysis of a sample of dust from the oil-fired plant of the Riverside Portland Cement Company, the acid-insoluble potash was found to amount to 1.9 per cent of the total, the slowly soluble potash to 6.5 per cent and the soluble potash to 91.6 per cent. The corresponding values obtained for the dust from the plant of the Security Cement and Lime Company, where coal is used for burning, amounted, respectively, to 4.4, 36.0 and 59.6 per cent. In the case of the dust from the Cementon plant of the Alpha Portland Cement Company, the proportion of slowly soluble potash is still greater and is sufficient to greatly depreciate the commercial value of the dust as a fertilizer.

BUREAU OF SOILS EXPERIMENTS

In experiments made some time ago in the Bureau of Soils, it was shown that the greater part of the potash in feldspar may be made to pass into solution by digesting with lime under a steam pressure of 10 to 15 atmospheres. In cement dust, as it escapes from the kilns, the slowly soluble and insoluble potash is already associated with a considerable percentage of free lime, and it was consequently thought that the greater part of these constituents might be recovered in readily soluble form by digesting the dust with steam alone under pressure. This has been found to be the case, and with dust from the Security and Cementon plants it has been found possible to recover in this way, in soluble form and with little increase in pressure, about 95 per cent of the total potash present.

In carrying out these experiments 20 g. of the dust were placed in a small autoclave provided with a steam gauge for indicating pressure. Water was

added to the dust in the autoclave and the latter then heated so as quickly to give the desired pressure. This pressure was then maintained constant for varying lengths of time in the different experiments. The amount of water added was just sufficient to give a paste with the dust at the end of each treatment.

Digesting beyond one-half hour was found to have little effect in increasing the amount of potash made soluble. Thus, after treating at 50 lbs. pressure for one-half hour the water-soluble potash in the Security dust amounted to 82 per cent of the total and only increased to 91 per cent in 8 hours. At 100 lbs. pressure 90 per cent of the total became soluble in one-half hour and upwards of 95 per cent in 8 hours.

With the Cementon dust similar results were obtained. With this dust, though, it was noticed that prolonged treatment seemed to decrease rather than increase the solubility of the potash. Thus, at 50 lbs. pressure, 81 per cent of the total potash present became soluble in one-half hour, 87 per cent in 4 hours and 82 per cent in 16 hours. At 100 lbs. pressure a maximum solubility of 93 per cent was obtained in 2 hours. Experiments at 150 and 200 lbs. pressure, which are expected to yield still higher results, are now in progress.

RECOVERABLE POTASH

This method of treating cement dust should be applicable whether it is desired simply to increase the soluble potash in the dust or to bring about a subsequent separation of the potash salts present. It has not been demonstrated that the method would prove as efficient under commercial conditions as in the laboratory tests, but if such would prove to be the case, then the average percentage of soluble potash that could be obtained in the dust from different plants should amount to from 90 to 95 per cent of the total. Assuming then that it would be practical to recover or render available, say, 90 per cent of the potash in the recoverable dust of cement plants, then the recoverable and available potash escaping from the cement plants of this country amounts approximately to 70,000 tons annually. If, however, the dust from all plants losing less than 1 lb. of potash per barrel of cement be considered as too low-grade for use as a source of fertilizer material and is omitted in the calculations, then the value for the available recoverable potash in the cement industry of this country will be in the neighborhood of about 67,000 tons annually.

This estimate is based on the amount of potash lost under present working conditions. It is possible, however, to bring about an increase in the amount lost by two different ways:

(1) By increasing the percentage of potash in the raw mix.

(2) By increasing by chemical or other means, the percentage of potash volatilized.

At the plant of the Riverside Portland Cement Company, the potash in the raw mix has been increased from 0.2 per cent to as much as 0.8 per cent. This was done by utilizing that portion of the clay deposit highest in potash and by enriching the raw mix with the addition of feldspar. The proportion

of silica to alumina in feldspar is, however, higher than in the argillaceous material ordinarily used in cement manufacture, and an extended use of this mineral by itself would therefore not be practical in all plants, particularly in those plants where a siliceous cement is already obtained. By use of the proper proportion of iron ore, however, in connection with the feldspar, the latter may then be used even in plants where siliceous cement is ordinarily produced, while in the case of plants producing aluminiferous cement a certain proportion of feldspar should be possible without the addition of any oxide of iron.

At the plant of the Security Cement and Lime Company, an increase in the potash volatilized has been brought about by use of ordinary salt. This is effected by adding the salt in the solid state both to the raw mix and to the coal used for fuel. The quality of the resulting cement is in no sense impaired by the addition of the salt for it is found that the total alkalies in the clinker when salt is added are actually less than when no salt is added. By this treatment the percentage of volatilized potash which at this plant normally runs about 38 per cent is increased to about 65 per cent.

INCREASING PROPORTION OF POTASH VOLATILIZED

Other reagents may also be used for increasing the amount of potash carried over in the dust. Thus an ingenious method devised by the Riverside Portland Cement Company makes use of calcium fluoride for this purpose. Volatilization of the potash then takes place largely in the form of the fluoride and as it escapes from the kilns it becomes associated with the salts of calcium carried over mechanically in the dust. It thus happens that when the dust is leached with hot water for the separation of the potash the latter passes into solution as the sulfate or carbonate while the fluoride remains as insoluble calcium fluoride. On using the residue for cement material the same fluoride is fed into the furnace again and may thus be repeatedly used in bringing about increased volatilization of the potash. By this cyclic process the volatilization at this plant has been increased from 60 to 90 per cent.

An increase in the proportion of potash volatilized may also be brought about by increasing the temperature of burning. This is illustrated in the analysis of a number of samples furnished us by the Tidewater Portland Cement Company and which represented variations in burning from that which gave a very soft clinker to that sufficient to give a very hard clinker. The results showed that the proportion of potash volatilized in the different steps varied from 30 to 62 per cent.

According to the analysis of the representative samples sent us from the different plants of the company the proportion of potash volatilized in the different plants varied from about 25 to 48 per cent. This variation is too great to be attributed to differences in the temperature of burning alone, and it is probable that a number of factors are due to being about this result. The average for dry process plants amounts to 41 per cent, and for wet process plants to 46 per cent. Both averages are above the value for the ordinary

tilization of potash that normally prevailed at the plant of the Security Cement and Lime Company, but below the 65 per cent volatilization that has now been secured at this plant. If it be assumed that the last-mentioned percentage volatilization could be attained by chemical or other means in all plants where a lower volatilization normally prevails, then it may be estimated that the recoverable available potash in the cement plants of this country would be increased from 67,000 tons to about 100,000 tons annually. This estimate represents a recovery according to our analyses of only between 50 and 55 per cent of the total potash entering the kilns in the different plants. At the plant of the Security Cement and Lime Company, where no steps are yet taken to make soluble the slowly soluble potash, the percentage of available potash recovered is somewhat less than this, but, at the plant of the Riverside Portland Cement Company the recovery of soluble potash is already considerably greater. Improvements over present methods of recovering potash are to be expected and it would therefore seem that an estimated possible average recovery of about 50 per cent should not be considered excessive. Whether or not this percentage can be economically recovered in all plants remains to be determined.

It may also be pointed out that the weight that can be attached to these estimates is also dependent on the representative character of the samples analyzed. Analyses of a number of samples corresponding to those which we have analyzed, but collected from six to nine months previous to the time our samples were taken, have also been made by other chemists and particularly by the Western Precipitation Company. In every case in which the results were compared there was found to be an agreement within the limits of experimental error. It is, of course, recognized that the analysis of further samples collected from some other plants might not show the same close agreement, but from the observations which have been made it is thought that as a whole the results obtained are representative.

COLLECTION OF CEMENT FLUE DUST

Cement flue dust is now being collected by the Cottrell process of electrical precipitation at the plants of the Riverside Portland Cement Company and the Security Cement and Lime Company; at several plants of the Universal Portland Cement Company; and at the Cementon Plant of the Alpha Portland Cement Company. At the Riverside plant the dust is being used for the preparation of concentrated potash salts, while at the Security and Cementon plants it is disposed of directly for use as a fertilizer. The dust from the Universal plants, being too low grade to serve as a source of potash, is simply returned to the kilns for manufacture into cement. Installations of the Cottrell process are now being considered by a number of other cement companies and operations have already been started on the installations at the Coplay, Dexter and Ironton Portland Cement plants, and at the plant of the Buffalo Potash and Cement Corporation, where a commercial installation

has been erected for the recovery of potash from flue-dust by use of the latter in the manufacture of cement.

Wet processes for precipitating cement dust are now in operation or are being installed for one or more kilns at the plants of the California Portland Cement Company, the Santa Cruz Portland Cement Company, and the Sandusky Cement Company.

SUMMARY

The constituents of the dust in all cement plants are much the same but may vary greatly in relative proportion. In the case of freshly precipitated dust collected in the normal operation of a cement plant the soluble constituents consist for the most part of the sulfates, chlorides, sulfides and polysulfides of potash, soda and lime. Chlorides occur only in small amount. The percentages of sulfides and polysulfides in the dust from different plants may vary widely and in the case of dust from some oil- or gas-fired plants may be entirely absent. Free lime is found in all cement dust, and in the water extract of all samples analyzed, the basic radicles were found to be in excess. It follows, therefore, that the potash in the water extract of freshly collected flue dust will be present to a greater or less extent in the form of the hydroxide. As the dust becomes carbonated, either by chemical treatment or by exposure to the air, the hydroxides present will change to carbonates, and by interaction of the carbonates with calcium sulfate in the dust the water-soluble potash will be obtained principally in the form of the sulfate which is the form universally recognized as of most value for use as a fertilizer.

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

SOLVENT GASOLINE¹

By C. OLIN NORTH
Received July 2, 1917

The sudden jump in the price of gasoline last year was of prime importance to the automobile owner, but if anything it affected the rubber companies more. Because of their high cost, gasoline had replaced to a great extent all other solvents for use in rubber cements and doughs. A small rubber factory making 1500 tires a day will use approximately 12,000 gals. per month, while a large company will require close to 10,000 gals. per day. In 1915 a good grade of solvent gasoline could be procured at 15 to 18 cents per gal., but in 1916 it jumped to 26 to 30 cents per gal.

Solvent gasoline is customarily of 70 to 72° B_e. gravity, though for certain purposes 80° B_e is required. It must be readily volatile and must be free from kerosene tails. A comparison of its rate of evaporation with those of some common solvents is as follows, when 2 cc. of each liquid were allowed to evaporate from a metal surface 3 1/2 in. square, under similar conditions:

Benzol (60° B _e)		Solvent	Gasoline
Commercial	14 min.	Naphtha, 107 min.	80° B _e , ... 4 min.
Toluol	33 min.	Turpentine, 142 min.	70° B _e , ... 8 min.

Distillation tests on representative samples of the three grades of gasoline, viz., Motor, Solvent, and Paint & Varnish Makers' Naphtha, resulted as follows:

¹ Submitted as partial fulfillment of the requirements for the degree of Chemical Engineer, Carnegie Institute of Technology, Pittsburgh, Pa.

	Motor Naphtha	Solvent Naphtha	Paint & Varnish Makers' Naphtha
Sp. gr. at 15° C.....	0.716	0.697	0.746
Gravity.....	65.5° Bé.	70.9° Bé.	57.7° Bé.
Distillation began.....	45° C.	46° C.	123° C.
5% distills below.....	77.5	64	133
10% distills below.....	85	69	136
15% distills below.....	91	73	138
20% distills below.....	96.5	76	141
25% distills below.....	99	79	143
30% distills below.....	102	82	144
35% distills below.....	105.5	85	144
40% distills below.....	108	88	145
45% distills below.....	111	90	148
50% distills below.....	116	94	149
55% distills below.....	120.5	97	150
60% distills below.....	121	100	152
65% distills below.....	127	102	153
70% distills below.....	131.5	106	156
75% distills below.....	138	111	158
80% distills below.....	144	116	163
85% distills below.....	154	121	166
90% distills below.....	161.5	125	174
95% distills below.....	177	137	180
5% lost during distillation			

The experiments described below were performed at the chemical laboratory of the Republic Rubber Company, of Youngstown, Ohio, in the years 1915-1916, and were undertaken with a view to securing a good grade of solvent gasoline at a reasonable price by cracking heavy kerosene or other heavy oil. The method and apparatus finally developed cannot, in a strict sense of the word, be called original, since features were contained which might rightly be considered an infringement on certain well-known patents. However, the development took place in logical steps and I feel that the work was of value in that I attempted to embody in my procedure such points as I considered of prime importance in other processes, and to improve on them to the best of my ability.

As in the Burton process, the pressure within the apparatus was built up by heating a comparatively large volume of oil. In common with the Rittman process the cracking was accomplished in the gas phase. Condensation was effected under pressure and in the presence of the non-condensable gaseous products of the reaction.

THEORETICAL CONSIDERATIONS—In comparison with the benzene-toluene process, the production of gasoline is comparatively easy. Rittman¹ considers the order of hydrocarbon formation to be as follows:

Heavy Petroleum Hydrocarbons \rightleftharpoons Light Petroleum Hydrocarbons (saturated and unsaturated) \rightleftharpoons Cymene \rightleftharpoons Xylene \rightleftharpoons Toluene \rightleftharpoons Benzene \rightleftharpoons Naphthalene, Diphenyl, etc. \rightleftharpoons Anthracene \rightleftharpoons Carbon and Gas.

It is evident that the production of gasoline requires but one step.

The factors influencing any reaction in the vapor phase are: (1) Temperature, (2) Pressure, (3) Concentration, (4) Duration.

TEMPERATURE—Since all organic substances decompose on application of heat, it is self-evident that the higher the temperature the greater the degree of decomposition. Heavy molecules are more unstable than lighter ones of similar structure. This fact must be considered in making the proper choice of cracking temperature. Any oil or kerosene heavier than gasoline can be used as a raw material for the production of gasoline if the correct cracking conditions are observed.

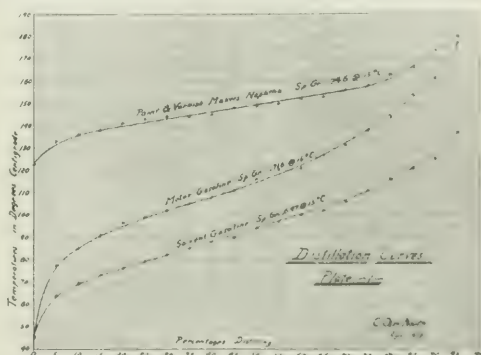
¹ THIS JOURNAL, 8 (1916), 331. Also Bureau of Mines Bulletin 114; Met. & Chem. Eng., March 1, 1916.

PRESSURE—The chief service of pressure is to produce saturated hydrocarbons. Heat breaks up the oil into saturated and unsaturated bodies, while pressure tends to increase the saturated at the expense of the unsaturated.

Unsaturated Hydrocarbons \rightleftharpoons Saturated Hydrocarbons.

Diminished pressure increases decomposition, but increased pressure works the other way. For example, diminished pressure favors the production of gas, while increased pressure aids in the formation of gasoline.

CONCENTRATION—The gases produced during cracking may be classed as condensable or non-condensable. In the first class may be placed gases condensing at, say, from 20° C. up (gasoline), and in the second such ones as hydrogen, methane, etc., which do not condense until very far below 20° C. These may be called fixed gases. It is quite in accordance with the law of mass action that the withdrawal, i. e., condensation of the condensable gases in the presence of the non-condensable, favors the formation of the condensable hydrocarbons. Therefore condensation should be effected



under pressure and in the presence of the non-condensable gaseous products of the cracking reaction.

DURATION—The time factor is intimately related to the temperature and pressure employed. Thus a higher temperature requires a shorter time for equilibrium to be established. It may also be regulated by

- 1—Varying the length of the cracker,
- 2—Introducing a catalyzer,
- 3—Changing the rate of oil supply.

In Rittman's process this is accomplished by varying the feed. But with my apparatus it was effected by regulating the fires under the kettle. I also found it advantageous to tilt the cracker tube about three-quarters of an inch at a horizontal angle of about 10° to a right angle. These served to prolong the sojourn of the gases in the reaction zone.

APPARATUS

The apparatus used in this study was simple, and only such parts were contained as might be found in any well-equipped plant or workshop.

CRACKER—The original kettle was a small dental appliance of one inch capacity. The volume of oil

contained proved to be entirely insufficient to get up proper pressure within the apparatus. For the next trial a 12-in. piece of double extra heavy wrought-iron pipe, 6 in. diameter, was capped at both ends, but because of poor threading the outfit leaked like a sieve when heated up, and was discarded.

Consequently it was decided to oxyacetylene weld the heads into the pipe, and a very satisfactory kettle was secured in this manner from a 12 in. section of double extra heavy wrought iron pipe 6 in. diameter. The capacity of this kettle was 340 cu. in., or 1.47 gal., amounting to 5550 cc. This allowed the use of a comparatively large quantity of oil, and insured a wider range of pressure. The kettle was carried by an angle iron stand built in such a way as to support the fire brick which surrounded it. A burner rack carrying the blast lamps was placed at proper height underneath. The fuel used was natural gas.

The whole was encased in fire brick arranged so that the flame from the burners on its way to the stack

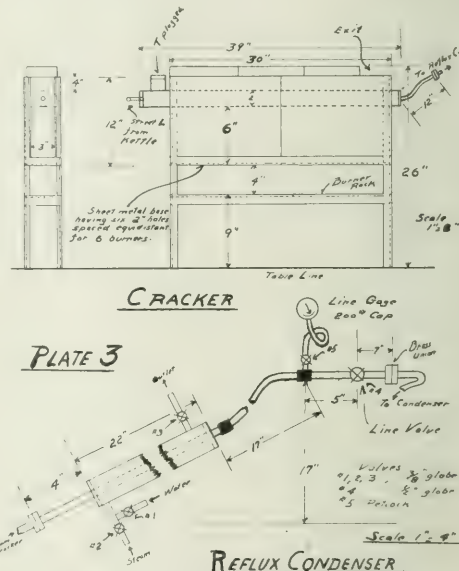
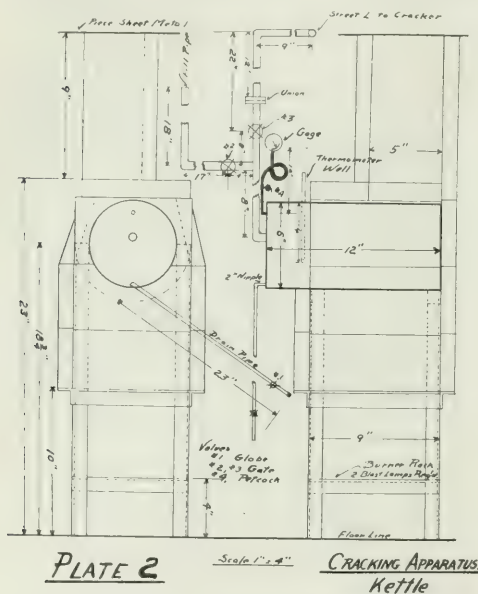
only in the kettle but in the cracking zone and reflux condenser as well.

(3) A $\frac{3}{8}$ -in. pipe fitted with a globe valve was placed as low down as possible on the end of the kettle, which was tilted slightly so as to allow almost complete draining.

(4) Connection was made with the cracker through a 38-in. length of $\frac{1}{2}$ -in. heavy, wrought-iron pipe. This was broken 12 in. from the top at a union, below which was placed a gate valve. The filling pipe, which also had a gate valve, was teed into the riser pipe 8 in. above the center of the kettle. The fill pipe was arranged in such a way that it could have been easily connected to a pump, which would have made the apparatus suitable for continuous running.

CRACKER—The cracking tube consisted of a 39-in. piece of double, extra heavy, wrought-iron pipe, 2 in. in diameter, plugged and tapped at both ends. A plugged tee was placed on the end next the kettle for the removal of any carbon.

A 30-in. section of the tube was encased in fire



completely surrounded the kettle. The bricks were cemented together with a mixture of fire clay and sodium silicate, which was found to set quite hard and to have very satisfactory heat-resisting properties.

The fittings were as follows:

(1) A pressure gauge of 200 lb. capacity connected to the kettle by a piece of $\frac{3}{8}$ in. pipe in which a small pet cock was placed for the release of air during filling.

(2) A thermometer well, which proved to be of no advantage except in the beginning of the run, since near the end of the experiment the kettle was often red hot. It should be mentioned here that the lack of a suitable pyrometer proved a decided handicap. Temperatures should have been accurately determined not

brick, supported by an angle iron rack which also carried a shelf upon which the burners (5 Bunsens and 1 Meker) were placed. The cracking zone found most satisfactory was a 12-in. section of the pipe, 6 in. from the kettle end of the cracking furnace, heated to a just visible red heat (525° C.).

REFLUX CONDENSER—For a reflux condenser a section of $\frac{1}{2}$ -in. wrought-iron pipe was jacketed by a 2-in. pipe 22 in. in length, which was bushed, plugged, and tapped at both ends. The jacket was fitted with both steam and water connections.

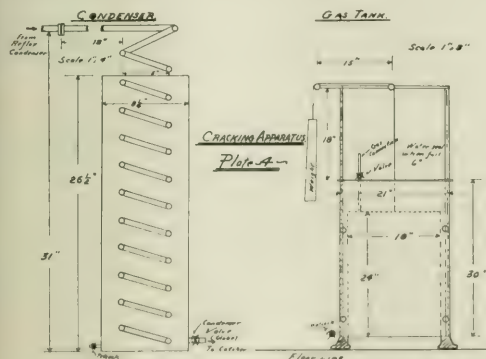
By changing the temperature of the reflux condenser the degree of cracking could be varied considerably. Thus, if kept very cold, the oil was continually returned

to the cracking zone and only gas allowed to escape. But if heated by 10 lbs. of steam (116° C.) a good yield of gasoline was obtained with comparatively low pressure (100 to 125 lbs.).

PIPING—The reflux condenser was connected through a union to the riser pipe from the cracker. Both this union and the one immediately above the kettle gave considerable trouble because of leakage. Practically all the difficulty was removed by the use of two copper gaskets in each one. On the upper side of the reflux condenser the union was of the sleeve type and gave no trouble. Between the reflux condenser and the condenser proper were placed the line gauge (200 lb. limit) fitted with a pet cock so that it could be cut out when desired, and the main line valve, a 1/2-in. globe valve. Beyond it was a ground joint brass union having one side brazed to brass pipe, which was in turn brazed to the condenser proper.

A reducing valve was tried in place of the main line 1/2-in. globe valve just before the condenser, but because of small particles of iron which were carried up it could not close properly and was therefore discarded.

CONDENSER—The first condenser tried was an old block tin coil 20 ft. in length and 3/8-in. internal diame-



ter. Because of its low strength, condensation under pressure could not be attempted and it was replaced by a copper coil which had been tested up to 175 lbs. This coil was part of an old instantaneous water heater and consisted of 15 ft. of 1/16-in. copper tubing 5/8-in. internal diameter, with coils 5 in. in diameter. The lower end of the coil was brazed to a piece of 1/2-in. brass piping which carried a 1/2-in. globe valve. This pipe led to the catcher. The coil was set in a heavy galvanized iron tank 8 1/2 in. in diameter and 26 1/2 in. high, open at the top but provided with a pet cock at the base for draining. Since rapid cooling was found necessary, the tank was packed with ice and salt before each run and the temperature kept around 5 to 10° C.

The catcher was a 6-liter bottle fitted with a siphon and gas outlet. The gas on leaving the catcher passed first through an empty bottle (a safety) to two scrubbers partly filled with paraffin oil, from which it was led to the gas tank.

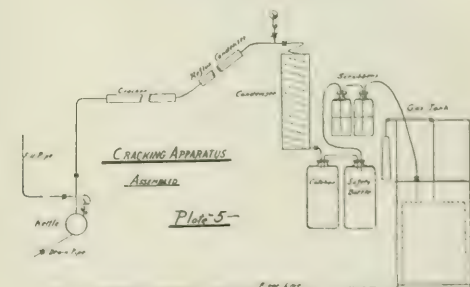
GAS TANK—The gas tank was built of heavy galvanized iron throughout, and all rivets were soldered both inside and out. The inner vessel was 18 in. in diameter by 24 in. high, and worked on rollers inside the main tank, which was 21 in. in diameter and 30 in. high. It was fitted with a 3/8-in. gas connection. When full there was a 6-in. water seal. The inner vessel was, of course, connected through a cable to a heavy weight and was operated in the usual manner. This tank was about three times too small.

SUPPORT—The kettle was placed on the floor, but a table 21 in. wide, 36 in. high, and 10 ft. long was used to carry the cracking furnace, the condenser, the catcher, and the scrubbers. The piping system was partly supported by chains from the ceiling.

METHOD OF OPERATION

While the procedure was varied considerably in the early experiments, the method found most satisfactory may be outlined as follows:

- (1) A charge of from 3 to 4 liters was placed in the kettle previous to lighting the fires under the cracker.
- (2) All the burners were lighted under the cracker but those near the kettle end were on full while the others were about half. When a section 12 in. long was at just visible red heat, the run was started. Care had to be taken that this temperature was held, since any variation would make the results worthless.



- (3) The steam (10 lbs.) was turned on in the reflux condenser, heating it to 116° C. When near the end of a run the oil was very hot and would be liable to heat the reflux condenser considerably higher than this. At such instances cold water was turned on for a short time.

- (4) The condenser proper was packed with ice, salt, and water, maintaining a temperature throughout of 5 to 10° C.

(5) The main line valve at the top of the condenser was closed, as was also the catcher valve (at the base of the coil). All gas in the tank was properly collected and the gas tank should be at its normal pressure (100 lbs.) which would drive off any gases, making it safe to open the tank for sampling purposes.

- (6) The steam being under the kettle was lighted and the gas in the tank was collected at the desired pressure (100 lbs.) and the run was started.

(7) Supposing the run to have been at 90 to 100 lbs. pressure, when 100 lbs. was reached on the line gauge near the top of the condenser, the line valve was opened and the line pressure dropped to 90, at which point it was closed. When the apparatus was working slowly perhaps 10 minutes were required to build the pressure up again to 100 lbs. per sq. in. Shortly before this was reached the condenser valve (at the bottom of the coil) was opened and the condensate allowed to flow into the catcher. The gases were as a rule retained on the assumption that condensation had not gone to completion. The end of the run was judged partly by

carried any further owing to the high cost of the raw material, high gas loss, and excessive carbon formation in the cracker.

B—CRUDE OIL

The crude oil used (Table I) was obtained from the Texas-Oklahoma field. The new apparatus was used in these experiments. The method of operation was the same as that previously described.

It appeared that by careful regulation of the conditions about 20 per cent of solvent gasoline could be secured (Table II). The tails could, of course, have been mixed with a new charge or run separately. Con-

TABLE I. PROPERTIES AND DISTILLATION ANALYSES OF MATERIALS USED IN EXPERIMENTS

A—PAINT & VARNISH MAKERS' NAPHTHA				B—CRUDE OIL				C—HEAVY KEROSENE	
ORIGINAL	Color of Distillate	Specific Gravity at 15° C.	Per cent of Total	ORIGINAL	Color of Distillate	Sp. Gr. at 15° C.	Per cent of Total	Sp. Gr. at 15° C.	Distillation Above 270° C.
0.763 (53.8° B _e)				0.853				0.830	
DISTILLATION:				DISTILLATION:					
Below 100° C.			Less than 1	Below 103° C	Water-white	0.708	2		
86 to 130°	Water-white	0.734 (60.9° B _e)	21.7	103 to 157°	Pale yellow	0.750	13		
130 to 150°	Water-white	0.754 (52.9° B _e)	25.0	157 to 180°	Pale yellow	0.770	6		
150 to 170°	Water-white	0.769 (52.1° B _e)	26.63	180 to 242°	Pale yellow	0.770	12		
170 to 190°	Water-white	0.781 (49.4° B _e)	13.34	242 to 300°	Light brown	0.842	20		
190 to 210°	Paint yellow	0.790 (47.4° B _e)	6.66	300 to 389°	Brown	0.847	20		
210 to 250°	Yellow	0.798 (45.9° B _e)	5.0	389 to 402°	Dark brown	0.860	12		
Res. above 250°	Orange		1.27	Residue	Black	Not detd.	16		
Per cent Loss			0.4						
TOTAL PER CENT			100.00				100		

the temperature of the kettle and by the volume of the condensate.

A—PAINT AND VARNISH MAKERS' NAPHTHA

The naphtha used in this set of experiments tested as indicated in Table I.

The apparatus used was the original one with the dental autoclave and the block-tin condenser. Condensation was effected at atmospheric pressure and there was not sufficient volume of oil to get up and maintain any pressure in excess of 45 lbs. The temperature of the cracker was varied, and was judged by the shade of red. The results are given in Table II.

All the gasoline fractions obtained had a yellow color

conditions most favorable were a pressure of 95 to 105 lbs. with the cracker heated to just visible red for about 12 inches.

As it was quite difficult to secure Oklahoma crude oil in Youngstown, in quantity at a reasonable figure, further experiments with crude oil were suspended.

C—HEAVY KEROSENE

A heavy grade of kerosene (Table I), known as heavy neutral, was next tried. Under normal conditions this oil may be secured on the open market at around 6 cents per gallon. The experiments were performed as previously described under "Operation." The cracking zone was kept at a dull red heat (525° C.).

The great difficulty, not only in this set of experiments

TABLE II—RESULTS OF CRACKING EXPERIMENTS

EXPERIMENT NO.	A—P. & V.-M. NAPHTHA				B—CRUDE OIL				C—HEAVY KEROSENE					
	1	2	3	4	1	2	3	4	1	2	3	4	5	6
Section	6-in.	12-in.	12-in.	12-in.	1	2	3	4	1	2	3	4	5	6
Temperature (a) ° C.	700	900	800	700	525	525	525	525	525	525	525	525	525	525
Average Pressure, Lbs.	30	45	20	10	30-40	60-70	75-85	95-105	75-85	85-95	95-105	105-115	115-125	125-135
Original Sample, Cc.	1000	1000	1000	1000	2000	2000	2500	3000	2000	2000	3000	3000	4000	4000
Total Oil Distilled, Cc.	600	200	430	630	1600	1750	2200	2770	1610	1725	2625	2685	3500	3575
Residue in Apparatus, Cc.	125	110	250	158	50	50	100	50	100	50	75	50	120	50
Per cent Recovery	72.5	31	65	78.8	82.5	90	92	94	85.5	88.8	90	91.2	90.5	89.4
Per cent Gas Loss	27.5	69	32	21.2	17.5	10	8	6	14.5	11.2	10	8.8	9.5	10.6
Fractionation of Oil Distilled—Yields in Per cent of Volume Distilled														
30 to 130° C.	16.67	11.00	46.5	36.5	11	16.0	18.5	21	11.3	9.5	16.0	15.1	18.8	16.8
130 to 150°	28.33	20.00	15.1	36.5	7	7.0	4.0	5	7.33	11.4	8.1	8.15	7.55	8.4
150 to 170°	18.3	21.45	17.2	25.3	5	7.1	3.0	6	7.33	8.1	10.5	6.5	9.5	11.0
Yields in Per cent of Original Sample														
GASOLINE														
Solvent (30 to 130° C.)	10	2.2	20.0	23	8.8	14	16.3	19.4	9.1	8.2	14.0	13.5	16.4	15.0
Motor (30 to 150° C.)	27	6.2	26.5	46	14.4	20	19.8	24.0	15.0	18.0	21.1	20.8	23.0	22.5
Specific Gravity at 15° C.														
Solvent (30 to 130° C.)	0.701	0.702	0.700	0.704	0.707	0.702	0.705	0.703	0.710	0.708	0.712	0.714	0.710	0.708
Motor (30 to 150° C.)	0.703	0.722	0.716	0.725	0.733	0.730	0.729	0.732	0.719	0.730	0.725	0.725	0.725	0.726

(a) Temperatures estimated by color of heated pipe: Dull Red, 525° C.; Dark Red, 700° C.; slightly less than Cherry Red, 800° C.; Cherry Red, 900° C.

and a characteristic pungent odor. According to Bacon and Hamor¹ this odor is due to a small quantity of sulfur compounds, naphthenic acids, and basic nitrogen compounds, probably of the pyridine type. They mention that it may be removed to a large extent by treatment with alkaline plumbite, cupric oxide, or sodium.

The experiments with P. & V. M. naphtha were not

¹ "American Petroleum Industry."

but in the preceding ones as well, was in holding the proper temperature in the cracking furnace.

Because of its low initial cost an oil such as this is perhaps the best material to start from in the preparation of gasoline.

SUMMARY

I—The proper temperature for the cracking furnace was a just visible red heat. Larger volumes of oil can be handled by increasing the length of the cracking zone.

II—The steam-heated reflux condenser by returning the heavier fractions to the cracking zone, increased the yield of gasoline.

III—Condensation was best effected under pressure.

IV—By proper regulation of the conditions, gasoline can be secured from any petroleum oil.

V—It is considered more economical to crack the oil with as little gas loss as possible, recover the gasoline, and work the tails over again. In this way the final products are gas, gasoline, and carbon.

VI—In this process excessive carbon deposition was not a factor.

VII—The most satisfactory materials are heavy kerosene and fuel oil.

CONCLUSION

The preparation of solvent gasoline is not difficult and is quite feasible when a supply of heavy kerosene or fuel oil can be readily obtained at normal price.

ACKNOWLEDGMENT

The writer takes this means of thanking the Republic Rubber Company for permission to publish the experimental data contained above. He is also indebted to Messrs. Seth R. Clark, A. Brill, and M. H. Daniels for their interest and for valuable suggestions rendered during the course of the experiments.

RESEARCH COMPOUNDING LABORATORY
GOODYEAR TIRE & RUBBER COMPANY
AKRON, OHIO

THE COMPOSITION OF LOGANBERRY JUICE AND PULP

By MILO REASON DAUGHTERS
Received June 27, 1917

The results given in this paper were obtained by following the directions given in the "Official and Provisional Methods of Analysis," *Bull.* 107 (Revised).

TABLE I—ANALYSES OF LOGANBERRY JUICE

SAMPLE No.	I	II	III
Sp. Gr. (16° C.)	1.0523	1.0477	1.0508
Per cent Acidity { as Citric.....	2.396	3.084	2.199
{ as Sulfuric.....	1.678	2.159	1.54
Water.....	88.96	89.15	90.548
Total Solids.....	11.04	10.87	9.452
Per cent Ash { Alkalinity.....	0.4139	0.5785	0.4226
{ K_2CO_3	0.4130	0.5075	0.288
Protein (N \times 6.25).....	0.3226	0.731	0.7375
Sugar (as invert sugar).....	6.36	5.37	8.39
Alcoholic Precipitate.....	0.502	0.872	0.4008
Caloric Value, per Liter.....	290	207	385

Sample I was raw unsweetened juice bottled by the Pheasant Fruit Juice Company of Salem, Oregon, during the summer of 1915. Sample II was collected from fresh berries by subjecting them to pressure with a Yale press, July 10, 1916. Sample III was obtained in the same manner as II but later in the season, viz., August 8, 1916. The higher moisture content¹ and lower total solids of Sample III are due to the fact that the sample was dried in a steam oven whereas I and II were dried *in vacuo* at 70° C.

Windisch and Schmidt² state that the ash of all

¹ The analysis of Sample III, Table I, beginning with the percentage of water was done by Mrs. Irene Allen of the laboratory. [Author's Note.]

² Windisch and Schmidt, "Contributions to the Knowledge of Fruit Juices," *Z. Nahr. Genussm.*, 17, 584.

fruit juices has an alkalinity of 10 to 12 per gram of ash, and sometimes, though rarely, a very little more or less. The alkalinity of one gram of ash of I and II was found to be 12.70 and 12.71, respectively.

TABLE II—PERCENTAGE COMPOSITION OF LOGANBERRY PULP

	Moist Pulp	Dried Pulp
Moisture.....	74.65
Total Solids.....	29.03
Protein (N \times 6.25).....	3.727	12.81
Fat (Ether extract).....	3.799	13.089
Carbohydrate (Nitrogen-free Ext.).....	11.06	38.11
Crude Fiber.....	8.389	28.89
Ash.....	0.695	2.394
Acid (as citric).....	1.367	4.706
Calories (per lb.).....	426	1458

The constants of the oil extracted from the finely ground dried pulp by means of petroleum ether, boiling point 44–65° C., are as follows:

Specific Gravity (15.5° C.)	Refractive Index (15.5° C.)	Solidifying Temperature	Iodine No.	Saponification No.
0.9260	1.4811	–33° C.	158.32	179.8

Comparing this oil with other drying oils, it lies between hemp seed oil and tung oil as judged by its iodine value and specific gravity. Its refractive index is high—near that of linseed oil.

DEPARTMENT OF CHEMISTRY
OREGON STATE AGRICULTURAL COLLEGE
CORVALLIS

THE FERTILIZING VALUE OF SOME HOUSEHOLD WASTES¹

By PHILIP E. BROWNING

The following table of analyses of the ash of certain household wastes is the result of work recently undertaken with the cooperation of John Phillips Street, of the Connecticut Agricultural Experiment Station, to determine the possible fertilizing value of such material. The table is by no means complete and we hope to be able to make a number of additions to it in the near future.

No attempt was made to secure very carefully ashed products, but rather to secure results which would be obtained by burning in an improvised incinerator under ordinary household conditions.

ASH	Per cent K_2O	Per cent P_2O_5
Banana stalks(a).....	49.4	2.34
Banana skins.....	41.76	1.25
Grape fruit skins(b).....	30.6	3.58
Orange skins.....	27.0	2.90
Lemon skins.....	31.0	6.3
Apple skins.....	11.74	3.08
Cantaloupe rinds.....	12.21	9.77
Raw white potato skin.....	27.5	5.18
Boiled sweet potato skin.....	15.89	7.29
Pea pods.....	9.00	1.79
Cucumber skins.....	18.00	1.88
String bean strings and stems.....	0.44	1.6
Tea leaf ash.....	1.99 N.	0.36
Coffee grounds (dried).....	0.67	0.36
Lamb chop bone ash (32.12 CaO).....	1.60	0.43
Burned egg shells.....	0.20	0.43
Tobacco.....	0.38	0.87
Peanut shell ash.....	0.38	0.8
Peach stones.....	6.04	3.25
Peach skins.....	36	8.81

(a) About 1 oz. of ash from one banana stalk.

(b) About 1 oz. of ash from one grape fruit.

(c) About 1 oz. of ash from one orange.

(d) About 1 oz. of ash from one lemon.

(e) About 1 oz. of ash from one apple.

(f) About 1 oz. of ash from one cantaloupe.

(g) About 1 oz. of ash from one pea pod.

(h) About 1 oz. of ash from one cucumber.

(i) About 1 oz. of ash from one string bean.

(j) About 1 oz. of ash from one tea leaf.

(k) About 1 oz. of ash from one coffee ground.

(l) About 1 oz. of ash from one lamb chop bone.

(m) About 1 oz. of ash from one burned egg shell.

(n) About 1 oz. of ash from one tobacco.

(o) About 1 oz. of ash from one peanut shell.

(p) About 1 oz. of ash from one peach stone.

(q) About 1 oz. of ash from one peach skin.

(r) About 1 oz. of ash from one banana stalk.

(s) About 1 oz. of ash from one banana skin.

(t) About 1 oz. of ash from one grape fruit skin.

(u) About 1 oz. of ash from one orange skin.

(v) About 1 oz. of ash from one lemon skin.

(w) About 1 oz. of ash from one apple skin.

(x) About 1 oz. of ash from one cantaloupe rind.

(y) About 1 oz. of ash from one raw white potato skin.

(z) About 1 oz. of ash from one boiled sweet potato skin.

(aa) About 1 oz. of ash from one pea pod.

(ab) About 1 oz. of ash from one cucumber skin.

(ac) About 1 oz. of ash from one string bean string and stem.

(ad) About 1 oz. of ash from one tea leaf.

(ae) About 1 oz. of ash from one coffee ground.

(af) About 1 oz. of ash from one lamb chop bone.

(ag) About 1 oz. of ash from one burned egg shell.

(ah) About 1 oz. of ash from one tobacco.

(ai) About 1 oz. of ash from one peanut shell.

(aj) About 1 oz. of ash from one peach stone.

(ak) About 1 oz. of ash from one peach skin.

(al) About 1 oz. of ash from one banana stalk.

(am) About 1 oz. of ash from one banana skin.

(an) About 1 oz. of ash from one grape fruit skin.

(ao) About 1 oz. of ash from one orange skin.

(ap) About 1 oz. of ash from one lemon skin.

(aq) About 1 oz. of ash from one apple skin.

(ar) About 1 oz. of ash from one cantaloupe rind.

(as) About 1 oz. of ash from one raw white potato skin.

(at) About 1 oz. of ash from one boiled sweet potato skin.

(au) About 1 oz. of ash from one pea pod.

(av) About 1 oz. of ash from one cucumber skin.

(aw) About 1 oz. of ash from one string bean string and stem.

(ax) About 1 oz. of ash from one tea leaf.

(ay) About 1 oz. of ash from one coffee ground.

(az) About 1 oz. of ash from one lamb chop bone.

(ba) About 1 oz. of ash from one burned egg shell.

(bb) About 1 oz. of ash from one tobacco.

(bc) About 1 oz. of ash from one peanut shell.

(bd) About 1 oz. of ash from one peach stone.

(be) About 1 oz. of ash from one peach skin.

(bf) About 1 oz. of ash from one banana stalk.

(bg) About 1 oz. of ash from one banana skin.

(bh) About 1 oz. of ash from one grape fruit skin.

(bi) About 1 oz. of ash from one orange skin.

(bj) About 1 oz. of ash from one lemon skin.

(bk) About 1 oz. of ash from one apple skin.

(bl) About 1 oz. of ash from one cantaloupe rind.

(bm) About 1 oz. of ash from one raw white potato skin.

(bn) About 1 oz. of ash from one boiled sweet potato skin.

(bo) About 1 oz. of ash from one pea pod.

(bp) About 1 oz. of ash from one cucumber skin.

(bq) About 1 oz. of ash from one string bean string and stem.

(br) About 1 oz. of ash from one tea leaf.

(bs) About 1 oz. of ash from one coffee ground.

(bt) About 1 oz. of ash from one lamb chop bone.

(bu) About 1 oz. of ash from one burned egg shell.

(bv) About 1 oz. of ash from one tobacco.

(bw) About 1 oz. of ash from one peanut shell.

(bx) About 1 oz. of ash from one peach stone.

(by) About 1 oz. of ash from one peach skin.

(bz) About 1 oz. of ash from one banana stalk.

(ca) About 1 oz. of ash from one banana skin.

(cb) About 1 oz. of ash from one grape fruit skin.

(cc) About 1 oz. of ash from one orange skin.

(cd) About 1 oz. of ash from one lemon skin.

(ce) About 1 oz. of ash from one apple skin.

(cf) About 1 oz. of ash from one cantaloupe rind.

(cg) About 1 oz. of ash from one raw white potato skin.

(ch) About 1 oz. of ash from one boiled sweet potato skin.

(ci) About 1 oz. of ash from one pea pod.

(cj) About 1 oz. of ash from one cucumber skin.

(ck) About 1 oz. of ash from one string bean string and stem.

(cl) About 1 oz. of ash from one tea leaf.

(cm) About 1 oz. of ash from one coffee ground.

(cn) About 1 oz. of ash from one lamb chop bone.

(co) About 1 oz. of ash from one burned egg shell.

(cp) About 1 oz. of ash from one tobacco.

(cq) About 1 oz. of ash from one peanut shell.

(cr) About 1 oz. of ash from one peach stone.

(cs) About 1 oz. of ash from one peach skin.

(ct) About 1 oz. of ash from one banana stalk.

(cu) About 1 oz. of ash from one banana skin.

(cv) About 1 oz. of ash from one grape fruit skin.

(cw) About 1 oz. of ash from one orange skin.

(cx) About 1 oz. of ash from one lemon skin.

(cy) About 1 oz. of ash from one apple skin.

(cz) About 1 oz. of ash from one cantaloupe rind.

(da) About 1 oz. of ash from one raw white potato skin.

(db) About 1 oz. of ash from one boiled sweet potato skin.

(dc) About 1 oz. of ash from one pea pod.

(dd) About 1 oz. of ash from one cucumber skin.

(de) About 1 oz. of ash from one string bean string and stem.

(df) About 1 oz. of ash from one tea leaf.

(dg) About 1 oz. of ash from one coffee ground.

(dh) About 1 oz. of ash from one lamb chop bone.

(di) About 1 oz. of ash from one burned egg shell.

(dj) About 1 oz. of ash from one tobacco.

(dk) About 1 oz. of ash from one peanut shell.

(dl) About 1 oz. of ash from one peach stone.

(dm) About 1 oz. of ash from one peach skin.

(dn) About 1 oz. of ash from one banana stalk.

(do) About 1 oz. of ash from one banana skin.

(dp) About 1 oz. of ash from one grape fruit skin.

(dq) About 1 oz. of ash from one orange skin.

(dr) About 1 oz. of ash from one lemon skin.

(ds) About 1 oz. of ash from one apple skin.

(dt) About 1 oz. of ash from one cantaloupe rind.

(du) About 1 oz. of ash from one raw white potato skin.

(dv) About 1 oz. of ash from one boiled sweet potato skin.

(dw) About 1 oz. of ash from one pea pod.

(dx) About 1 oz. of ash from one cucumber skin.

(dy) About 1 oz. of ash from one string bean string and stem.

(dz) About 1 oz. of ash from one tea leaf.

(ea) About 1 oz. of ash from one coffee ground.

(eb) About 1 oz. of ash from one lamb chop bone.

(ec) About 1 oz. of ash from one burned egg shell.

(ed) About 1 oz. of ash from one tobacco.

(ee) About 1 oz. of ash from one peanut shell.

(ef) About 1 oz. of ash from one peach stone.

(ef) About 1 oz. of ash from one peach skin.

(eg) About 1 oz. of ash from one banana stalk.

(eh) About 1 oz. of ash from one banana skin.

(ei) About 1 oz. of ash from one grape fruit skin.

(ej) About 1 oz. of ash from one orange skin.

(ek) About 1 oz. of ash from one lemon skin.

(el) About 1 oz. of ash from one apple skin.

(em) About 1 oz. of ash from one cantaloupe rind.

(en) About 1 oz. of ash from one raw white potato skin.

(eo) About 1 oz. of ash from one boiled sweet potato skin.

(ep) About 1 oz. of ash from one pea pod.

(eq) About 1 oz. of ash from one cucumber skin.

(er) About 1 oz. of ash from one string bean string and stem.

(es) About 1 oz. of ash from one tea leaf.

(et) About 1 oz. of ash from one coffee ground.

(eu) About 1 oz. of ash from one lamb chop bone.

(ev) About 1 oz. of ash from one burned egg shell.

(ew) About 1 oz. of ash from one tobacco.

(ex) About 1 oz. of ash from one peanut shell.

(ey) About 1 oz. of ash from one peach stone.

(ey) About 1 oz. of ash from one peach skin.

(ez) About 1 oz. of ash from one banana stalk.

(fa) About 1 oz. of ash from one banana skin.

(fb) About 1 oz. of ash from one grape fruit skin.

(fc) About 1 oz. of ash from one orange skin.

(fd) About 1 oz. of ash from one lemon skin.

(fe) About 1 oz. of ash from one apple skin.

(

LABORATORY AND PLANT

METHOD OF STAINING TO DISTINGUISH BETWEEN BLEACHED AND UNBLEACHED SULFITE PULPS¹

By CHARLES G. BRIGHT

The principle of the method is first to stain the fibers with Cross and Bevan's ferric ferricyanide solution, which colors the unbleached sulfite green on account of the lignin contained in it, and leaves the bleached sulfite colorless. This alone gives a good distinction, but by subsequently staining with a red substantive dyestuff, the green of the unbleached is changed to a very pure blue, the bleached being colored red, thus giving a most striking contrast.

The problem is to adjust the treatment with the two solutions to bring out the sharpest contrast. If the treatment with red is too severe some of the unbleached fibers are likely to be colored purplish, or in extreme cases take on a dull, dirty red color. On the other hand, if the treatment with ferric ferricyanide is continued for too long a time or at too high a temperature, the reagent has a tendency to decompose and form a deposit on the slide as well as on the bleached sulfite, so that the latter turns a dull purplish color when subsequently stained with red.

The results depend on three factors—namely: (1) the concentration of the solution, (2) the temperature at which each is applied, and (3) the length of time each is allowed to act. In experimenting with this method these factors were varied separately and the combination which gave the best results was chosen.

The solutions are prepared according to the following procedure:

FERRIC FERRICYANIDE

SOLUTION A. Tenth Normal FeCl₃ — 2.7 grams FeCl₃ 6H₂O per 100 cc.
SOLUTION B. Tenth Normal K₃Fe(CN)₆ — 3.29 grams per 100 cc.

After diluting to the mark with distilled water filter through dry filters into clean, glass-stoppered bottles—protect from dust. Equal volumes of Solutions A and B are mixed fresh whenever the reagent is used.

SUBSTANTIVE RED

Benzopurpurin 4B extra (Bayer Co.).....	0.4 gram
Oxamine brilliant red BX (Badische Co.).....	0.1 gram
Distilled water.....	100 cc.

NOTE: Have the water hot and stir in the dyes slowly.

The stain is placed in a tall, narrow cylindrical beaker, which is set into a water bath. The slides are suspended in the beaker by a clamp which holds them at their upper ends, the clamps resting across the top of the beaker. The bath is heated by a small Bunsen burner with a pilot flame. The burner can be turned on full to heat the bath up to the required temperature (35 and 45° C.); then by turning off the burner and regulating the pilot flame the bath can be kept at the required temperature without much difficulty. A thermometer is suspended in the beaker of stain beside the slides. The beaker should be as small as

possible so as not to use up too much stain at one time.

METHOD OF STAINING WITH FERRIC FERRICYANIDE

Mix equal volumes of fresh Solutions A and B and heat to 35° C., regulating the water bath so that it will remain within one degree of the temperature named, for 15 minutes. The dry slide is then dipped in water to moisten it uniformly, so that air bubbles will not be formed when it is immersed in the stain. If air bubbles are formed the fibers under the bubbles will not be stained. If dipping in water still leaves bubbles, they can be removed by blowing across the slide from the edge. The slide is then suspended in the stain and left there for 15 minutes at 35° C. It is then removed and washed by dipping in and out of a beaker of distilled water six times and repeating the process in a fresh beaker of water. The slide can then be placed wet into the red solution, but it is perhaps best to dry it out so that the fibers will be stuck on tightly again in case they have been loosened to any extent by the treatment.

APPLYING THE SUBSTANTIVE RED STAIN

A fresh solution of stain is heated to 45° C., and the slide, after moistening and excluding bubbles as before, is suspended in the solution for 5 minutes at 45° C. and immediately washed in two beakers of distilled water. The slide is then dried and a cover glass placed on with a drop of balsam.

DIRECTIONS FOR INSURING BEST RESULTS

To get the clearest, brightest results, distilled water must be used throughout, and the staining solutions must be fresh. The two solutions for ferric ferricyanide will keep well if placed in separate bottles. Equal volumes are mixed together immediately before using. The red solution should be made freshly each time for the best results, as it gets thick and stringy on standing, especially when it is being heated up continually.

Staining under the conditions described gives on unbleached sulfite perhaps the deepest blue it is possible to obtain without depositing blue on the slide and on the bleached sulfite; the method also produces the best red on the bleached without turning the unbleached purple. Unbleached sulfite from different mills varies considerably in lignin content, hence some samples stain a deeper blue than others. The foregoing conditions give a satisfactory blue on a sample of high-grade imported unbleached pulp as well as a better color on the average run of unbleached pulps, the latter being not so well cooked as a rule. With pulp containing more lignin it is possible to use a slightly stronger treatment with the red and thus get a better color on the bleached without affecting the unbleached.

After the analyst has had a little experience with the method he can tell by the color of the unbleached

¹ Presented at the Spring Meeting of the Technical Association of the Pulp and Paper Industry, Neenah, Wis., May 24 and 25, 1917. Reprinted from *Paper* 20 (Aug. 29, 1917), No. 25, p. 11.

whether he may safely continue the staining with the red for 6 or possibly 7 minutes at 45° C. At first, however, it is better to follow the directions as given. It is of prime importance to wash out, or neutralize, every trace of alkali in the fibers, as the blue is decolorized by alkali.

This method of staining will in general give a distinction between pure cellulose fibers and those which contain lignin. Rags, bleached sulfite, soda pulp or any thoroughly bleached material are stained red, while unbleached sulfite, groundwood, jute, or any lignified materials are stained blue. The principal application lies in the estimation of unbleached pulp in book papers. A considerable saving can be made by using unbleached sulfite instead of bleached, hence it is important to know how much unbleached pulp there is in a sheet.

KIMBERLY-CLARK COMPANY LABORATORIES
NEENAH, WISCONSIN

SOME SUGGESTIONS CONCERNING THE PREPARATION OF AMMONIUM CITRATE SOLUTION AND THE DETERMINATION OF INSOLUBLE PHOSPHORIC ACID¹

By PHILIP MCG. SHUEY

The preparation of ammonium citrate solution used in the determination of available phosphoric acid is usually looked upon as a very long and tedious process. Very often considerable time is expended in making up the solution to conform with the two requisites, neutrality and specific gravity, particularly in striking the neutral point.

Generally the method consists of first making a solution of citric acid, and then adding ammonia numerous times, in varying quantities, until the neutral point is reached, thus requiring a test for neutrality after each addition of ammonia, and as there is necessarily considerable guess-work attached to this process the operator may at times overstep the mark, making the solution too alkaline, requiring the addition of more citric acid, and probably another long period of numerous additions of ammonia and a corresponding number of tests.

In order to save unnecessary loss of time and labor, the writer found by experiment that the neutral point could be reached at once by simply calculating the amount of ammonia required for a given amount of citric acid, according to the following equation:



As commercial citric acid contains one molecule of water of crystallization, the proportion is 210.08 parts of citric acid to 31.102 parts of ammonia, or a ratio of 1.000 of NH_3 to 4.111 citric acid.

The calculation for making up a solution using 4 lbs. of citric acid has been found, theoretically and experimentally, to be as follows:

4 lbs. = 1814.37 g., which requires 441.34 g. of NH_3 . This is equivalent to 1760 cc. of aqueous ammonia containing 28 per cent NH_3 .

The sp. gr. is 0.9554 at 15° C., but at the time the

experiments were conducted, the temperature was 23°, and the sp. gr. therefore 0.89554.¹

$1576.2 \div 0.89554 = 1760$ cc. aqueous ammonia required.

The above may be summed up as follows, also to show the amount of water required, and the volume of solution resulting:

Commercial Citric Acid	4 lbs.
Water	6961 cc.
Concentrated Ammonia (28%)	1760 cc.
Gain in Volume from Ammonium Citrate	791 cc. approximately
Total Volume	9512 cc. approximately
Specific Gravity, 1.09 at 20° C.	
Temperature of both ammonia and water when measured, 23° C.	

Commercial citric acid appears to be very uniform in composition. This is shown by having used the above formula several times with practically the same result, the solution testing neutral to corallin in each case.

Further, a weighed portion of a sample of citric acid was dissolved in water and titrated with a standard caustic soda solution, using phenolphthalein as indicator, and the result was very nearly 100 per cent in acidity.

In the operation of dissolving the citric acid, it is advisable to add the ammonia just after the water. This materially hastens solution for obvious reasons.

There has apparently been a good deal of inconsistency on the part of many of us with regard to a strictly neutral solution. The insoluble phosphoric acid in acid phosphate, for example, may be determined with practically identically the same result whether or not the weighed portion is previously washed with water, and, in practice, the washing is rarely done more than a few times, when, in reality, a large number of washings would be required to get rid of all the acid.

Cyanamid, on the other hand, is very alkaline, and also gives off ammonia in the presence of water. A few washings would get rid of but a small portion of the alkalinity, yet the determination of insoluble phosphoric acid has been found to be extremely close to the theoretical in a large number of experiments in which Cyanamid was present in considerable amounts, and in some cases the acid phosphate was present in very small quantity.

In the case of acid phosphate that has not been previously washed before digestion, it is equivalent to using a slightly acid citrate solution, or one containing approximately 0.5 per cent of free citric acid, which is not enough to dissolve the already strongly acidulated tricalcium phosphate remaining.

In the case of ground tannage, whale guano, meat guano, fish, and such other materials that have not been strongly acidulated, it may be important for the solution to be strictly neutral, the way to the neutral point of applied acids need be limited to be sufficiently accurate, and if a case doubtful that such a solution would not give consistent results as compared with those found from the use of a solution prepared by the use of an electric indicator in some other more sensitive indicator.

Submitted for discussion December 15, 1916; accepted February 1, 1917.

¹ Presented before the Fertilizer Division at the 35th Meeting of the American Chemical Society, Boston, September 10 to 13, 1917.

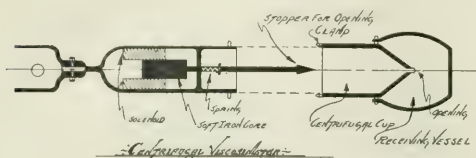
A SUGGESTED FORM OF VISCOSIMETER

By W. C. COPE

Received July 21, 1917

The usual form of viscosimeter is based on the proposition of passing a given quantity of oil or other liquid contained in a cylindrical vessel at a specified temperature through an orifice of definite dimensions in a variable length of time. The viscosity of the liquid under examination, then, is obtained by comparing the time taken for passing a like volume of liquid, such as rape seed oil, through the orifice under similar conditions.

A criticism of instruments of this kind is: (1) the height of column of liquid is variable and the first half of the liquid collected comes through in less time than the second half due to less head of liquid in the viscosimeter; (2) an oil of the nature and consistency of engine oil at ordinary laboratory temperature will flow only a few cubic centimeters per minute (to get any data on such an oil the temperature must be raised and this will not indicate the viscosity at the lower temperature); (3) time may not be the proper medium for a basis of comparison.



A suggested form of viscosimeter which is shown in the accompanying drawing is based on a different principle and is therefore not subject to the above criticism. It is described as follows: an arm of a centrifuge holds a cylindrical or other shaped cup having an orifice of definite dimensions which is closed by means of a cone needle valve actuated by a spring. A receiver is attached to the cup to retain any liquid passing through the orifice. The receiver is easily detached from the cup and by reason of its flat bottom will be perfectly stable when placed on a balance pan.

A definite quantity of oil or other liquid under examination is placed in the cup and the centrifuge is whizzed at the desired speed when the valve is raised by passing electric current through a solenoid which excites the soft iron core attached to the valve. After a given time the current is shut off, whereupon the valve is closed by the spring.

A definite quantity of liquid will pass through the orifice in a definite period of time by varying the speed. Hence it is seen that temperature, time, and volume are constant and force variable. Knowing the length of the centrifuge arm and the speed of rotation, the force required to pass the liquid may be easily calculated by the well-known formula. Viscosity, then, would be measured in terms of acceleration due to gravity (g), which is a rational system.

The centrifuge could be driven by a motor and the speed varied by means of a variable speed countershaft

cone. A tachometer would indicate the speed at any time. Temperature of test could be controlled by carrying out the operation in a constant temperature room or enclosing the centrifuge in a case in which the temperature could be regulated.

It seems to be impossible to arrive at any definite agreement as to a standard instrument for viscosity while using the present system of time variation. It is believed that an agreement could be had on some modification of the principle suggested.

The suggested form of apparatus is offered with the hope that it will raise discussion and accelerate investigation leading to the adoption of a standard viscosimeter.

E. I. DU PONT DE NEMOURS & COMPANY
EASTERN LABORATORY, CHESTER, PA.

A CONVENIENT AUTOMATIC DEVICE FOR RAPIDLY WASHING PIPETTES

By AUBREY VAIL FULLER

Received September 11, 1917

Without doubt the piece of glass apparatus in daily use in quantitative analytical work most difficult to cleanse thoroughly is the ordinary transfer pipette.

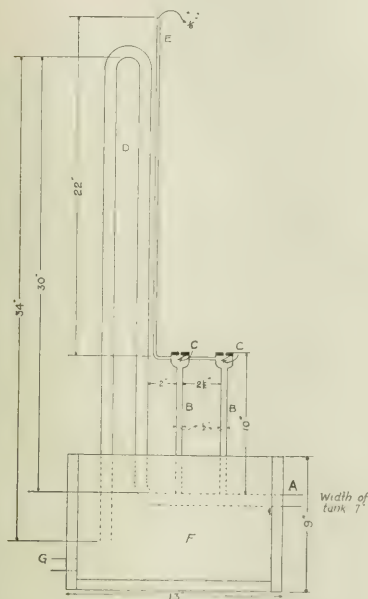
In order to surmount these difficulties and to render the procedure simpler and less time-consuming the writer has devised the automatic washing apparatus pictured.

A is the inlet tube, which is connected with the water supply either by means of rubber tubing or by being permanently piped thereto. *B, B* are the pipette carriers, provided at their enlarged ends with short rubber stoppers bored with $\frac{3}{8}$ -in. holes. These stoppers are fitted on their lower faces with gate valves *C, C*, made by cementing small squares of sheet rubber to them so as to form a flap over the holes, the function of these valves being to prevent the escape of water from the carrier not in actual use. *D* is a syphon and *E* a breather pipe, permitting the escape of air which would otherwise be compressed as the water rises in the carriers. The entire pipe system is supported in a copper-lined wooden tank, *F*, provided with an outlet, *G*.

The operation of the device is as follows: The supply tap is opened until water flows from the syphon intermittently as in the familiar Soxhlet apparatus. The pipette to be washed is then placed tip-up in one of the carriers. Water rises in both pipette and syphon, but on encountering the constriction at the tip of the former, has its flow arrested, while it freely rises to the bend in the latter and syphons out, emptying the pipette. The process repeats itself indefinitely, and one, or several pipettes of different sizes, may be washed simultaneously and without attention. In a two-carrier apparatus as illustrated, a 5 cc. and a 200 cc. instrument may be washed side by side.

The cross-section of the syphon pipe is determined

by the speed of washing desired. Using $\frac{3}{4}$ -in. pipe, a 50 cc. pipette may be washed free from the ordinary cleansing mixture ($\text{H}_2\text{SO}_4 + \text{K}_2\text{Cr}_2\text{O}_7$) on the third emptying, the time consumed being about 20 seconds.



It is to be noted that it is imperative in order to obtain positive operation that the internal diameter of the syphon bend must be the same as that of the limbs. The use of the ordinary "return bend" is therefore excluded, and if a separate fitting is to be employed, it must be of the so-called recessed type.

The detailed form of the apparatus may, of course, be varied to suit conditions. In many cases it might be found convenient to mount the piping directly in the laboratory sink, in which event the overflow tank could be dispensed with.

BIOCHEMICAL DIVISION, BUREAU OF ANIMAL INDUSTRY
U. S. DEPARTMENT OF AGRICULTURE, WASHINGTON, D. C.

AN ASBESTOS STOPPER

By JOSEPH B. NICHOLS

Received September 19, 1917

Having occasion to perform a distillation involving the use of fuming sulfuric acid at a temperature of about 350°C ., and desiring to use a Pyrex flask so as to observe the behavior of the substance, some difficulty was experienced in finding a suitable stopper. The following procedure was used with very satisfactory results: A cork of the proper size was obtained, and from it a mold made of plaster of Paris. Two glass tubes of the size of the delivery tube and thermometer were placed

in it, and some asbestos-magnesia mixture, as used for steam packing, was mixed with long-fibred asbestos and worked with water into a thick paste. This was tamped into the mold, as much water pressed out as possible, and the whole dried upon the steam bath. The stopper held together perfectly and was just plastic enough, not being totally dry, to be pressed down firmly in the flask. When heated, it became hard, and was unaffected by the fumes. On completion of the distillation, it was removed with no difficulty, and on moistening became plastic enough to be fitted into the flask for a second distillation.

The author hopes this simple device may be useful to others working at a higher temperature or with chemicals which would affect a cork or rubber stopper.

2222 BANCROFT WAY
BERKELEY, CALIFORNIA

A NEW FORM OF SAFETY PIPETTE

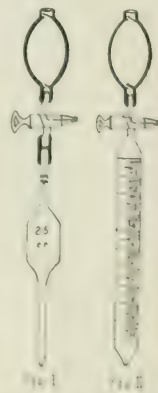
By A. S. BEHPMAN

Received April 24, 1917

In pipetting acids, alkalis, poisons, etc., the chemist is frequently confronted with the possibility of drawing up some of the solution into his mouth. Not finding any of the several forms of safety pipettes on the market eminently satisfactory for many purposes, the writer finally devised the following simple and effective plan.

Though the basic idea lends itself to a number of modifications, the most compact and convenient one is illustrated in the accompanying two sketches. As will readily be seen, the essential feature of the device is a provision for permitting two inlets to the pipette proper—one of these being connected with a source of suction, the other with the outside air. A very satisfactory arrangement is a 3-way stopcock used in conjunction with a stiff atomizer bulb, properly valved.

Fig. I shows the device connected to an ordinary pipette by means of a short, stout piece of rubber tubing. Fig. II shows it made integral with a graduated pipette of the type of Mohr's.



To operate, the 3-way cock is turned so as to connect the pipette with the bulb. The pipette is then filled a little above the mark by pressing and releasing the bulb one or more times, the bulb valves acting to prevent the back flow of the liquid. With a stiff bulb, pipettes of even 25 to 50 cc. capacity can usually be filled with one pressure and release of the bulb. The stopcock is then turned so as to permit the suction of the outside air, by which means the liquid is jet down to the mouth, and subsequently delivered.

RECEIVED BY THE EDITOR, MARCH 1, 1918

ADDRESSES

ANALYSIS AND TESTING OF PREPARED ROOFINGS

By HERBERT ABRAHAM

Received May 8, 1917

Prepared roofings are composed of one or more layers of fabric impregnated with bituminous matter of relatively soft consistency, which are cemented together and surfaced with layers of bituminous matter of harder consistency. The fabric is ordinarily composed of a fibrous felt, although in certain cases this is used in conjunction with a woven fabric consisting either of burlap or cotton duck.

The bituminous matter may consist either of asphaltic compositions or of coal-tar residues, but these are rarely used together. In this paper, we consider only prepared roofings manufactured from asphaltic compositions.

Prepared roofings are marketed in the form of rolls, usually 36 or 32 in. wide, measuring 108 sq. ft. in area, known commercially as a "square," which is sufficient to cover 100 sq. ft. of roof surface, allowing for the usual 2-in. lap at the joints.

It is customary to pack sufficient nails and liquid lap-cement in the core of the roll to affix the roofing to the roof of a building. The rolls are wrapped in paper and headed with metal, paper, or cloth, or a combination of the last two. The heads serve to keep the roll of roofing in shape, and prevent the nails and cement from falling out of the core.

Roll roofings are marketed in various weights known to the trade as "plies." The term "ply," however, is a misnomer, as it does not, as one would suppose, refer to the number of layers of fabric contained in the roofing. It is customary to manufacture the so-called "one-ply" to weigh 35 lbs. gross per square including the paper wrapper, heads, nails and cement in addition to the roofing itself. The net weight of the roofing per square ranges from 2 to 4 lbs. less than the gross weight. The gross weight of "two-ply" roofing is 45 lbs., and that of "three-ply" roofing 55 lbs. per square. Heavier weights are also manufactured, especially in the case of roofings surfaced with moderately coarse or coarse mineral matter, which in certain cases weigh 100 lbs. per square or over. At the present time there is no standard practice followed in manufacturing the heavier weights, each manufacturer being guided by his own ideas on the subject.

METHODS OF MANUFACTURE

In manufacturing prepared roofings, the fibrous felt is first saturated by passing it through a bath of the melted bituminous impregnating material, which soaks into the felt and fills up its pores. The saturated felt may then be coated immediately with the melted bituminous surface coating, while it is still hot, or else it may be wound into large rolls, allowed to cool, and coated later. Both methods are used, one being known as the continuous and the other as the intermittent process of manufacture. Each is claimed to have its particular advantages.

The coated roofing may be wound up in rolls without any further treatment, or it may be sprinkled on the surface with a fine dusting finish of mineral matter to prevent the convolutions of the roll from sticking together in transit or storage. Ground talc, mica and silica are used for this purpose. As they are sprinkled on while the roofing is hot, a certain proportion becomes embedded in the surface coatings and cannot be removed by mechanical means. Most of the dusting finish, however, is detached, and either blows away or else is washed off the roofing by the first rain-storm after it has been applied to a building.

In other cases, moderately coarse to coarse mineral particles are purposely embedded in the surface coating, either to enhance the appearance of the roofing, or else to reduce its cost by making up weight. Popular finishes of this character consist of small rounded grains of sand, coarsely ground particles of talc, angular particles of crushed slate or greenstone (which may either be of a reddish or greenish color), angular particles of feldspar, granite, etc., or even fairly large pebbles or gravel. These are embedded in the surface coating as firmly as possible, so that they may durably attach themselves, and become an integral part of the roofing. In all cases, however, more or less of the mineral particles fail to embed themselves and hence we distinguish between the "detached" and "embedded" mineral matter, the proportions of which serve as a criterion as to the efficiency with which the manufacturing process has been performed.

In some cases it is customary to mix mechanically a certain proportion of finely powdered mineral matter with the surface

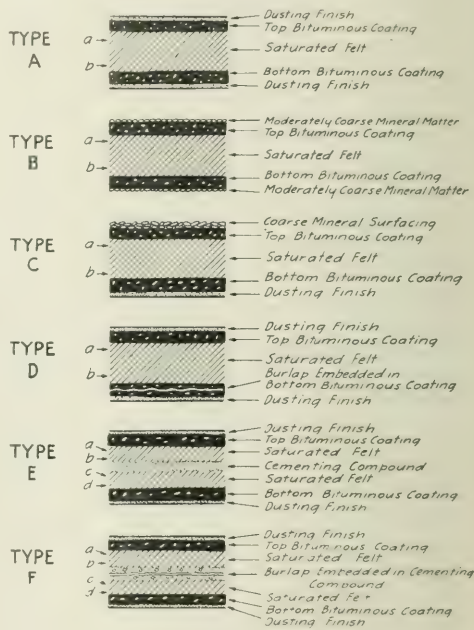


FIG. 1

coatings before they are applied to the roofing and while they are still in a molten condition, and for one or more of the following reasons:

- (1) To impart a color to the surface coating. For this purpose, bright mineral pigments of various colors are used and intimately mixed throughout a bituminous coating of a special composition.
- (2) To increase the weather resistance of the bituminous mixture.
- (3) To serve as an extender and reduce the cost of the finished product.

Where the roofing is composed of more than one sheet of fabric very fine mineral matter may be similarly mechanically mixed with the bituminous layer used to cement them together, for reason (2) or (3).

The various forms of prepared roofing are legion. For all general purposes, however, they may be divided into six types shown in Fig. 1.

TYPE A represents a layer of felt saturated and coated with bituminous matter. The surface coatings may be either finished plain or dusted with very fine mineral matter, and they may be either applied smooth and level, or with a veined appearance.

TYPE B is similar to Type A, but surfaced on *both* sides with moderately coarse mineral matter embedded in the coatings.

TYPE C is similar to Type A, but surfaced on *one* side with coarse mineral matter embedded in the coating.

TYPE D is composed of a layer of saturated felt and a layer of burlap or cotton duck cemented together and coated on top and bottom with bituminous matter. It is finished on the surface similar to Type A.

TYPE E is composed of two layers of saturated felt cemented together and coated with bituminous matter, being finished on the surface similar to Type A.

TYPE F is composed of two layers of saturated felt, cemented together with a layer of burlap in between, and coated with bituminous matter. Its surface is finished as in Type A.

Where burlap is used, it is merely embedded in the bituminous cementing or coating material without previously being saturated, due to the fact that burlap, on account of its structure, will not absorb the bituminous saturation in the same manner as felt.

PHYSICAL TESTS OF THE FINISHED ROOFING

The original material is tested for pliability, weight, thickness and tensile strength.

Pliability is tested by cutting lengthwise from the center of the roll a strip 1 in. wide, and commencing with the largest, successively bending it around various cylinders under water at temperatures of 77 and 32° F., respectively, recording the cylinder on which the surface cracks. Five cylinders are used in the test, measuring 2 1/2, 2, 1 1/2, 1 and 1/2 centimeter in diameter, respectively. A convenient apparatus for this purpose is shown in Fig. 2. The roofing should be bent parallel to itself, through an arc of 180°, at a uniform speed, and in exactly 2 seconds time.

The pliability is expressed in figures from 1 to 10, as follows:

GRADE PLIABILITY TESTS

- 1 May be bent through an arc of 180° in one direction (*i. e.*, flat on itself), and then through an arc of 360° in the other direction (*i. e.*, flat on itself) without cracking the surface coating.
- 2 May be bent flat on itself (*i. e.*, through an arc of 180°) without cracking the surface coatings, but will crack when bent through an arc of 360° in the other direction.
- 3 Surface cracks when bent through an arc of 180° flat on itself.
- 4 Surface cracks on the 2 1/2-cm. cylinder.
- 5 Surface cracks on the 1 1/2-cm. cylinder.
- 6 Surface cracks on the 1-cm. cylinder.
- 7 Surface cracks on the 2-cm. cylinder.
- 8 Surface cracks on the 1 1/2-cm. cylinder.
- 9 Both the surface and the interior of the sheet crack on the 2 1/2-cm. cylinder without, however, cracking *entirely* through the sheet.
- 10 The roofing cracks *entirely* through the sheet on the 1-cm. cylinder.

Weight, in lbs. per 100 sq. ft., is determined in accordance with the method to be described later.

Thickness, in mils. (thousandths of an inch), is determined with a micrometer caliper, with flat bearing surfaces about 1/2 in. in diameter.

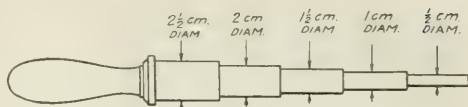


FIG. 2

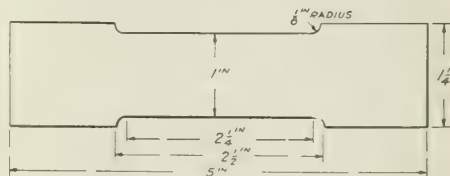


FIG. 3

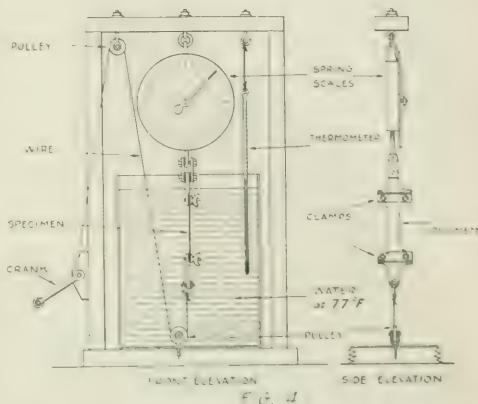


FIG. 4

Tensile Strength is determined by subjecting a specimen cut, in the direction of the length of the roll and of the dimensions shown in Fig. 3, to a tension which is increased at a uniform speed of 3 lbs. per second, the specimen being maintained at a uniform temperature of 77° F. during the test. A simple and effective instrument for finding the tensile strength is shown in Fig. 4. Ten such tests are averaged.

HEATING TESTS

(1) **Heating to 125° F. for 100 Hrs.**—A strip of the roofing is cut, exactly 12 in. x 12 in., care being taken not to disturb any of the detached mineral matter on the surface, and suspended in an oven from a chain which is fastened through holes in the upper edge of the strip. The piece of roofing should be allowed to hang freely and maintained at a temperature of 125° F. for 100 hrs. At the end of this time the roofing is allowed to cool. The pliability, weight, thickness and strength are redetermined, and the changes from the original values expressed in percentages. Any change in the appearance of the surface should also be noted, as well as softening of the mineral matter, absorption of the surface by the felt, any yellowing of the surface, blistering, etc.

Heating to 300° F. for 100 Hrs.—The same procedure is followed for the heating to 300° F. The loss in weight would indicate the volatile matter being driven off, and the change in the surface coatings would indicate the softening of the surface coatings. Any change in the appearance of the surface should also be noted, as well as softening of the mineral matter, absorption of the surface by the felt, any yellowing of the surface, blistering, etc.

dry out rapidly on exposure to the elements. Any yellowing of the mineral matter on the surface would indicate the presence of unstable oils in the bituminous matter.

(2) *Exposure to Air Saturated with Moisture at 77° F. for 100 Hrs.*—Accurately cut a strip of roofing 18 in. \times 18 in., and weigh. Remove the detached mineral particles from both sides of the sheet with a moderately stiff brush, and reweigh (area equals 2 $\frac{1}{4}$ sq. ft.). Suspend in a tight box containing sufficient water at the bottom to saturate the air with moisture. Cover tightly and allow the specimen to remain in the moist air for 100 hours at 77° F. As the moisture enters more readily through the cut edges of the sheet than through the surface itself, 6 in. should be trimmed from the edges at the termination of the test, leaving a strip measuring exactly 12 in. \times 12 in., representing the central portion of the original specimen, and weighing $\frac{4}{9}$ ths of the latter. Ascertain the weight, thickness and tensile strength of the 12 \times 12 portion at the end of the test, and calculate any variation from the original figures in percentage. The increase in weight should be figured on the basis of the original material including the detached mineral matter.

(3) *Immersion in Water at 77° F. for 100 Hrs.*—This test is run exactly the same as in the preceding, only in this case the specimen should be immersed entirely in water at 77° F. for 100 hours. An 18 in. \times 18 in. sheet of roofing should be used in making the test, and this should be trimmed to 12 in. \times 12 in. before redetermining its weight, thickness or strength.

Heating tests Nos. 2 and 3 show the susceptibility of the roofing to the action of dampness and water.

A skeleton of the physical tests just described is shown in Table I.

TABLE I—PHYSICAL TESTS OF PREPARED ROOFINGS

Original Material	After Heating to 125° F. for 100 hrs.	After Exposing to Air Saturated with Moisture at 77° F. for 100 hrs.	After Immersing in Water at 77° F. for 100 hrs.
Pliability at 77° F. <i>P</i>	<i>P</i> ₁
Pliability at 32° F. <i>p</i>	<i>p</i> ₁
Weight in lbs. per 100 sq. ft. <i>w</i>	<i>w</i> ₁	<i>w</i> ₂	<i>w</i> ₃
% Decrease in Weight.	$\frac{w - w_1}{w} \times 100$
% Increase in Weight.	$\frac{w_2 - w}{w} \times 100$	$\frac{w_3 - w}{w} \times 100$
Thickness in Mils. <i>t</i>	<i>t</i> ₁	<i>t</i> ₂	<i>t</i> ₃
% Decrease in Thickness ..	$\frac{t - t_1}{t} \times 100$
% Increase in Thickness.	$\frac{t_2 - t}{t} \times 100$	$\frac{t_3 - t}{t} \times 100$
Tensile Strength at 77° F. <i>s</i>	<i>s</i> ₁	<i>s</i> ₂	<i>s</i> ₃
% Decrease in Strength.	$\frac{s - s_2}{s} \times 100$	$\frac{s - s_3}{s} \times 100$
% Increase in Strength.	$\frac{s_1 - s}{s} \times 100$

A variation of these tests consists in first subjecting a specimen of the roofing to the action of moist air or water for 100 hrs., then drying at 125° F. for 100 hrs., re-subjecting to the action of moist air or water for another 100 hrs., and finally repeating the drying process for 100 hrs.

Although these tests throw considerable light on the behavior of the roofing towards atmospheric heat and moisture, nevertheless they fail to record one very important factor, namely, the effect of atmospheric oxidation. At the present time we know of no accelerated test by which this can be accurately measured. The effect of oxidation can be recorded only by actually submitting the roofing to an exposure test for a lengthy period of time. This question will be taken up in another paper.

SEPARATING PREPARED ROOFING INTO ITS COMPONENT PARTS

The mineral matter, bituminous matter and fibrous matter present are distributed in the following manner:

MINERAL MATTER

- 1—Detached } *Very Fine Mineral Matter* (e. g., finely ground talc, mica or silica) Types A, D, E and F (on top and bottom) also Type C (on bottom only).
- 2—Embedded in the top surface coating } *Moderately Coarse Mineral Matter* (e. g., sand, coarsely ground talc and coarse mica flakes) Type B (on top and bottom).
- 3—Embedded in the bottom surface coating } *Coarse Mineral Matter* (e. g., crushed slate, crushed brick or tile, crushed feldspar or granite, small pebbles or gravel) Type C (on top only).
- 4—Admixed with the top surface coating } May or may not be present. If present, consists of very fine mineral matter (e. g., Types A, B, C, D, E and F
- 5—Admixed with the bottom surface coating } fine mineral matter (e. g., Types A, B, C, D, E and F
- 6—Admixed with the cementing layer } clay, silica, limestone, shale colored mineral oxides, etc.) Types E and F

BITUMINOUS MATTER

- 1—Contained in the top surface coating (all types).
- 2—Contained in the bottom surface coating (all types).
- 3—Contained in the cementing layer (Types D and F).
- 4—Contained in the felt present in either one layer (Types A, B, C and D) or distributed in several layers (Types E and F).

FIBROUS MATTER

- 1—One or more layers of felt (all types).
- 2—Burlap or other fabric (Types E and F).

The separation of prepared roofing into its component parts is carried out as follows:

Weight per 100 Sq. Ft.—Carefully unpack the roll, taking care not to detach any of the mineral surfacing or dusting finish. Weigh the roofing after removing the wrapper, ends, nails and lap-cement packed in the core of the roll. Measure the length and breadth of the roll with a steel tape, recording the dimensions to $\frac{1}{16}$ in. Calculate the area in square feet.

Figure the weight of the finished roofing in lbs. per 100 sq. ft. (1)

Cut several strips exactly 3 in. wide across the sheet.

NOTE—With roofing 36 in. wide, these strips will measure exactly $\frac{3}{4}$ sq. ft., and with roofing 32 in. wide, they will measure $\frac{2}{3}$ sq. ft. Find the weight of each strip in grams.

Calculate the weight of the roofing in lbs. per 100 sq. ft. (2)

NOTE—With 36 in. roofing, wt. in lbs. per 100 sq. ft.

$$= 0.294 \times \text{wt. 3 in. strip in g.}$$

$$\text{With 32 in. roofing, wt. in lbs. per 100 sq. ft.}$$

$$= 0.331 \times \text{wt. 3 in. strip in g.}$$

CHECK—Result (1) should equal result (2).

Detached Mineral Matter—Remove the detached mineral particles from both sides of the 3-in. strips with a moderately stiff brush or cloth and reweigh in grams.

Calculate the weight Detached Mineral Matter in lbs. per 100 sq. ft. (3)

Dry Felt and Burlap; Total Embedded and Admixed Mineral Matter; Total Bituminous Matter—Extract one of the 3-in. strips in a Soxhlet extractor with benzol. Dry the extracted fabric together with any adhering mineral matter at 110° C. Cool in a desiccator and weigh the felt as rapidly as possible before it has an opportunity to absorb moisture from the air. Repeat the drying, until the weight is constant. Carefully brush off, weigh and set aside the adhering mineral matter.

Calculate the weight of each layer dry felt or burlap in lbs. per 100 sq. ft. (4)

NOTE—Use the separated felt or burlap for examining its physical and chemical characteristics according to the methods described later.

Separate the mineral matter from the benzol extract by filtering or centrifuging, wash clean with successive portions of benzol, dry and weigh. Combine with the mineral matter brushed off the extracted felt.

Calculate the weight of the total embedded and admixed mineral matter in lbs. per 100 sq. ft. (5)

Screen through a set of standard sieves of different mesh. A mere inspection of the particles retained by the various screens will enable one to separate the moderately coarse or coarse embedded mineral matter from any very fine admixed mineral matter present in Types B and C.

- Calculate the weight of moderately coarse or coarse embedded mineral matter in lbs. per 100 sq. ft. for Types B and C.
 Calculate the combined weights of very fine embedded mineral matter and admixed mineral matter in lbs. per 100 sq. ft. for Types A, D, E and F.
 Calculate the total weight of bituminous matter in lbs. per 100 sq. ft., i. e., $[1] - [(3) + (4) + (5)]$ (7)

Bituminous Saturation in the Felt—Warm a strip about 2 in. wide cut lengthwise from the roll, and tear off the coatings as shown in Fig. 5, taking care that in so doing as little as possible of the saturated felt is removed with the coatings, and, on the other hand, that *none* of the coatings or cementing layer remains adhering to the strip of saturated felt. The small arrows to the left of the various types of roofing illustrated in Fig. 1 indicate approximately where the layers should be separated. This can readily be accomplished with a little practice and dexterity. Where the roofing is composed of one layer of felt, as in Types A, B, C and D, the zone between the arrows *a* and *b* should be separated. Where the roofing is composed of two layers of felt, as in Types E and F, separate the zones between the arrows *a* and *b*, also *c* and *d*, respectively. In this manner, about 25 g. of the saturated felt (free from the coating or cementing layers) are obtained from each layer. Weigh and extract each portion separately in a Soxhlet with benzol. Dry

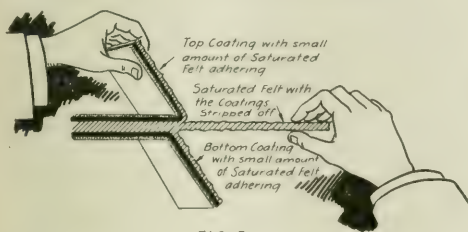


FIG. 5

the extracted felt at 110° C. to constant weight, desiccate and weigh. Calculate the weight of bituminous saturation by difference, and evaporate the benzol extract to exactly this weight.

NOTE—Use the residue of bituminous saturation recovered from each layer of felt for examining its physical and chemical characteristics, according to the methods described later.

- Calculate the per cent of bituminous saturation carried by each layer of dry felt..... (8)
 Calculate the weight of bituminous saturation present in each layer of the felt in lbs. per 100 sq. ft. [i. e., (8) \times (4)]..... (9)

Weights of Bituminous Matter in the Coatings and Cementing Layer—TYPES A, B, C AND D—The combined weights of bituminous matter in the top and bottom coatings expressed in lbs. per 100 sq. ft. may be calculated by subtracting (9) from (7).

To find the respective weights of bituminous matter in the top and bottom surface coatings, take a 3-in. strip cut across the sheet of roofing, from which the detached mineral matter has been removed, and split it lengthwise by tearing the felt midway between the points *a* and *b* (Fig. 1). Weigh and extract each section separately in a Soxhlet. Desiccate and weigh the dry felt in each section (and the burlap in Type D), also separate and weigh the total embedded and admixed mineral matter. Calculate the weight of bituminous saturation present [i. e., weight of dry felt \times (8)]. From the original weight of each

section subtract the combined weights of dry felt, bituminous saturation, embedded and admixed mineral matter. The difference represents the weight of bituminous matter in the surface coating carried by that particular section.

- Calculate the weights of bituminous matter in the top and bottom coats, respectively, in lbs. per 100 sq. ft..... (10)

IN TYPES E AND F—Take a 3-in. strip freed from the detached mineral matter as previously described, and split it into three sections, by tearing through the felt midway between the points *a* and *b*, also *c* and *d*, respectively (Fig. 1). Weigh and extract each of the three sections separately in a Soxhlet. Separate, and in each case weigh the dry felt (also the burlap in Type F), and the total mineral matter. Following the method previously described:

- Calculate weights of bituminous matter in the top and bottom coats respectively in lbs. per 100 sq. ft..... (11)
 Calculate weight of bituminous matter in the cementing layer in lbs. per 100 sq. ft.
 Calculate weight of very fine mineral matter admixed with the cementing layer in lbs. per 100 sq. ft.

Very fine Embedded Mineral Matter also admixed Mineral Matter, in the Top and Bottom Coatings, respectively—TYPES A, D, E AND F—Take another 3-in. strip from which the detached mineral matter has been brushed off, and remove the *outer* layer of the top and bottom coatings, respectively, by means of moderately rough sand paper. Enough of the surface should be scraped to remove every vestige of the very fine embedded mineral matter, and at the same time care should be taken *not* to cut

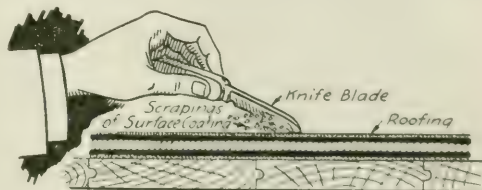


FIG. 6

completely through the surface coatings into the saturated felt underneath.

With Types A and D, split the scraped sheets lengthwise, midway between the points *a* and *b*. With Types E and F, split the scraped sheets lengthwise midway, respectively, between the points *a* and *b*, also *c* and *d*, discarding the central section. Extract the scraped outer sections separately with benzol, as before, recovering and weighing:

- The dry felt present in the respective scraped sections..... (12)
 The admixed mineral matter present in the scraped sections..... (13)
 The total bituminous matter present in the surface coating and saturating the felt in the respective scraped sections..... (14)
 The dry burlap in Type E.
 Calculate the bituminous matter present in the felt in the respective scraped sections $[8] \times 100 \times (12)]$ (15)
 Hence the bituminous matter present in the surface coating remaining on the respective scraped sections $\times (14) - (15)$ (16)
 The proportion of very fine mineral matter admixed with the bituminous matter in each coating $\times (13) \div (16)$ (17)
 Total weight of very fine mineral matter admixed with the respective coating in lbs. per 100 sq. ft. $\times (17) \times (16)$ in Types A and D or $(17) \times (13)$ in Types E and F..... (18)
 And weight of very fine mineral matter embedded in the surface of the respective coatings in lbs. per 100 sq. ft. $\times (13) \times (18)$ (19)

NOTES—(1) The *Admixed Mineral Matter in the Cementing Layer*.—Enough of the detached mineral matter found in the surface coating should be removed to make a representative portion of the

surface coating with a sharp knife. This is accomplished by holding the knife at right angles to the sheet of roofing resting on a firm, level surface, and rapidly drawing the blade sideways under moderate pressure (Fig. 6). Care should be taken to avoid scraping entirely through the surface coating. This is important. Weigh the scrapings, and then dissolve in benzol. Separate the mineral matter by filtering or centrifugating, and wash with successive portions of benzol. Dry and weigh the mineral matter. Calculate the weight of bituminous matter in the scrapings by difference, and evaporate the combined benzol extracts on the water bath to exactly this weight, completing the evaporation if necessary in an oven. Both surface coatings should be treated separately in this manner. In Type D the bottom coating can readily be removed by cooling the specimen in an ice-chest and rapidly tearing off the burlap, which will carry most of the bottom coat with it. This should be extracted, filtered and the extract evaporated to obtain the pure bituminous matter present.

With Type F the central web of burlap can be torn out, and the bituminous matter contained in the cementing layer separated in the same manner.

With Type E the bituminous matter can be separated from the cementing layer between the sheets of felt, by cooling in an ice-chest, rapidly tearing the specimen in two along the plane of the cementing layer, scraping and separating the bituminous matter as described for the surface coatings.

Use the residues of bituminous matter for examining their physical and chemical characteristics.

TESTING THE RAW FELT

Ash—The ash is determined by incineration and expressed in percentage.

Fibers Present—The percentage composition of the fibers is determined microscopically by staining them with a solution of zinc-chloride (composed of 20 g. of zinc chloride dissolved in 12 cc. of water to which is then added 4 g. of potassium iodide and 0.1 g. of iodine), and counting under a microscope having a magnification of about 100 diameters. The individual fibers are recognized by their characteristic shapes and the colors to which they are stained by the zinc-chloride solution. The percentages are ascertained by counting the fibers in a number of fields and finding their average. The following classes of fibers are reported:

Rag Fibers	Cotton fibers—stained wine-red
	Wool fibers—unstained by the solution
	Jute and manila fibers—stained a yellowish brown
Paper Fibers	Mechanical wood pulp—stained lemon-yellow
	Chemical wood pulp—stained grayish purple to purple

"Number"—This is an arbitrary figure adopted by the trade, corresponding to the weight in pounds of a ream consisting of 480 sheets, each measuring 12 in. \times 12 in.

Thickness—This is expressed in mils.

Mullen Strength—Since the raw felt is not susceptible to changes in temperature (as is the case with the finished roofing) it may be tested for tensile strength by means of the Mullen tester. The specimen is accordingly tested at room temperature by increasing the tension at a uniform speed of 2 lbs. per second until it ruptures.

Thickness Factor—This is equal to the thickness in mils divided by the "number" of the felt.

Strength Factor—This is equal to the Mullen strength in pounds divided by the "number" of the felt.

TESTING THE RAW BURLAP OR DUCK

Weight—In the case of burlap and cotton duck, the weight is figured in ounces per square yard, which is the customary way of designating these.

Thickness—Expressed in mils.

Mullen Strength—Determined as described for testing the raw felt.

BITUMINOUS COATING, SATURATION AND CEMENTING COMPOUNDS

These should be examined by means of the following tests:

Specific Gravity at 77° F.—Standard Method.

Hardness or Consistency at 115°, 77° and 32° F.

Fusing Point—Kraemer-Sarnow or Ball and Ring Method.

Volatile Matter—Standard Method.

Flash Point—Standard Method.

Saponifiable Constituents.

MINERAL SURFACING AND ADMIXED MINERAL MATTER

These should be subjected to a granularmetric analysis by passing them through a set of sieves and finding the percentage retained on the various sieves. Further knowledge can be gained regarding the character of the mineral matter, where required, by subjecting it to a quantitative analysis.

STANDARD PAINT COMPANY
WOOLWORTH BUILDING
NEW YORK CITY

TECHNICAL PHOTOGRAPHY AND ITS USE IN INDUSTRIAL AND COMMERCIAL ORGANIZATIONS

By JOHN H. GRAFF¹

It is not the aim of this paper to discuss the different technical manipulations of photography, but to illustrate how photography can be used technically for better efficiency and to good advantage in science, engineering, industry, and commerce, and how it is needed not only in big corporations or large engineering or research laboratories, but how practically no concern is so small that it can afford to be without photography in one form or another. With the exception of a very few large concerns that had some sort of photographic department for the sake of photographing salesmen's samples, etc., there was until very recently no concern that had installed a photographic department as a unit in their business—a photographic department whose first and foremost duty it was to serve all the other departments and the company as a whole; the writer believes himself to be one of the first in this line. He installed such a department in one of the larger concerns of the country for the sake of efficiency in each and all of the departments, and the photographic department of this concern to-day serves over fifty different departments of the corporation, so that what was a dream three years ago is to-day a necessity which none of the departments could be without.

It is clear that to serve fifty different departments efficiently, many technical problems must be solved, and the manager of the new department must not only be a photographer in the fullest sense of the word, but also must have a general knowledge of drawing, engineering in its different branches, elementary chemistry and physics, microscopy, business management, buying, selling and advertising—in other words technical photography. Embracing all this, the writer hopes to see some day the "Photographical Engineer," who has had fundamental practical and theoretical college training for this purpose.

Now, then, can technical photography be used in an industrial

¹ Technical Photographer of the Berlin Mills Co., Berlin, N. H.

or commercial organization so that it justifies a department of its own? A photographic department as such is of little or no value if it is not fitted for the particular conditions for which its service is expected; but I can give in this paper only a general outline of how photography can be used to good advantage in almost any concern or corporation.

I—To make copies, reductions and enlargements of maps, drawings, blue-prints, pencil sketches, typewritten matters, articles in magazines and books, photographs, prints, paintings, etc. This may be done either by contact prints in a large printing machine—as blue-prints, maduro prints (brown), Umbra prints (black and white), etc., or by the reproduction method with the Photostat or similar machines, or through the direct photographic method on plates to be printed or enlarged afterwards. The first method, of course, is known to every engineer and almost all commercial men; the others, however, need some explanation.

I know of no better efficiency device than the Photostat; its uses are manifold for copying drawings, maps, typewritten matter, pencil sketches and blue-prints, and the work is both cheap, quick and satisfactory, if the originals are not larger than the copying board and the sizes of the reproduction are within the capacity of the machine. Patching different parts of a print together is in many cases not satisfactory, as proper registering of lines can never be done.

For larger drawings and prints it is necessary to use plates and it will probably some time in the future be possible to use films (ordinary Process or Process Panchromatic) for line work. From these, prints or enlargements can be made to any size required, but it is well to remember that all enlargements of drawings and maps, etc., should be soaked in a glycerin bath before drying, so that they will remain flexible and soft.

Other copying or reproduction methods could be listed, but I mention only the "Photo Copier" mostly used for copying letters or documents, where four different exposures can be made on a 4×5 plate, and the "Dry-printing method," whereby any tracing can be reprinted on tracing cloth, ordinary linen or any kind of paper in as many copies as wanted, and, as the name implies, the prints are not bathed in water or any kind of chemical solution, and are naturally free from all shrinkage.

But no matter which method is the most practical to use in any case, it is evident that it is of both direct and indirect gain to be able to reproduce any drawing or map to any scale or size required, to save the original drawings and standardize the filing system, to reproduce copies of blue-prints and pencil drawings without having to trace same, to get uniform copies of book and magazine articles for filing purposes, and to have exact copies of deeds, contracts, and other documents and specifications, free from all possible human errors or misunderstandings.

II—To make photographic records of constructions, progress of constructions, machinery, tools, instruments and experimental apparatus. This is of importance, not only for the engineer and contractor for use in reports, for filing and for future reference, but for comparisons, estimates, controversies, advertising and many other cases too numerous to mention. No engineer or department head in charge should be without a first class hand camera, equipped with a good lens, and whether the service of a practical photographer is used or not, the responsible man in charge should at all times take a photograph of those observations which are worthy of report. It should be needless to mention that explorers, estimators, inspectors, commercial reporters and agents should always be equipped with the best of hand cameras and all of their reports and observations should be illustrated, the film or plates being developed, printed, cleaned, and filed in the company's own photographic department.

III—To compile true and correct photographic data for con-

troversies, court and accident cases. Nothing can be better for a true record than a photograph, and nothing is more convincing in a controversy, court or accident case, than a correct photographic illustration of same. Still nothing can be more misused, for good and many reasons. Photographic copies of maps, etc., are time and again not accepted by recorders of deeds. Photographic exhibits are denied admittance in court cases and the judge gets the blame instead of the photographer. But how can anything else be expected? Photography cannot lie, but not all photographers understand photography in general, and technical photography in particular.

It is about time that a state or federal examination be required for a license to take photographs of this kind. To pass such an examination, it should be required that, besides being able to explain the principles of photography, the applicant also should know the following:

- 1—How to photograph a drawing to a certain scale.
- 2—How to place a drawing so that all straight lines will photograph geometrically straight.
- 3—How to light a tracing so that he does not photograph the wrinkles instead of the lines, or both.
- 4—Where to use a Process plate and where not to use it.
- 5—The different principles of ordinary, Orthochromatic and Panchromatic plates, and their uses.
- 6—The principles of color filters and how to use same.
- 7—The different actions of color filters under daylight and different artificial illuminations.
- 8—Construction and use of all practical photographic cameras and equipment.
- 9—The construction of lenses and their proper use, focal lengths, achromatism and apochromatism, etc.
- 10—Practical geometry and perspective.

After a thorough examination for colorblindness, the applicant should finally be required to promise, under oath, that he will make all such photographs to the best of his knowledge and with the correct equipment and material.

Until such a time arrives, money and time will be spent uselessly, and many a disappointment will be had, but the court will not be to blame. Corporation heads demand not only college degrees or some similar education of the most of the men in their employ, but for some even a state or federal license. Even milkmen must have licenses to deliver milk, but when it comes to making a photographic record, deciding right or wrong, loss or gain, almost any one who can put his head under a focusing cloth is good enough.

IV—To prepare the right kind of photographs for newspapers, magazines or catalogues. This, of course, is again more or less in connection with the advertising end of a business, but no business will do much independent advertising without finding that it pays both indirectly and directly to have this done in their own department under the proper supervision.

V—Direct photography for advertising and the salesman's remedies.

It has been proved that the best of printing on the best of paper is the cheapest and best advertising, and, by the advance of photography, a still better advertising medium can be used—the photographs themselves—in the following ways:

- 1—Collectively on exhibitions to the general public.
- 2—As educational demonstrations to the retailer or middleman, as, for example, showing samples of window decorations, special products to be made of an article, methods of using same, comparison with inferior articles, or comparison of different physical properties, etc., in various ways.
- 3—As direct photographic samples of the articles where the real merchandise would be impracticable to carry in sample trucks. All of the foregoing matters can be done photographically in one or two photographs (as compared with many in the former ways) and the marketing salesman need make but a single trip to the place where the goods are only then used, and return home, but also that of the salesman. The great advantage with all points of consideration of the above is that these methods are physical processes and have no artificial bias to distort the

selling points to the best advantage. In short, the advertising manager and the photographer must work hand in hand, and together bring the advertising campaign to success.

VI—*To make direct color photographs for lithographic cuts, salesmen's illustrations, scientific purposes and court cases, where true color renderings are of importance.* This, however, is new, but is fully practical if handled properly and in fact is much more advanced and even more used in Europe than here; it offers unlimited opportunities for the technical photographer. Catalogs and magazine advertisements can be illustrated with correct and beautiful color prints, a thing which was impossible before. It is of practical importance for records and scientific research, and, if properly done by one who knows how, is of inestimable value in court and accident cases.

VII—*To make lantern slides in black and white or through direct color photography for advertising or for collective departmental education of the company's employees.* Here again we meet a photographic problem which has great possibilities, but as an advertising medium has often been misused because it has not been handled with technical skill and has not been organized for systematic follow-ups. As an advertising medium it is not only available for the manufacturer and wholesaler but also for the small merchant and retailer, in particular if directed and prepared by the manufacturer.

As an educational medium, lantern slides are invaluable. Such education not only raises the standard of the employees from the lowest to the highest, but it gives each one better understanding of his particular work in his own department and of his relation to the company as a whole. It brings all new methods and things of daily business interest before him and gradually elevates him from an ordinary laborer to a live unit in his department, so that, before long, he works for the pleasure of it and to advance the work itself.

VIII—*To make photomicrographs for scientific research and comparison of raw materials, and to record all microscopic observations not only for scientific purposes but also for manufacturing, buying, selling, and advertising.* The scientist has, for many years, made photomicrographs for his own particular scientific purposes and educational demonstrations, but it took a long time before this work began to be of any commercial value. To-day, however, with the strict demand for efficiency, the close competition and the almost undetectable substitutes of every kind of merchandise, commercial photomicrography is a necessity—the greater the business, the greater the need.

We must realize that nearly all physical and many chemical differences, no matter how small, can be detected with a microscope; and, therefore, they can be photographed and standardized.

Microscopic observations can be interpreted only by those with special training and long practice with same, but a photomicrograph can readily be understood by any intelligent man, in particular if he can make comparison with other photographs of standardized examples of the same product. Many commercial objects have already been standardized in their different forms and compositions and photographic charts of these can be bought with full descriptions for comparison, but much is yet to be done and in many cases each one must work out his own solution. If intelligently done and if proper records are kept, it will not be long before photomicrographic work will be of immeasurable value for comparison in manufacturing, for protection and checking in buying and awarding bids and as illustrative explanation in advertising and selling.

Many more uses of photography could be mentioned, but the subject is so many-sided that each industry and commercial establishment must be treated separately, if a true and convincing proof of its need for technical photography should be made.

How large, then, must a concern be before it has practical use for a photographic department?

Not all industrial or commercial concerns need or can afford a \$5000 equipment, but no up-to-date business of any kind, efficient and worth its salt, can afford to be without a photographic equipment of some kind. What the small industrial and commercial man cannot afford to do alone, he can do through his Chamber of Commerce, manufacturer, wholesalers' or jobbers' society; and no commercial association or agency for mutual benefit to members, either for importation, exportation, general distribution or what not, can afford to be without a photographic equipment if it aims to give efficient service.

"But who, then," I have been asked, "shall take care of my photographic work? Technical photographers evidently do not go begging for work, and besides I want to experiment only gradually and spend a small amount for an equipment."

Technical photographers are not born, and the best man any one could get, to start in an experimental way, would be a live young man already in one's employ, interested in the business and with intelligence and education enough to find what he is lacking, learn and apply the knowledge he acquires. For bigger concerns, however, the problem is more difficult, but there are intelligent young photographers to be found who are educated enough to apply themselves to technical and commercial problems, and, on the other hand, technical men are more and more taking up photography; it will not be long before the "Photographical Engineer" has a recognized profession.

How shall the beginner and experimenter properly select his equipment, arrange the room he can spare, select his material and get the proper instructions, so that no more money is spent than necessary?

Looking at it from the standpoint of advancement of photography, no one will be better situated and served than the industrial or business man who takes up photography for his own use. The manufacturers of photographic materials and instruments, from the very beginning of photography, have built their success on practical and thorough demonstrations to each individual user of their material. When amateur photography advanced, literature of the most instructive kind was freely distributed, traveling schools were organized and equipped and sent from city to city all over the country, giving demonstration lectures free of charge and for each advancement in photography new subjects were added. Just so, when the demand comes from the industrial and business man, he will not only be offered all the experience of photography in general, but his own point of view will be studied to assure the best possible fulfillment of his requirements.

As the engineer to-day orders a certain machine to fit his own local conditions, demands a certain capacity and so much to spare in case of increase of production, specifies drawings, costs, etc., the business man can to-day simply state his requirements in photography, the room he has to spare, cost limitation and his possible future demand, and he will not only be supplied with material fitting the conditions specified, but, when eventually decided, an expert will install the equipment and not leave the place before everything is understood and runs smoothly.

Photography applied to science, engineering, industry and commerce has come to stay.

CHAIRMAN'S ADDRESS¹ FERTILIZER DIVISION AMERICAN CHEMICAL SOCIETY

By J. E. BRACKENRIDGE

There has been some discussion as to the advisability of holding meetings during the war time, but it seems to me the

¹ Presented before the Fertilizer Division at the 55th Meeting of the American Chemical Society, Boston, September 10 to 13, 1917.

American Chemical Society has followed a right course in planning for their regular meetings, for there was never a time that we needed inspiration to push ahead in our various lines of work as much as we do now.

The Fertilizer Division of the American Chemical Society, I believe, has been the means of giving inspiration to many of us with the result that much has been accomplished in our division.

Our committees as a rule have been composed of State Chemists, Independent Chemists and Chemists of the Fertilizer Industry. By the representation of the Control Chemists, Referee Chemists and Industrial Chemists on committees, all sides of a problem can be presented and worked out to the mutual advantage of all.

The first step in analytical work is securing a fair and just sample. Last year our division took up that work and showed very plainly how different methods of sampling were used in various states, and that there was no Official Method of sampling. The committee referred the matter to the A. O. A. C., which organization appointed a committee to report an Official Method at their next meeting.

This method should include type of sampler, amount of sample drawn, amount sent to state laboratory, method for quartering at laboratory, including what size sieve the whole sample shall be put through before quartering. When we take into consideration the different specific gravities of various materials which enter a complete fertilizer, we see the need of a sample tube which will take material from top to bottom of bag. Acid phosphate weighs from 60 to 65 lbs. per cu. ft.; sulfate of ammonia, 53 lbs.; nitrate of soda, 65 lbs.; potash salts, 55 to 79 lbs.; tankage, 29 to 47 lbs.; blood, 39 lbs.; bone, 47 lbs.; land plaster, 72 lbs.

Considering the different specific gravities of the various materials it would seem reasonable to believe that, regardless of how well the materials were mixed in the factory, in transit a separation might take place and a sample that did not include some material all the way from top to bottom of bag would not be a fair sample.

I believe an official method based on the method used by the Indiana Station¹ would be fair and just to the Fertilizer Industry and do away with many deficient analysis complaints.

I would like very much to see the Indiana sampling tube adopted as the official sampling tube. Further, I would like to see the amount of samples to be taken at least 20 tubefuls from as many sacks, if shipment sampled includes that number; if not, 20 tubefuls taken from what was in shipment, the sampling tube to be inserted at one ear of the bag and run diagonally to the opposite bottom corner. This whole sample of 20 tubefuls, which would make about 5 to 6 lbs. should be sent to State Laboratory, where it should be screened through a No. 10 mesh sieve and then quartered before final preparation of the sample to be analyzed. If the above method should be adopted there could be no adverse comment on sampling.

This past year my attention has been called to the difficulty of securing closely agreeing results on nitrogen determinations, especially when nitrate nitrogen is present. On the same carefully prepared sample there was a difference of 0.20 per cent nitrogen on 2^d per cent nitrogen grade when tested by State Chemist, Independent and Industrial Chemists. Here I believe is a chance for some good work to be done and would recommend that the coming year the Fertilizer Division study this, to the end that the methods in use for determining nitrogen including nitrates be carefully tried on carefully prepared samples, having cooperation of State Chemists, Independent Chemists and Chemists of the Fertilizer Industry. If it is not possible to reduce the analytical error to at least 0.1 per cent nitrogen,

the fertilizer manufacturers must sacrifice more than seems fair on one element alone.

It is very gratifying to learn that our country is able to meet the emergency in nitrogen supply, and that the General Chemical Company and Solvay Company¹ offer a means of making this country independent of working under foreign patents.

In securing the available phosphoric acid necessary for the fertilizer business, sulfur is being successfully used to meet the shortage of pyrites for making sulfuric acid. Here is a chance for the careful chemist to see that the sulfuric acid is used to the best advantage, and that acid phosphate going into the trade has not been over-acidulated but has a free acid as low as possible. This can be accomplished by correct formulas for acid phosphate manufacture, together with right curing conditions.

Coming to the third element in Fertilizer Industry we find this country increasing the supply of potash. In a paper by R. K. Meade,² presented before the Institute of Chemical Engineers the prospects for potash production in this country are outlined from a Chemical Engineer's standpoint. We have a paper on the program covering the potash production in U. S.

I would, however, like to outline my own experience in rendering potash in feldspar soluble by mixing finely ground feldspar with rock dust, fluorspar and sulfuric acid.

As to the supply of feldspar in this country I would say that careful prospecting revealed no large amount of feldspar that would test as high as 10 per cent K_2O , and we were forced to seek a supply in Canada, where feldspar can be found in large quantities, testing 10 per cent K_2O and better.

Brief of a German Patent No. 188,651 (Oct. 2, 1906) entitled "Process for the Manufacture of Sodium Silicofluoride and Fertilizers," by A. G. Rütgerswerke reads as follows:³

"Substances containing fluorine and silicon, as, for example, feldspar (orthoclase), are added in definite quantities to the charge of raw materials for the manufacture of superphosphates. The vapors evolved in the subsequent working up of the charge are converted into sodium silicofluoride in the usual manner. The superphosphate obtained is specially valuable owing to its content of potassium."

It was found that the fluorine in phosphate rock was not sufficient to get good recovery of potash from feldspar, consequently fluorspar had to be added to furnish more fluorine. The feldspar required 40 per cent of its weight of sulfuric acid and was very hard on grinding machinery. The recovery of K_2O was 65 to 70 per cent, allowing for keeping the final mixture in dry enough condition to handle. The final product would test about 10 per cent "available P_2O_5 " and 1.20 to 1.50 per cent "water-soluble potash."

The cost of feldspar delivered, plus cost of sulfuric acid and fluorspar used, together with heavy cost of crushing and grinding feldspar, made the proposition uneconomical.

An attempt was made to recover the potash in feldspar by mixing fluorspar feldspar and sulfuric acid leaching the soluble salts and evaporating. Crystals were obtained which tested 21 per cent K_2O , but the cost per unit of K_2O was too high to offer any inducement for further work.

I believe this division should concentrate its efforts this coming year on the following: (1) To obtain an official method for sampling and have it adopted in as many states as possible. (2) To try out the methods for nitrogen to include nitrates, and see if it is not possible to keep the experimental error down to at least 0.1 per cent nitrogen.

AMERICAN AGRICULTURAL CHEMICAL SOCIETY
NEW YORK

¹ *THE JOURNAL*, 9 (1917), 1055.
² *Met. Eng. Chem.*, 17 (1917), No. 1, 18.
³ *U. S. Pat. No.* 1,277,000, 27.

¹ Purdue University Agr. Expt. Sta., Lafayette, Ind., Bull. 106.

METALLURGICAL SYMPOSIUM

Four papers read at the 55th Meeting of the American Chemical Society, Boston, September 10 to 13, 1917

PHYSICO-CHEMICAL DATA NEEDED BY METALLURGISTS

By J. W. RICHARDS

Metallurgical chemists are vitally concerned with the energy involved in the chemical reactions useful in metallurgical operations. These energies are based primarily on thermochemical data, and raise the question of the sufficiency of these data for metallurgical purposes.

They are woefully insufficient, and this from two standpoints: (1) thermochemical data at ordinary temperatures and (2) data permitting their evaluation at higher temperatures.

THERMOCHEMICAL DATA AT ORDINARY TEMPERATURES

These are the figures of the thermochemical tables. They give the heats or energies of formation of compounds as determined in the laboratory, starting and ending at or about room temperature. They enable us to figure out easily the energy of a chemical reaction beginning and ending at ordinary temperatures, when the heats of formation of all the substances concerned are contained in the tables. They give us no exact information at all about the energy of the chemical reaction at temperatures other than the ordinary room temperature.

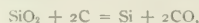
Even so, the tabulated data are often lacking. Thermochemists active in the past, such as Thomsen and Berthelot, gave us the energy of formation of most common compounds, but chemists have been increasing rapidly the list of known compounds and the thermochemical laboratories have not kept pace with them, but have fallen far behind.

Let us mention a few directions in which thermochemical data of the ordinary kind are sadly deficient or lacking: Combinations of metallic oxides with silica, forming silicate slags; combinations of metallic sulfides with each other, forming mattes; combinations of metallic arsenides with each other, forming speisses; combinations of metals with each other, forming alloys; heat of formation of iron pyrites, FeS_2 ; heats of formation of metallic arsenides, antimonides, nitrides, phosphides, silicides, carbides; heats of formation of metallic arsenates, antimonates, phosphates, tungstates, borates, molybdates, titanates, vanadates, chromates, manganates, aluminates. There are enough of these lacking data, needed now in metallurgical chemistry, to keep a dozen thermochemical laboratories busy for ten years. For every one which is being published (and this applies to antebellum conditions), a dozen or a score are urgently needed. Here is a wide field in which the thermochemist can be of immediate assistance to the scientific metallurgist.

THERMOCHEMICAL DATA AT HIGHER TEMPERATURES

The larger part of metallurgical reactions are carried on at temperatures above the ordinary, running up to 3000°C . in electric furnaces. But, for any temperature above the ordinary, the thermochemical data are not exact, and the energy involved in the reaction is different from what it is beginning and ending at room temperature.

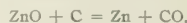
As an example: If we are reducing liquid silica in an electric furnace, at 1800°C ., to liquid silicon and CO gas, the energy calculated for the equation



taking the tabulated heats of formation of SiO_2 and CO, applies only to $15\text{--}20^\circ \text{C}$., and not to the actual conditions under which the reaction is taking place. Moreover, it applies only to solid

SiO_2 being reduced to solid Si, and not to the reaction when both these are in the liquid state.

As a further example: Distilling off zinc vapor from a mixture of ZnO and C, at a working temperature of 1050°C ., the energy absorbed is far from being the difference between the tabulated values used in the equation



because this involves the formation of solid zinc, while as the operation is actually performed, zinc vapor is produced. For such a reaction, the tabulated thermochemical heats of formation are only the starting point from which to evaluate the heat of the reaction at any temperature and for any physical state of the reacting substances and products.

A concise statement of the method of evaluating what is needed metallurgically from what is given by the ordinary tabulated thermochemical data, is as follows: The heat absorbed in a reaction at any temperature t is equal to the heat absorbed at ordinary temperature, as given by using the tabulated thermochemical data, increased numerically by the heat necessary to raise the reacting substances from ordinary temperature to t (including heat absorbed in any change of state—fusion or vaporization), and diminished by the heat which would be given out by the products of the reaction in cooling from t to room temperature (including likewise heat evolved in any change of state—condensation or solidification).

For these calculations, it is seen that we must, therefore, have some or all of the following data: Specific heats of all the substances involved in the reaction, in the physical state they possess at ordinary temperature; their latent heats of fusion (solidification); specific heats in the liquid state; latent heats of vaporization (condensation); specific heats in the gaseous state.

The physical chemist must be looked to for these data. There is no longer occasion to say that this work is the function of the physicist; three-fourths of the work of the physical chemist is physics and physical measurements, and the metallurgical chemist needs these data so badly that the physical chemist must make it his business to provide them for him. And they need providing, badly. Not one-tenth of the data which scientific metallurgists need and should have, is known and tabulated. We will briefly review what is needed.

SPECIFIC HEATS

These have been well worked at, but mostly only for temperatures between 100 and 0°C ., or room temperature. Such an average value for a short range is of little use to the metallurgist. He needs the specific heat curve, from its actual value at 0° to its actual value at the melting point, then its values in the liquid state to the boiling point, then its value for the gas or vapor. He wants a whole range of values, for all temperatures, while the tables usually give him only one. Or, putting it in another way, he wants the total heat content from any temperature down to zero.

Such heat content curves are known for some of the elements and for a few compounds, but not for many. Most of the determinations concern the substance only in the solid state, while it is needed also for the liquid and gaseous states. Out of forty metals, the specific heats of perhaps ten are known in the liquid state, and of only two as gases; of metallic compounds, which are much more numerous, the above statement may be repeated, with approximate accuracy. There are at least a hundred important metallic compounds which need to be studied in these respects.

LATENT HEAT OF FUSION

One has only to look in the best book of physicochemical tables published, to realize the paucity of information on this topic. For every one known there are a dozen important ones unknown. It would well repay any large metallurgical firm to hire an investigator to determine such of these factors as it is interested in. For instance, there are at least a dozen typical kinds of cast-iron, and there exists only a doubtful value for one kind. No reliable determinations have been made on steel, of any kind. No determinations are published for any kind of brass or bronze. The recent enlarged use of the electric furnace for melting metals has accentuated this deplorable lack of data on which to base metallurgical engineering calculations.

LATENT HEAT OF VAPORIZATION

What has just been said regarding latent heat of fusion applies with much greater urgency to the heat of vaporization. It has been experimentally determined for only three metals, and six metallic compounds, so that it is almost an unknown quantity. Yet we need it for all metals which are distilled, and for all metals and substances which are vaporized (at great expenditure of power) at the high temperatures in electric furnaces. The latent heat of vaporization of zinc, for instance, represents probably 25 per cent of the net thermal work done in a zinc retort, yet it is experimentally unknown. Metallurgists are looking expectantly to physical chemists for these experimental values, so necessary for correctly interpreting and studying chemical reactions at high temperatures.

VAPOR TENSION

One more topic of very similar nature which is pressing for investigation is the vapor tension of the metals and metallic compounds at various temperatures. For a few elements we have their vapor tension curves through a large range for the liquid element. For the solid element these are lacking, except for arsenic, selenium, iodine, phosphorus and sulfur. Yet the vapor tension of zinc below its melting point is the working force in the sherardizing process. Almost all metals lose weight in being melted, both before they melt and after melting, yet the data on which properly to study this phenomenon quantitatively are almost entirely lacking. In producing silicon, 25 per cent of the product is lost by vaporization; silver evaporates before it melts, like blocks of ice in a current of cold, dry air. Important consequences could be multiplied; the need of further accurate data is urgent.

EXAMPLE

As an example of what is needed in the way of physico-chemical data, we will instance zinc

Heat content solid, $0.0^\circ \text{C.} = 0.00000 \pm 0.000001$

Heat in solid at melting point, 45.2 calories

Latent heat of fusion, 12.6 calories

Heat in liquid at melting point, 67.8 calories

Specific heat liquid, 0.129 , not determined for all temperatures.

Heat in liquid at boiling point, 119.0 calories estimated

Latent heat of vaporization, 146.0 calories calculated from the vapor tension curves.

Heat in vapor at boiling point, 605.8 calories

Specific heat of vapor, 0.145 , calculated on theoretical grounds

Vapor tension liquid, 1.0×10^{-5} mm. ± 0.005 , $T = 817$ calculated from "Barn" observations

Vapor tension at the melting point, 0.003 mm. of mercury

Vapor tension solid, $\log 7$ mm. ± 0.005 , $T = 861$

Vapor tension at $0^\circ \text{C.} = 1 \times 10^{-10}$ mm. of mercury

The completeness of the data for zinc will emphasize, by comparison, the poverty of our data for other important metals, alloys and compounds. For brass and bronze, for instance, the most important alloys next to steel, we know only their specific heat from room to room, and the total heat content at the melting point, for only one variety of each.

If any properly equipped chemists are looking for experimental work which will be of immediate assistance to the metallurgical industries, we urge them to look at this field, with its great opportunities for service, and "do their bit" in this direction.

LEHIGH UNIVERSITY
SOUTH BETHLEHEM, PA.

RECENT DEVELOPMENTS IN CONNECTION WITH THE USE OF SULFUR DIOXIDE IN HYDROMETALLURGY

By EDWARD R. WETZEL

The researches on the metallurgy of copper conducted under the auspices of the Mellon Institute of Industrial Research since 1913 have aroused considerable interest but only preliminary announcements of the results of the experimental work have been made up to the present time. This contribution reports briefly upon the present status of the investigations and the results presented show the industrial value of the author's method for treating low-grade copper deposits.

The increasing adaptation of flotation to the treatment of low-grade copper ores has somewhat discouraged the use of leaching methods and accordingly these processes have not made the progress expected; but the field is still open for oxidized ores where flotation has not thus far been successfully applicable. Successful flotation assumes that the copper content of the ore is in the form of disseminated mineral. In the case of ores wherein the copper compound is diffused throughout the mass of gangue, such as is undoubtedly true of the copper silicate ores found at Inspiration, it is certain that flotation is out of the question and that some leaching process must be used. With the exception of the ammonia leaching process, all the hydrometallurgical processes in use are based upon the employment of sulfuric acid as the leaching agent and the copper is then precipitated by one of three methods: *viz.*, electrolytic, gas or iron. Of these methods, the electrolytic has received the preference, although in a few instances the iron process has been installed.

The experimental plant at Thompson, Nevada, was erected under the author's supervision and placed in operation by him on the first of April, 1916. The process employed therein is based upon the precipitation of copper by means of sulfur dioxide. Prior to its development, the use of sulfur dioxide for precipitating copper had been frequently suggested but was evidently not followed up on a sufficiently large scale to make apparent the defects and merits of the process.

The application of this process to large scale experimentation has developed several new features, as described in United States Patents issued to the author. These have so materially reduced the cost of operation in the experimental plant that it is now clear that the process possesses many advantages over the other competitor, the electrolytic process. The various innovations rendered imperative the elaboration of a process of physico-chemical detail for dealing with low-grade sulfidized and sulfate copper ores. In fact, the various chemical problems involved in the investigation had been satisfactorily solved and were available for use three years prior to the construction of the necessary mechanical equipment of the plant.

Of especial interest was the method of precipitating the copper from the solution and the process for the concentration of sulfur dioxide from various types of other combustion gases. The method of treatment is applicable to either treatment of "oxide" or "sulfate" copper ores. One hundred per cent yield of treatment is obtained by percolation in large tanks, but for best results a 60 per cent efficiency has been found with counter-current flow of solution. In precipitation, the solution is neutralized with lime and sprayed with sulfur dioxide and is then filtered and concentrated by evaporation to three or four times the original volume. The precipitation of metallic copper on a large scale when the solution

is brought to a temperature of 160° C., under a pressure of 100 lbs.

The results of the first year's operation, based upon the treatment of 5 tons of ore per day, show conclusively that the author's sulfur dioxide process can be operated continuously without interference from accumulated impurities in the solution. During this time various ores were treated, some containing a very high iron content, while others were high in lime, and in every case a satisfactory recovery of the copper content was obtained.¹

Theoretically, only twice the quantity of sulfuric acid originally present in combination with the copper is regenerated. In actual practice, however, the amount of sulfuric acid regenerated is above this amount. In fact, during the operation of the process it has been necessary to neutralize sulfuric acid with lime, in order to keep down the volume of the solution on hand. The copper assays, when melted, over 99 per cent pure and contains oxygen as the sole impurity. This copper is disposed of without further purification. The chief advantage of the process over other metallurgical procedures consists in its simplicity of construction and operation; no skilled labor is necessary and fewer men are required per ton of ore treated. The actual recovery of metallic copper approximates 90 per cent.

The mechanical arrangements are such that the processes of dissolution and precipitation are continuous. Heat is conserved by returning the hot precipitated solution through a heat exchanger in countercurrent to the flow of fresh solution to the precipitator. The latter is a lead-line cylinder through which the solution flows from bottom to top. The necessary temperature is obtained by circulating oil of high flash-point from a heater through the jacket surrounding the lead lining. Precipitated copper is discharged through a bottom gate into a receptacle, from which it is periodically removed, washed and melted.

An interesting phase of this research work and one of prospective economic importance is a process of concentrating the sulfur dioxide fumes or other gases weak in that constituent, which has been developed by Mr. G. A. Bragg. The plant was in continuous operation for one year, when it was decided to close down in order to increase the daily capacity and to install this method of concentrating sulfur dioxide.

MELLON INSTITUTE OF INDUSTRIAL RESEARCH
PITTSBURGH, PA.

THE IMPORTANCE OF THE FLOTATION PROCESS IN THE METALLURGY OF COPPER

By E. P. MATHEWSON

The flotation process has revolutionized the metallurgy of copper. Recently constructed plants, costing millions of dollars, have been discarded or scrapped and the flotation process introduced. Notable examples of this are the Washoe Reduction Works at Anaconda and the plants of the Utah Copper Company at Garfield, Utah.

It took considerable time to convince the copper metallurgists of the country that the flotation process was a success, but as soon as a satisfactory demonstration of the process was made, which occurred after numerous failures, these metallurgists took up the new process with avidity, scrapped their old plants and rebuilt to adopt this modern system of concentration.

The *Mining and Scientific Press* of San Francisco, under the able direction of T. A. Rickard, has published an immense amount of information about flotation and has given out the following figures, which are astounding when one considers

¹ Among the ores treated were silicious ores containing approximately 70 per cent of SiO₂ and high-lime ores running about 25 per cent of CaO. The excess acid resulting in the treatment of silicious ores was used in the extraction of copper from ore high in lime.

that the application of the process on anything more than an experimental scale is only a few years old:

FLOTATION—THE LEADING PROCESS IN THE METALLURGICAL FIELD	
TREATMENT	Tons per Annum
FLOTATION	30,000,000
Copper smelting	26,000,000
Gravity concentration	25,000,000
Gold and Silver milling	13,000,000
Lead smelting	5,500,000
Copper leaching	2,000,000
Zinc smelting	1,000,000

Of the figures given above, that for copper leaching is, perhaps, a little low, but it is so much smaller than the figure for flotation that it does not signify. Prior to the adoption of the flotation process in copper concentration the losses were seldom less than 20 per cent, whereas now they are seldom over 8 per cent. The figures published by the Anaconda Copper Mining Company indicate that the concentration loss in the most modern gravity concentration plant in existence was 17 per cent; now, with flotation, the loss is given at a trifle over 4 per cent. Other large establishments can show equally amazing results. The savings are now so great and the economies so extensive, due to the introduction of the process, that the so-called hold-up by owners of patents on the process cannot possibly cripple the users of the process, even if exemplary damages be allowed by the Courts.

The slime problem, the bugbear of copper metallurgists for a generation, has been solved by flotation. Many copper metallurgists will recall the numerous experiments conducted with a view to recovering the values from slime and the enormous sums of money expended in putting up plants that recovered only 60 per cent of the values from these slimes and which were considered marvels in their day. These plants, like the concentrators, have gone into the discard and now from the most pernicious slimes, savings of 90 per cent of the values by means of the flotation process are quite common.

Strange to say, the process is a rule-of-thumb development. The practical application of the process was first made on an extensive scale with zinc. Copper metallurgists never imagined in those days that the process would ever be applied in their specialty, but to-day the tonnage treated by the process is largely made up of copper ores, zinc long ago taking a secondary position.

Each particular ore seems to require a special treatment. This is because no satisfactory theory has as yet been evolved regarding the process. Many students are working on the problem with some promise of success, but at this writing we know less about flotation itself than we do about the true nature of electricity, while the results of the flotation process are as well known as the effects of electricity. Naturally, a process creating such enormous profits and handling such large tonnages has produced a great amount of litigation. We have had cases involving millions of dollars tried in various courts and the end is not yet. However, as indicated above, there is money enough in the process to pay for all the litigation and still leave a good return on the investments.

BRITISH AMERICA NICKEL CORPORATION, LTD.
TORONTO, CANADA

CHEMICALS USED IN ORE FLOTATION¹

By OLIVER C. RALSTON² AND L. D. YUND³

The flotation of minerals from ore-pulps, as practiced at present, involves the use of a small amount of a flotation "oil" which so modifies the water in the pulp that a froth is formed and that certain valuable minerals are gathered in the froth. The froth must have sufficient persistence to allow time for

¹ Published by permission of the Director, U. S. Bureau of Mines.

² Metallurgist, U. S. Bureau of Mines, Salt Lake City Station.

³ Metallurgical Research Fellow, University of Utah, 1916. Now Metallurgist, Stimpson Equipment Co., Salt Lake City.

separation from the body of the residual ore-pulp. This paper does not deal with the subject of flotation "oils" but rather with the other chemicals which are occasionally added to ore-pulps for one reason or another.

The development of ore flotation in a few years to a stage where over 100,000 tons of ore are treated every day in the United States, and half as much again in the rest of the world threatened, for a time, to upset disastrously market conditions for various products such as pine oil, coal creosotes, coal tar, etc. Incidentally, flotation has also opened a market for other chemicals which formerly could not be used in the western intermountain districts. Chemical engineering has never flourished in these districts on account of the smallness of the market but it is hoped that ore flotation will now open up new fields for the chemical engineer. The signs of the times point toward the speedy development of sulfuric acid plants at various smelters which are now wasting their sulfur in smoke, and on these plants many other industries will depend. Certain other chemicals will not require sulfuric acid in their manufacture but will soon find a market in these regions, due to the demands of flotation mills and of hydrometallurgical plants.

I shall outline briefly the most important of these chemicals and attempt to set forth the reasons for their use or the theories as to why they have certain definite effects.

ACIDS

Almost the only acid used for flotation work is sulfuric acid which costs less than most of the other available commercial acids. No one knows why the addition of sulfuric acid to certain pulps improves the flotation work. We do know that it often produces a cleaner flotation froth containing less gangue, and also that higher extractions are often made. Further it can reduce the amount of oil necessary to produce the same frothing effect. However, the addition of acid to an ore pulp sometimes proves fatal to good flotation, especially with some copper ores in which a part of the copper has been oxidized by weathering. Such an example is the ore at Inspiration, Arizona. In this latter case the trouble may be due to the formation of enough copper sulfate to spoil flotation, copper sulfate having been found deleterious in the flotation of a number of copper ores. The oxidized copper minerals dissolve easily in very dilute sulfuric acid solutions while the natural copper sulfides are not attacked.

When the addition of sulfuric acid causes an improvement in the flotation of a definite ore, its exact function is rather a difficult thing to explain, and theories are very conflicting. The phenomenon has been known since the very early development of the art. The Potter-Delprat processes depend on the acid to develop bubbles of gas through interaction on the carbonate minerals in the ore (such as calcite) in order to form a froth, and bubbles of air were not beaten into the pulp. Consequently it was natural that some of the early theories claimed that the addition of acid to a pulp being treated by air flotation caused an increased number of gas bubbles to form in the pulp and hence facilitated frothing out all the desirable mineral particles. The fallacy of this argument has long been felt.

Fanciful electrostatic theories have been advanced to explain flotation and the statement has been made by one theorist that the addition of an electrolyte to the water of the pulp allowed the electrostatic charges on the gangue particles to be conducted away while the charges on the particles of the desired minerals were insulated by a surrounding film of flotation oil. This electrostatic theory was soon exploded as it rested on a misapprehension as to just what caused charges to appear on suspended particles. The surfaces of small particles suspended in a liquid usually tend to adsorb more ions of one electric sign than of the other sign and hence carry apparent electrostatic charges. The thing to be noted, however, is that these charges

on the particles are not conducted away by the presence of electrolytes but their existence is dependent upon the presence of ions in the solution. The surfaces of oil droplets and of air bubbles likewise adsorb ions from solutions, and a certain parallelism between the charges on these various particles of matter and the conditions of good flotation has been observed. Just what is the inner connection has never been explained. It is an interesting fact that one mill in Colorado was reported to receive very pure water from melting snow and that flotation of its ore in this water was very unsatisfactory until the water was contaminated with an electrolyte, sulfuric acid being acceptable among other things.

Bancroft¹ calls attention to the fact that the acid in ore flotation may not react because of the replaceable hydrogen atom but by cutting down the concentration and consequently the adsorption of the hydroxyl ions. The connection which he wishes to draw with flotation is that "in acid and neutral solutions air seems to be adsorbed by organic liquids much more readily than by water," and he thus derives a reason for the attachment of the air bubbles to the oiled sulfides. The preferential adhesion of the oil to the valuable sulfide minerals in the presence of gangue minerals is well known.

The "surface tension" theorists have claimed that the addition of the proper electrolytes, like sulfuric acid, so alters the surface tension of the water that frothing can take place. This may be true without conflicting with the colloidal theory but we would call attention to the very small amounts of acid which sometimes produce a marked effect on flotation and the small resulting changes in surface tension of the water. Small amounts of electrolytes are sometimes known to produce profound changes in colloids and we feel more inclined toward the colloidal theory.

Nevertheless it is not right to claim that the replaceable hydrogen atom has nothing to do with the improvement in flotation results when acid is added. Allen and Ralston² have called attention to the fact that if an ore sample is ground dry it is usually necessary to use acid in its flotation, while it is often possible to grind this same ore in a wet condition in a ball- or pebble-mill and obtain the same flotation results without the use of acid. The natural inference is that the dry grinding has caused oxidized films to form on some of the particles of natural sulfides and that the sulfuric acid was needed to dissolve these films, leaving a clean unaltered surface for the action of the flotation oil and the air bubbles. This, of course, is only a special case and does not claim exception to the colloidal theory in the least.

As to the amounts of acid which are generally used and the ores on which it is generally applied, the amount used is usually the minimum which has been found to produce a given effect. It varies from 2 or 3 lbs. of sulfuric acid per ton of ore contained in 3 to 5 tons of water to as much as 100 or 200 lbs. of acid. When a large excess of acid is necessary we usually feel that it must be dissolving off oxidized films while small amounts of acid are probably effective in causing selective adsorption effects. Acid seems to be necessary in the flotation of many sphalerites and iron pyrites. Occasionally a pernicious copper ore needs acid. The Anaconda, Montana, flume constitute an example of such an ore. The present tendency among flotation men is to find substitutes for acid.

COPPER SULFATE

So much has been said about the "flotation mystery" involved in the improved results obtained at the Massey, Tennessee, plant of the American Zinc, Lead & Smelting Co., that a word should be said here. There is no doubt that the use of less than

¹ Walder D. Bancroft, *Ore Flotation*, McGraw-Hill, Eng. 14, 74-163, 631.

² *Mineral and Smelting Eng.*, Jan. 1 and Aug. 8, 1916.

1 lb. of copper sulfate per ton of ore, suspended in over 4 tons of water, has caused very much increased recoveries of the sphalerite in their ore and allowed cleaner work. The same effect has been noticed in many other mills treating zinc sulfide ores although an improvement in the flotation is not necessarily the invariable result of adding copper sulfate to zinc sulfide ores.

At Mascot, the large scale plant was unable to produce commercial results on the ore which had yielded good results in laboratory tests. A bucket of pulp taken from the mill and tested in the laboratory gave good results where the mill failed. At last it was realized that the bronze castings used in the laboratory machine might account for the difference and the hanging of a plate of copper in the mill pulp while it was passing through the large flotation machines corrected the difficulty, and led to the discovery of the effect of salts of copper on flotation of sphalerite. The method by which this discovery was made deserves commendation.

So much then for the fact. Copper sulfate added to the pulp improves the flotation of sphalerite but it has been called a flotation mystery because no one could explain it. Copper sulfate is deleterious in the flotation of silver ores¹ and of copper ores, its effects being overcome by precipitation with such a reagent as hydrogen sulfide, sodium sulfide or sodium carbonate.

Neither silver minerals nor copper minerals precipitate copper ions from solutions but it is well known that natural zinc sulfide reacts with copper sulfate solutions, precipitating copper sulfide. In fact, this reaction is used in the Huff electrostatic separation process for separating zinc sulfide from minerals of the same specific gravity and which are likewise poor electric conductors, such as barite. By soaking the mixture of minerals in a dilute copper sulfate solution a thin imperceptible film of copper sulfide is formed over the zinc sulfide particles and after drying they then act like good conductors and can be caused to jump off of the electrostatic separating machines, leaving the barite behind.

The suggestion is inevitable that in the case of improved flotation of sphalerite the copper going into solution is precipitated as copper sulfide on the surfaces of the zinc sulfide particles, making them capable of better flotation. Why the modified particles float better is the true mystery. Whether the increased electric conductivity of the surfaces of the particles has anything to do with it or whether copper sulfide has some inherent property of being more easily "oiled," is hard to say. Some rather simple experiments in the physical laboratory might well be suggested by what has been said above.

Some other effects which have not been previously recorded have been reported to us by F. G. Moses, one of the engineers of the General Engineering Co. He had observed the appearance of the tailing from the flotation machines treating a sphalerite ore, when it was passed over a slime-table (as a pilot to indicate the work of the flotation machine by the size of the concentrate streak produced). Before the addition of copper sulfate the slime in the tailing seemed impalpable but afterwards it has the appearance of curdled milk (flocculated). However, in a second mill the slime in the tailing still seemed to be deflocculated. In both instances the finely ground zinc sulfide in the concentrate seemed to be flocculated and in the second case the grade of the concentrate was raised considerably by passing it through a drag classifier from which some of the deflocculated gangue slime could overflow. This observation by a young engineer who kept his eyes open may be of a great deal of importance. We have often noticed the flocculated condition of the concentrate in flotation froths but had been inclined to attribute it to the oil which supposedly collected the

material into little flocs. Evidently the copper sulfate could assist in this flocculation, for it is well known that heavy metal ions are strongly adsorbed. In colloid chemistry it is usual to find very small amounts of such chemicals producing striking effects and it is probable that the extremely small amounts of copper sulfate involved in the case at hand are sufficient only for some colloidal reaction, be that what it may.

The condition of the concentrate and gangue particles, with regard to their degree of flocculation, has not been sufficiently investigated and we are hence confronted with the necessity of determining just what becomes of the copper introduced into such ore-pulps. Is it precipitated as copper sulfide or is it adsorbed?

LIME AND ALKALIES

Of late there has been a tendency to use various alkalies as addition agents in flotation, with the result that in many places they are competitors of acid. Of course, the best thing to do, if possible, is to find an oil mixture that will not call for any addition agent, but as long as the use of these further addition agents increases the extraction of the desired mineral or improves the grade of the concentrates enough to more than pay for the amount of addition agents used, they will not be displaced. The use of alkaline addition agents has advantages in lessening the corrosion of the machinery and often diminishes the amount of oil necessary. With alkaline pulp the oils can be added to the pulp ahead of the final grinding machinery so that the tube- or ball-mills can be caused to disseminate the flotation oil before the pulp reaches the flotation machinery.

Few people have reported any observations on the phenomena produced by the use of these addition agents beyond the improvement of the metallurgical results. There is no doubt but that soluble heavy-metal salts are precipitated by the use of these various alkaline substances and it is also well known that these heavy metal compounds are often deleterious to flotation, so that their removal by precipitation is imperative. Whether more than the amount of alkaline agent necessary to react with the deleterious salts should be added is not known. It is known that in a number of instances it has been possible to float a "tarnished" ore by the addition of various alkaline sodium salts where the same flotation oils did very little good when used on the ore alone. If sodium sulfide were the alkali used this would not be surprising as it could be easily seen that the sodium sulfide would react with copper carbonates and other oxidized minerals, forming sulfides and thus causing their flotation, but when sodium hydroxide brings about the same results it makes it seem possible that the thin films of oxidized material are dissolved off of the faces of the natural sulfide particles. This would be possible with zinc, copper or lead ores since the hydrates of these metals are somewhat soluble in sodium alkaline solutions. Instances of improvement of the grade of work with ores containing each of these metals are known. I have not heard of many instances of the improvement of the flotation of pyrite by the use of such addition agents. British Patent 5856 of 1914, granted to Minerals Separation and DeBavey's Processes Australia Proprietary, Ltd., states definitely that in the flotation of such tarnished ores the water in the circuit should be distinctly alkaline toward phenolphthalein. Sodium carbonate is the alkali preferred.

The use of caustic soda at a number of mills has resulted in some degree of satisfaction, especially with the porphyry copper ores. At the September, 1916, meeting of the American Institute of Mining Engineers, during the discussion of one of the papers, it developed that the Old Dominion mill at Globe, Arizona, was using caustic soda to the amount of 1 lb. per ton of ore. According to the metallurgist, Mr. Cramer,¹ this resulted

¹ An Occasional Correspondent, "Effects of Soluble Compounds of Ore on Flotation," *Min. Sci. Press*, Dec. 18, 1915.

¹ *Trans. Am. Inst. Min. Eng., Bull.* 119 (1916), 1891.

in a much less viscous froth which tended to lay more flatly in the flotation machine and was more easily broken down and ran more easily in the froth launders so that not so much water was required. This, in return, allowed better work in the overcrowded Dorr thickeners where the flotation concentrate was thickened before filtering. Further, the extraction was somewhat increased, the grade of the concentrate was raised and hence less "insoluble" was left in the concentrate. At still another mill a reduction in the flotation oil necessary also resulted.

It is noticed that such alkalis cause a weaker, more mobile froth. The effect of the addition of alkali to a ball of stiff clay lying on a board is well known. A drop of alkali will cause the clay to flatten out whereas the same amount of water does not. The alkali deflocculates the clay so that it "liquefies." The cause of the decreased viscosity of the froth in a flotation machine is hence easily understood. The higher extraction of the desirable mineral is also easily explained, because the alkali tends to deflocculate the gangue slimes and, therefore, any desirable mineral particles entrained in the gangue flocs will be liberated and become available for flotation. As a result of this, not so much excess of flotation oil and agitation will be necessary in the attempt to break up the flocs mechanically and bring the oil and air in contact with the sulfide minerals. Not so much air being necessary to bring the mineral particles to the surface there will not be such a large proportion of mechanically entrained gangue in the froth concentrate. In other words, all the effects above noticed can be explained on this assumption.

Of the various alkalis used, caustic soda, sodium silicate, sodium carbonate, sodium sulfide and lime are the principal commercial ones. Sodium silicate is a more powerful deflocculent than sodium hydrate, possibly due to a "protective" action of the colloidal silicic acid formed in dilute solutions. It was used for a while with success in the flotation plant of the Utah Leasing Co. but was later displaced by sodium carbonate. Our own experience with many different types of minerals, at the Salt Lake Station of the Bureau of Mines, has been that sodium carbonate is the most desirable alkali as it does not tend to deflocculate the gangue slimes so permanently, allowing easier thickening and filtration of the flotation concentrate and tailing.

A rather surprising claim is made in U. S. Patent 1,203,341 of October 31, 1916, granted to Allen C. Howard of the Minerals Separation Co. He claims that if alkaline substances are made up into a strong solution and the proper amount dripped into the first cell of a series of flotation machines a better result is obtained than where the circuit water which contains the ore is already alkaline to the same extent. Attempts to check this claim by experimentation in our laboratory have failed to justify it. The patent claims that in the mill of the Caucasus Copper Co., in the Caucasus, Southern Russia, this effect is quite marked. We fail to understand just how this can be so, and strongly suspect that the patent is actually attempting to claim the use of these alkalis in the manner in which they are most naturally used, in the form of a strong solution, the proper amount of which is dripped into the pulp at the most convenient point in the flow sheet. To avoid infringing the patent the alkali would have to be previously mixed with all the mill water before the ore was ground in it, which might easily prove more expensive and less easily performed.

Lime is not such a desirable addition agent as the alkaline sodium compounds and while it may cause desirable effects when added in small amounts an excess is often harmful. Lime and most other calcium compounds are merely flocculants of gangue lime, rather than deflocculants of the alkaline sodium compounds are. This may explain the difference between the two, although it has been continually hinted that we know entirely too little about the condition of flocculation of the ore

pulp during flotation. It is very probable that in the cases noticed where lime improves the flotation it functions in precipitating other less desirable soluble impurities such as the iron sulfates. At the Miami mill it was found that if lime were added to the pulp before entering the ball mills a somewhat increased extraction resulted whereas the addition of lime directly at the head of the flotation cells resulted disastrously. Supposedly the lime had to be allowed time enough to react with all the soluble or semisoluble impurities of the pulp before going to flotation so that there would be no raw caustic lime to cause trouble.

Sodium sulfide and calcium sulfide, or polysulfides, are used in the flotation of oxidized ores of lead and of copper. Hydrogen sulfide is also in use for the same purpose in the flotation of copper sulfide ores. The oxidized minerals are "sulfidized" by these chemicals and can be floated in the same manner that the natural sulfides can be floated. However, there is no objection to using sodium sulfide or the other sulfides to precipitate soluble heavy metal salts from solution. Hence these soluble sulfides can serve a double function. Three mills are now in operation using sodium sulfide in the sulfidizing of lead carbonate ores and several copper mills use it for oxidized copper compounds. The method is fairly satisfactory because only small amounts of the sodium sulfide are used, the lead carbonate particles being merely coated superficially with a film of lead sulfide which can be oiled and floated. As little as 3 lbs. of sodium sulfide per ton of a certain ore containing 15 per cent lead is successful in causing the flotation of over 90 per cent of the lead minerals. In case the ore contains manganese dioxide or basic iron sulfates or lead peroxide minerals these tend to use up the sodium sulfide before the lead carbonate is satisfactorily sulfidized. Since such minerals are fairly common in the oxidized ores of lead the method can be applied to only those ores which are free from such constituents. Hydrogen sulfide is in use in the mill of the Magna Copper Co., at Superior, Arizona, sulfidizing copper carbonates.

Of all the alkaline compounds mentioned above, lime is then cheapest but not the most desirable. Sodium carbonate is not only highly desirable but also can be obtained more cheaply than most of the other sodium compounds. In fact most of the flotation work which calls for the use of sodium carbonate is situated in the intermountain region not far distant from the alkaline lakes and natural trona deposits of the arid and semi-arid regions. An outlet for some of this natural soda has long been desired. At the present time most of the soda in use by flotation mills is shipped in from the east and is much purer and more expensive than the work demands.

Sodium sulfide also costs too much when delivered into the intermountain country from the middle west or the east. It can be made from nitre cake or from sodium sulfate by reduction. Sodium sulfate is available in a fair degree of purity from deposits on the bottom of Great Salt Lake or from Seaford Lake in California.

ORGANIC COMPOUNDS

Organic acids, like tartaric acid, citric acid, etc., and their salts, have been mentioned in British Patent 11,127 of 1914, granted to Geo. A. Chalmers, one of the Minerals Separation engineers. About the crude materials of preparation were added to the pulp in both the *Amesbury* Mountains and the *Barro Mountain*, New Mexico, and after the grinding stage was over. The liquid was then added into the pulp as it entered the first mill, in amounts varying from one to six lb. per ton of ore. Both of the ore mentioned were noted for the high percentage of soluble gangue, but in the latter case especially in the residual ore. The theoretical results were not so greatly increased. The effect of the organic acids was noted to be a better frothing or concentration of the gangue slimes. These organic acids and their salts are known to have a low dissociation constant and the theory

advanced in Chapman's patent is that these reagents do not flocculate the gangue slime so quickly but that the sulfide minerals escape entrainment in the flocs so that they are collected by the oil and air into the froth before flocculation of the gangue. To quote the words of the patent, "The effect of electrolytes upon colloids (as is known) depends *inter alia* upon the valency and upon the ionizing power or dissociation constant of the electrolyte. Tartaric acid is divalent and as compared to ordinary mineral acids it has a low dissociation constant. Citric acid has similar properties but is trivalent. Many other electrolytes such as organic acids and their salts also have similar properties as electrolytes and the choice of a suitable electrolyte for the purposes of this invention can be readily determined by a preliminary test."

This is a most interesting theory but I have noticed that citric acid, which is mentioned above, usually does not flocculate gangue slimes but rather exerts the reverse effect. It is probable that the effects of organic acids in flotation will be found to be as erratic as their adsorption effects, commonly known to colloid chemists.

SILICOFLUORIDES

British Patent 4,938, of 1914, granted to Sulman and Minerals Separation, calls for the use of silicofluorides as a substitute for acid in the flotation of ores. It is claimed that these compounds give the desired results. The complex fluorine salts have rather unusual ionization and other chemical constants and hence it might easily happen that their effects on flotation would be unusual and hard to predict. The diversity of the various compounds mentioned as having been patented by the Minerals Separation Co. shows how far their engineers and chemists have gone in developing the process of flotation.

A test of Broken Hill (Australia) tailing was made in London tap water without the addition of potassium fluoride and another test was made with this addition agent present to the extent of 3.4 lbs. per ton of ore. The oil used in each test amounted to 2.0 lbs. of eucalyptus oil per ton of ore. The data on the two tests are as follows:

Percentages in	ORDINARY FLOTATION	WITH SILICOFLUORIDES
Heading.....	Zinc 19.0 Lead 7.0	Zinc 19.0 Lead 7.0
Concentrate.....	Zinc 29.0 Lead 9.3	Zinc 36.1 Lead 14.7
Tailing.....	Zinc 14.4 Lead 2.5	Zinc 4.8 Lead 1.6
Recovery.....	Zinc 56.0 Lead 70.2	Zinc 86.2 Lead 88.5

The patent also makes a good suggestion that the silicofluorides can be prepared by adding hydrofluoric acid to the ore pulp. This produces soluble silicofluorides of the bases in the pulp. The main value of a substitute for sulfuric acid would be for ores containing a great deal of calcium carbonate or other acid-consuming materials in the gangue.

MISCELLANEOUS

CALCIUM SULFATE is a compound which has been added to ores containing colloidal gangue, although its success has been somewhat erratic. It was once used in one of the Broken Hill mills and its effect was that of an electrolyte. It is very sparingly soluble so that there can never be a high concentration of its ions in solution and it is hence more or less equivalent to the tartrates in providing ions rather slowly or in smaller quantity so that supposedly the flocculation of the gangue slime will not entrain particles of the desired mineral.

SODIUM MANGANATE AND SODIUM CHROMATE are two oxidizers recommended for differential flotation of two or more floatative minerals. They seem to deaden one or the other of the floatative

minerals so that it will not float. The exact mechanism of this deadening action is not known, for while chromates will deaden galena particles in the presence of sphalerite, manganese compounds have the reverse effect. They are very efficient in this type of work but there is a wide-spread impression among metallurgical men that they are too expensive. To be sure, the market prices on the chemicals usually sold are rather high but high purity of these compounds is not essential. There is no apparent reason why they should not be made by fusing local manganese or chromium ores with sodium carbonate. Manganese ores are usually easily available in most zinc and lead districts although the chromium ores are harder to obtain. Mill managers who have considered only potassium permanganate of the usual high commercial purity might well give their attention to the more cheaply prepared sodium manganate.

SULFUR DIOXIDE, SODIUM SULFATE AND SODIUM THIOSULFATE are inhibitors of flotation, if used in sufficient amounts. If sulfur dioxide is applied to an ore pulp, the first effect is one similar to that obtained when sulfuric acid is added to the pulp, an improvement in the flotation. However, if the sulfurous acid is allowed to act on the ore long enough to form sulfites the result will be non-selective flotation and the gangue will be floated with the desired mineral particles. The great use of such compounds has been found in differential flotation, the basic idea being to add just enough of one of these inhibitors to deaden the surfaces of one kind of floatative minerals while another group is only slightly affected and can still be floated. Mixtures of sphalerite, galena, pyrite and chalcocopyrite or any two of them usually need separation and, in case they need to be finely ground to be liberated from each other mechanically, differential flotation methods are in demand.

CHLORIDE OF LIME is a reagent said to be very good for differential flotation of sphalerite in the presence of pyrite.

SODIUM CYANIDE—In most cyanide mills whose tailings have been tested by flotation it has been found that the cyanide left in the tailing is deleterious to flotation. E. J. Atckisson has informed us that in some tests made by him with the ore of the Amparo Mining Co., of Mexico, this effect was noticed unless the amount of cyanide present was less than 0.007 per cent on the weight of the ore or 0.0018 per cent in the mill water, under which conditions improved flotation results were obtained over what could be done in water containing no cyanide.

At the mill of the Ohio Copper Co., Lark, Utah, mine water containing a rather high percentage of the sulfates of iron and similar impurities is used in the flotation and the addition of a small amount of cyanide has been found greatly to improve the flotation.

It is probable that in both these instances complex double cyanides are formed with the solutes in the mill water and it may even be that some of the most undesirable impurities are precipitated by the cyanide. So far as we know very little has been done in the study of the cyanogen compounds for flotation.

CONCLUSION

The use of certain chemicals in the flotation concentration of ores has been described and theories of the action of these chemicals have been explained. The use of chemical addition agents in ore-pulps during flotation is only in its infancy and as the process is better understood operators will make greater use of chemical addition agents which will allow them to obtain the highest economic results. The possibilities of such applications are almost unlimited and it is probably along lines of this kind that some of the great advances in ore flotation will be made.

CURRENT INDUSTRIAL NEWS

AUSTRALIAN WOLFRAM

A report, says *Chemical Trade Journal*, 61 (1917), 10, has been issued by the Director of Mines on the wolfram deposits at Hatches Creek in the northern territory of Australia. It is stated that the reefs are numerous, well-defined, with considerable persistence in size along the line of outcrop, and with the introduction of capital and better transport facilities the field is destined to become an important producer in the future. Without the introduction of capital for the development of the mines and the erection of crushing and concentrating machinery, there is likely to be a diminution in the production, as all the easily worked wolfram near the surface has been obtained. Although a great number of the reefs carry payable ore if worked on a large scale, together with suitable crushing machinery, they will not pay with the primitive methods now in use. From present appearances there are, on the other hand, a number of reefs which will prove highly payable for some considerable time to come.—A. MACMILLAN.

BONE FAT EXTRACTION IN GERMANY

The collection and utilization of bones has become a very important factor in German war industry. The *Berliner Tageblatt* describes the following various uses to which the bones may be put:

Fresh bones are subjected to a pressure of 4 to 6 atmospheres in autoclaves and fat for food purposes is thus extracted to the extent of 14 to 16 per cent of the raw bones. From cooked bones, if still fresh, 6 to 8 per cent of edible fat is extracted. The jelly remaining is worked into extract of beef or gravy cubes. The bones are then used for fodder and manure.

From bones no longer fresh, and unfit for the above purposes, a fat for technical purposes is extracted amounting to 8 to 10 per cent. The bone brew and bones are used for fodder and manure. The fat is used in glycerine, oleine, stearine and pitch. Recently, by a special refining process, it has been possible to use this fat also for food purposes.

A third class of bones has the fat extracted in an open boiler by a process not destroying the bones, which are then used for the manufacture of buttons, knife-handles and other bone goods. Neat's-foot oil is the extract from the fresh feet which, again, is used in making torpedo-lubricating oil. The jelly waste, as far as possible, is used for human consumption.

In Berlin, permission has been given to the magistracy to supervise the extraction of edible fat from fresh bones including the fresh waste from private houses and hotels.—M.

SUBSTITUTE FOR PINE ROSIN

According to a recent German patent (No. 208,391), a substitute for pine rosin may be obtained as follows: Lignites which show a woody structure and are derived from conifers are extracted with suitable solvents, the solution being afterwards filtered off and evaporated. The rosin, so obtained, gives a lustrous, conchoidal fracture and is brown in color. It may be refined by melting in a pan fitted with stirrers and treating with a small percentage of caustic potash, milk of lime or sodium aluminate which is added in a thin stream with energetic stirring. The clear rosin is filtered off after settling. The rosin soaps are used for the recovery of their contained rosin in the extraction of fresh lignite. The rosin obtained by this method can be used in soap making or in paper making, in which latter case it is converted into a rosin paste with carbonate of soda or caustic soda and afterwards, in the pulp, into an alumina rosin soap by means of sodium aluminate. The rosin can also be used in place of pine rosin in making lacquers, varnishes and lubricants. M.

KOREAN VEGETABLE DYES

The British Consul at Seoul has forwarded particulars regarding the production of dyestuffs in Korea from the leaves of a species of maple tree known to Koreans as the "Shinnamu." The tree is very common throughout Korea, and, according to the Director of the Technical Institute of Korea, is not found elsewhere, except to some extent in that part of Manchuria immediately to the north of the Yalu River. It is stated that, if the dye should prove of commercial value it could be produced in very large quantities in Korea. The cost of production is put at 12 cents per lb.

With colors obtained from the "Shinnamu" extract, cotton goods can be dyed black, indigo, dark grey, grey, or khaki. In dyeing silk and pongees, black only can be used, and the chief value of the extract is for loading purposes, silk yarns or materials becoming over 30 per cent heavier after treatment.

Particulars of the methods of using a yellow or khaki dye produced in Korea from the flower of the "Enju" or "Pagoda" tree have also been forwarded by the Consul. Silk, wool and cotton are all susceptible of treatment with this dye. Samples of the above may be seen at the Board of Trade Offices, London.—M.

NORWAY'S STEEL PRODUCTION

For some time means have been discussed for increasing Norway's production of iron and steel, so as to make the country more independent of foreign supplies, a shortage of which might prove a most serious matter, not only for the Norwegian industry, but also and even more so from a military point of view. The Strømmen works will receive a subsidy of 51,200 kroner so as to be able to increase their production of steel from 5,000 tons to 10,000 tons per annum.

In order to increase the Norwegian production of steel from 12,000 tons to 24,000 tons and to put down a rolling mill having a minimum production of 10,000 tons of rolled products, the Christiania Spikerverk is to receive, for a period of 5 years, a premium of 8 kroner per ton of rolled steel made. The new installations of the Strømmen works, says *Engineering*, 104 (1917), 26, are not to commence operation until war mobilization takes place and the steel to be produced there will be ingots for projectiles, etc. The Christiania Spikerverk, on the other hand, is to start under a new scheme in peace time only and its rolled products are to be mainly for use in ferro-concrete work.—M.

IRISH CHEMICAL INDUSTRIES

Brief data concerning the chemical industries of Dublin and district are given in the Year-book for 1917 of the Dublin Chamber of Commerce. As might be expected in a country so largely dependent upon agriculture, the manufacture of fertilizers is an important industry of Dublin. The factories are among the largest in the United Kingdom, an average of 100,000 tons of chemical manures being turned out annually. The weekly production of sulphuric acid is said to be about 100 tons. The fertilizer industry in Ireland employs upwards of 20,000 men, while other major factories in Dublin City, Drogheda, Limerick, and Waterford give employment to an equal number of workmen. A considerable branch of traffic in bone appears in the context of fertilizers, and this is said to have been further developed. Other branches of the chemical industry which are fairly well established and around the City of Dublin are the manufacture of soda ash, soda ash from waste, and soda ash from waste, and the heavy development of these manufactures at Limerick.—M.

TUBING FOR ELECTRIC WIRES

In a recent issue of the *Electrical World*, Mr. R. Radcliffe describes the following plan for making tubing for the protection of electric wires:

Coat a straight brass or iron rod heavily with melted paraffin and allow to cool. Then mix one part of plaster of Paris with $2\frac{1}{2}$ parts of water, adding a small quantity of lime. Tear muslin strips one inch wide and dip in the mixture. After allowing them to absorb all they will hold, wind them smoothly around the rod, working slantwise, end to end. Enough layers may be applied to give the desired thickness. When the plaster is thoroughly hardened, beat the metal core until the paraffin is soft enough to permit removal of the rod. Tubing made in this way is a non-conductor, heat-resisting, slightly flexible, and can be cut into desired lengths with a hacksaw.—M.

CEMENT FROM SUGAR BEET

Experiments in French plants, says *La Revue* of Paris, commenced early in 1917, have resulted in the production of an excellent cement as a by-product of beet sugar refining. The first step in the production of sugar from beet consists in boiling them. It has, therefore, been customary to throw away as valueless the scum formed on the cauldrons. This scum, however, has been found to contain large quantities of carbonate of lime, and it has been estimated that 4000 tons of the carbonate can be recovered from 70,000 tons of beet. To this quantity of carbonate, 1,100 tons of clay are added, the resultant product being a cement, which is described as being of perfect quality. The beet scum is pumped into large reservoirs and allowed to evaporate for a certain length of time before being mixed with the clay. It is then stirred or beaten for an hour before being fed into a rotary oven such as is used for making Portland cement.—M.

PHOSPHORUS PRODUCTION IN JAPAN

Like potassium chlorate, phosphorus is also being produced beyond the home demand, says a Tokyo contemporary. Soon after the outbreak of war, the Nippon Chemical Industry Company, the Tokyo Electro-Chemistry Company, and the Fizi Chemical Industry Company, succeeded in manufacturing it, and their total production is about 100,000 lbs. per month, which is more than the home demand. The price, once \$600 per 100 lbs., has been reduced to \$120 per 100 lbs. This overproduction has caused an export to China and Russia. The export, however, has been restricted and must not exceed 3,000 lbs. of red phosphorus and 5,000 lbs. of yellow phosphorus. The new phosphor ore is imported from Oceania and electric power is rather cheap in this quarter so that the phosphorus manufacturing industry is certainly hopeful after peace is restored.—M.

MONAZITE SAND

The mineral survey now being conducted in Ceylon in co-operation with the Imperial Institute has, says the *Chemical Trade Journal*, led to the discovery of beach deposits of monazite sand which will usefully supplement the commercial supplies of thorium required for the manufacture of incandescent gas mantles. Samples of the sand have been investigated by the Imperial Institute, London, and the results are so promising that the Ceylon Government has arranged to work the deposits. Suitable British concentrating machinery has been selected by the Institute for the purpose, after experimental trials, and will be shipped shortly to Ceylon. It is interesting to note that the work of the mineral survey has shown that Ceylon can furnish several other thorium minerals besides monazite. Among these is thorianite, the richest known source of thorium. This new mineral, when it first came on the market, was sold in England at as high a price as \$8,000 per ton.—M.

ENGLISH CHINA CLAY

Progress is being made, says the *Chemical Trade Journal*, 61 (1917), 186, with the promotion of the Associated China Clays, Ltd., which is the title of the new centralized organization for the disposal of the wares of china clay producers. The scheme owes its origin to the war, it having been shown that during periods of depression all engaged in the trade suffered from the unrestricted competition between the various producers, involving severe cutting of prices in order to get into the restricted markets prevailing at such times. The agency is not, in any sense, a trust, and, in the fixing of prices, regard will be made to demands and to the competition of other clays and other materials which may come into competition with English clays.—M.

ACTION OF LIGHT ON BRIGHT COLORS

According to an article in the *Färber Zeitung*, the cause of the action of light on coloring matter is that the absorbed light rays set the molecules of the coloring matter in vibration. Brilliant colors owe this property to the fact that the molecules do not greatly influence the amplitude of vibration of the entering light waves, so that the intensity of the transmitted (reflected) and absorbed waves is only slightly reduced. Consequently, the amplitude of the absorbed waves remains large and the resulting vibrations of the molecules are very considerable and, by reducing the forces of affinity, are the cause of the high photochemical activity of the bright colors.

In the case of dull colors the amplitude of the chemically active waves is small and the molecules of the coloring matter are not caused to vibrate to the same extent although, even in these, decomposition may be set up.

For a color to be fast to light, its molecules must be very stable, a condition which is fulfilled by large molecules of simple closed constitution free from reactive side chains and substituents. A beneficial effect is produced by increasing the size of the molecule by chemical combination with the fiber such as takes place in dyeing wool. Coloring matters are also stabilized by metallic oxides, as is shown by the effect of the formation of lakes with mordants (aluminum, iron, etc.) and, after treatment with copper sulfate, in improving the fastness to light.—M.

CELLULOSE ESTER LACQUERS FOR LEATHER TRADE

According to a contemporary, cellulose ester lacquers and the like for the leather trade can be prepared from cellulose scrap by dissolving in amyl acetate, amyl formate, amyl and propyl alcohol, ether-alcohol, acetone, chlorinated hydrocarbons (tetrachlorethane) and diluents, such as light benzene, benzol, toluol, methyl alcohol, oil of turpentine, etc.; an opaque lacquer is obtained by using a solvent that is of high boiling point, or not quite anhydrous. Oils, such as castor oil and linseed oil, are sometimes employed to give increased flexibility and resins to impart body and lustre. The coloring matters may consist of pigments or dyestuffs that are soluble in alcohol though the former are liable to render the lacquer brittle by catalytic oxidation of the oil. The use of ultramarine and certain color lacquers that are sensitive to free acids should be avoided.—M.

JAPAN'S COPPER ORE OUTPUT

Japan's copper ore output in 1916 was 111,562 tons as compared with 83,017 tons in 1915 and 78,700 tons in 1914. The exports for 1916 amounted to 57,402 tons as against 56,528 tons for 1915 and 43,305 tons for 1914. Russia buys 60 per cent of Japan's copper exports, the United Kingdom 20 per cent, while France, the United States and India share the rest. The consumption of copper ore in Japan has increased considerably during the last three years, amounting to 59,690 tons in 1916 compared with 27,723 in 1915 and 32,045 tons in 1914.—M.

FERRO-SILICON ANALYSIS

Dr. Herwig in a recent issue of *Stahl und Eisen* points out that it is possible to dispense with expensive platinum crucibles in analyzing ferro-silicon alloys and to use iron crucibles if, instead of the usual carbonate of soda or potash method, sodium dioxide is used in the ignition mixture. Great care must be taken to reduce the ferro-silicon to as fine a powder as possible, to remove all coarse particles and to mix the powdered silicon thoroughly and very uniformly with the dioxide, as otherwise dangerous ebullition might take place which would nearly empty the crucible and the spattering endanger the analyst's eyes. The author gives a comparative list of 22 analyses made—one half by the sulfate, the other by the dioxide method of ferro-silicons ranging in silicon content between 10.75 and 90.78 per cent. The differences in the results obtained by the two methods range only between +0.05 and -0.13 per cent.—M.

MELTING POINTS OF FIREBRICKS

The melting point of a firebrick is understood to be the lowest observed temperature at which it exhibits transition from the rigid to the liquid state. Mr. William M. Barr states in *Industrial Engineering* that the melting points of 45 samples of firebrick including fireclay, bauxite, silica, magnesia and chromite brick have been determined in an electric vacuum furnace, the temperature being measured by an optical pyrometer, and the following melting points found: Kaolin, 1,740° C.; pure alumina, 2,010° C.; pure silica, 1,600° C.; bauxite, 1,820° C.; bauxite clay, 1,795° C.; chromite, 2,180° C.; magnesite brick, 2,165° C.—M.

BRITISH BOARD OF TRADE

During the month of August the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.

MACHINERY AND PLANT FOR

Making wire brushes for beating wool
Making firelighters
Making textile name tabs
Manufacture of horn and bone buttons
Making conical paper tubes for use in textile machinery
Waterproofing paper by coating with pitch
Advertising novelties
Anemometers for measuring the consumption of air in refrigerators
Bolts and handles for toy trunks
Collar studs, metal, for export
Combs, amber, for export
Cryolite
Crystal corundum
Darning cups used in making camel hair brushes

Eucalyptus red gum
Feldspar for china manufacture
Frames for ladies handbags
Gingelly or Sesame oil
Heavy steel spoons, electro tinned
Leather patch for hat-making machines
Metal frames for bags and purses
Needles (steel) for gramophones and phonographs
Photo-fumes, metal, especially tin
Red sulfide of arsenic
Saccharin
Sedum oil
Strontium carbonate
Stannic chloride
Stearic acid slabs
Sulfur (3 tons) flowers, 2 tons roll
Synthetic essential oil of mustard
Thumbles, nickel, for Italy

FENCING WIRE FOR SOUTH AMERICA

In view of the world's demand for meat, a demand that is likely to continue after the war is over, most of the South and Central American governments are urging the extension of the cattle-raising industry and some are financing the less wealthy landowners in the matter of fencing in their properties. Thus, says the *Times Trade Supplement*, a strong call is being experienced for fencing wire of which but a small portion can be satisfied. There are, moreover, no factories producing this material in South America, every single coil having to be imported. The class of fencing mostly met with is that made of two or three strands of wire stretched along a line of posts—mostly wooden—posts, but galvanized barb wire is also in request. Shortly before the war, Germany had acquired a large share of this trade.—M.

OIL-BREAK SWITCHGEAR

A pamphlet has been issued by the British Thomson-Houston Company, describing 3-phase switchgear of the iron-clad, draw-out, oil-break type, intended for mining and industrial service where compact, totally enclosed, dust-proof and drip-proof apparatus is required. The oil-switch instruments (if they are mounted with the oil-switch) and automatic features are mounted on a sliding carriage and connected to the bus-bars or cables through plug-contacts. The parts are designed to be readily accessible, so that all the essential pieces can be freely inspected after they have been rendered "dead" by withdrawing the carriage. The switches are of the free-handle type, so that they cannot be held closed on a short circuit or heavy overload, and have an accelerated gravity break, a double break on each pole and an ample head of oil. Barriers are inserted between phases, exceptionally large clearances are allowed between all live parts and earthed metal work, and there is no metal used in the neighborhood of the sparking fingers. The handles are interlocked so that it is impossible to withdraw or close the isolating contacts unless the oil-switch is in the off position, nor can the switch body be opened or the oil break removed unless the isolating contacts have been separated making all parts "dead." The cover must be removed before the isolating switch contact can be closed, and it is impossible to push the switch home accidentally before the cover has been replaced. The switches can be electrically interlocked with a controller or other starting apparatus by means of a patent device which is fitted in conjunction with the low-voltage release, and is so arranged that not only will the switch open when the line voltage falls but also cannot be closed again until the controller or starter handle is moved to the off-position.—M.

WAR AND RUSSIAN TRADE DIVERSION

The enormous effect on Russian trade brought about by the war is well illustrated by some recently published statistics. In 1913, the total imports were valued at Rs. 1,220,539,000. Of this total Germany contributed more than half, viz., Rs. 642,765,000. In 1916, the total had grown to Rs. 1,716,518,000, and the German trade had died away to Rs. 9,064,000. On the other hand, that of the United Kingdom had increased to Rs. 616,100,000, that of the United States to Rs. 422,388,000 and that of France to Rs. 170,211,000. In addition, the trade through Finland also showed a big increase. The imports of copper last year were 1,675,000 pounds (1 pound = 36.113 lbs.) as compared with 678,000 pounds in 1915. Imports of nickel were 344,000 pounds against 122,000 pounds and of aluminum 289,000 pounds against 211,000 pounds. The great bulk of the copper came from the United States and there were also consignments from Japan.—M.

AEROPLANES

A writer in *La Nature* for August 4 discusses the special features which aeroplanes of the chase and bombardment types should possess for adequately carrying out the work assigned to them. He takes as example of the two classes, the "Gotha" type *7 p.*, the type which has been prominent in recent air raids, and the albatross. The "Gotha" type is characterized by extensive plane area, high engine capacity and its powerful armament. The latest type carry 600 kilos of bombs. The power necessary is furnished by two motors of 100 to 180 h. p. each. The plane cover an area of about 100 sq. meters, while the total length of the aeroplane is 12 meters and the span 21 meters. A speed of 120 kilom. per hour can be attained. The D. I. type has a Mercedes engine of 100 h. p., a plane area of about 24 sq. meters, a length of 9 meters and a span of 4 meters. It has a speed of 100 kilom. per hour. Further interesting details of the construction of these two types of aeroplanes are given in the article quoted.—M.

SCIENTIFIC SOCIETIES

TENTATIVE STANDARD METHODS FOR THE SAMPLING AND ANALYSIS OF COMMERCIAL FATS AND OILS, OTHER THAN THOSE OF THE COCONUT, BUTTER AND LINSEED GROUPS

The following methods have been adopted by the *Committee on the Analysis of Commercial Fats and Oils of the Division of Industrial Chemists and Chemical Engineers of the AMERICAN CHEMICAL SOCIETY* as tentative standards for the use of the trade, pending their official adoption by the American Chemical Society.

They are the result of thirty months continuous and conscientious effort on the part of the committee and they have given excellent satisfaction in the hands of the members of the committee and others who have used them, and have been found to answer the commercial needs of the fat and oil industry in a satisfactory manner.

They are published here for the purpose of adoption by any contracting parties so desiring and for the purpose of eliciting suggestions and criticisms from fat and oil chemists. Communications on the subject of the methods should be addressed to W. D. RICHARDSON, c/o SWIFT & COMPANY, CHICAGO, and will be presented to the committee at their regular monthly meeting next following.

The committee is now working on methods designed to apply particularly to the coconut, butter and linseed groups, and these methods, when adopted by the committee, will include SAPONIFICATION NUMBER, IODINE NUMBER and REICHERT-MEISSL NUMBER. When completed they will be incorporated in the methods printed below.

TENTATIVE STANDARD METHODS FOR THE SAMPLING OF COMMERCIAL FATS AND OILS

Adopted September 22, 1916

Any or all of the following tentative standard methods may be used or inserted in contracts at the option of the parties concerned.

TANK CARS

1. **SAMPLING WHILE LOADING**—Sample shall be taken at discharge end of pipe where it enters tank car dome. The total sample taken shall be not less than 50 lbs. and shall be a composite of small samples of about one pound each, taken at regular intervals during the entire period of loading.

The sample thus obtained is thoroughly mixed and uniform 3-lb. portions placed in air-tight 3-lb. metal containers. At least three such samples shall be put up, one for the buyer, one for the seller and the third to be sent to a referee chemist in case of dispute. All samples are to be promptly and correctly labeled and sealed.

2. **SAMPLING FROM CAR ON TRACK**¹—(a) *When contents are solid.*² In this case the sample is taken by means of a large tryer measuring about 2 in. across and about 1½ times the depth of the car in length. Several tryerfuls are taken vertically and obliquely toward the ends of the car until 50 lbs. are accumulated, when the sample is softened, mixed and handled as under (1).

(b) *When contents are liquid.* The sample taken is to be a 50-lb. composite made up of numerous small samples taken from the top, bottom and intermediate points by means of a bottle or metal container with removable stopper or top. This de-

¹ Live steam must not be turned into tank cars or coils before samples are drawn, since there is no certain way of telling when coils are free from leak.

² If there is water present under the solid material, this must be noted and estimated separately.

vice, attached to a suitable pole, is lowered to the various desired depths, when the stopper or top is removed and the container allowed to fill. The 50-lb. sample thus obtained is handled as under (1).

(c) *When contents are in semi-solid conditions, or, when stearine has separated from liquid portions.* In this case a combination of (a) or (b) may be used, or, by agreement of the parties, the whole may be melted and procedure (b) followed.

BARRELS, TIERCES, CASKS, DRUMS, AND OTHER PACKAGES

All packages shall be sampled, unless by special agreement the parties arrange to sample a lesser number; but, in any case, not less than 10 per cent of the total number shall be sampled. The total sample taken shall be at least 20 lbs. in weight for each 100 barrels, or equivalent.

1. **BARRELS, TIERCES AND CASKS**—(a) *When contents are solid.* The small samples shall be taken by a tryer through the bung-hole or through a special hole bored in the head or side for the purpose, with a 1-in. or larger auger. Care should be taken to avoid and eliminate all borings and chips from the sample. The tryer is inserted in such a way as to reach the head of the barrel, tierce, or cask. The large sample is softened, mixed and handled according to TANK CARS (1).

(b) *When contents are liquid.* In this case use is made of a glass tube with constricted lower end. This is inserted slowly and allowed to fill with the liquid, when the upper end is closed and the tube withdrawn, the contents being allowed to drain into the sample container. After the entire sample is taken it is thoroughly mixed and handled according to TANK CARS (1).

(c) *When contents are semi-solid.* In this case the tryer or a glass tube with larger outlet is used depending on the degree of fluidity.

(d) *Very hard materials, such as natural and artificial stearines.* By preference the barrels are stripped and samples obtained by breaking up contents of at least 10 per cent of the packages. This procedure is to be followed also in the case of cakes shipped in sacks. When shipped in the form of small pieces in sacks they can be sampled by grab sampling and quartering. In all cases the final procedure is as outlined under TANK CARS (1).

2. **DRUMS**—Samples are to be taken as under (1), use being made of the bung hole. The tryer or tube should be sufficiently long to reach to the ends of the drum.

3. **OTHER PACKAGES**—Tubs, pails and other small packages not mentioned above are to be sampled by tryer or tube (depending on fluidity) as outlined above, the tryer or tube being inserted diagonally whenever possible.

4. **MIXED LOTS AND PACKAGES**—When lots of tallow or other fats are received in packages of various shapes and sizes, and especially wherein the fat itself is of variable composition, such must be left to the judgment of the sampler. If variable, the contents of each package should be mixed as thoroughly as possible and the amount of the individual samples taken made proportional to the sizes of the packages.

TENTATIVE STANDARD METHODS FOR THE ANALYSIS OF COMMERCIAL FATS AND OILS, OTHER THAN THOSE OF THE COCONUT, BUTTER AND LINSEED GROUPS

Adopted September 22, 1916

SAMPLE

The sample must be representative and at least 3 lbs. in weight and taken in accordance with the STANDARD METHODS FOR THE SAMPLING OF COMMERCIAL FATS AND OILS (given above). It must be kept in an air-tight container in a dark, cool place.

Soften the sample by means of a gentle heat taking care not

to melt it. When sufficiently softened, mix the sample thoroughly by means of a mechanical egg beater or other equally effective mechanical mixer.

MOISTURE AND VOLATILE MATTER

APPARATUS: *Vacuum Oven*—The committee Standard Oven.

Moisture Dish—A shallow glass dish, lipped, beaker form, approximately 6 to 7 cm. diameter and 4 cm. deep shall be standard.

DETERMINATION—Weigh out 5 grams (± 0.2 gram) of the prepared sample into a moisture dish. Dry to constant weight *in vacuo* at a uniform temperature, not less than 15° C., nor more than 20° C. above the boiling point of water at the working pressure, which must not exceed 90 mm. of mercury.¹ Constant weight is attained when successive dryings for 1-hr. periods show

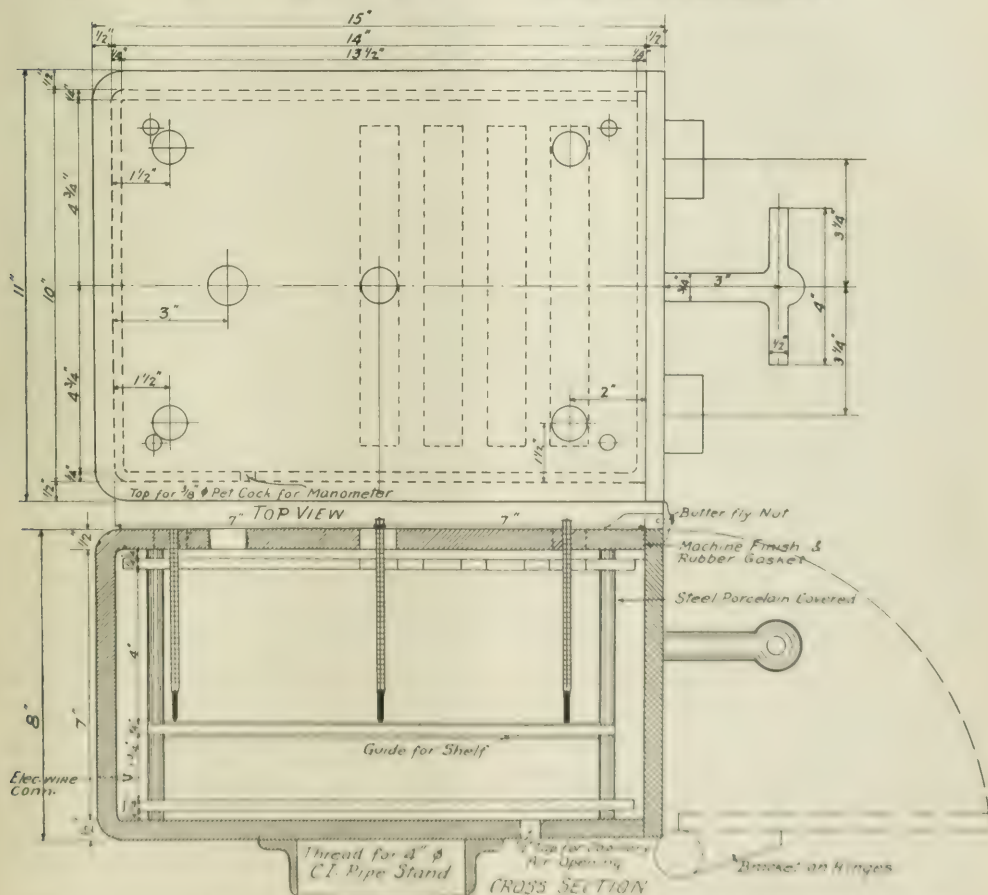
an additional loss of not more than 0.05 per cent. Report loss in weight as MOISTURE AND VOLATILE MATTER.¹

SUGGESTION FOR ROUTINE CONTROL WORK

The following method is suggested by the committee for routine control work: Weigh out 5- to 25-gram portions of prepared sample into a glass or aluminum² beaker or casserole and heat on a heavy asbestos board over burner or hot plate, taking care that the temperature of the sample does not go above 150° C. at any time. During the heating rotate the vessel gently on the board by hand to avoid sputtering or too rapid evolution of moisture. The proper length of time of heating is judged by absence of rising bubbles of steam, by the absence of foam or by other signs known to the operator. Avoid overheating of sample as indicated by smoking or darkening. Cool in desiccator and weigh.

¹ Results comparable to those of the Standard Method may be obtained on most fats and oils by drying 5-gram portions of the sample, prepared and weighed as above, to constant weight in a well constructed and well ventilated air oven held uniformly at a temperature of 105 to 110° C. The thermometer bulb should be close to the sample. The definition of constant weight is the same as for the Standard Method.

* Caution: Aluminum soap may be formed



INSOLUBLE IMPURITIES

Dissolve the residue from the *moisture and volatile matter* determination by heating it on a steam bath with 50 cc. of kerosene. Filter the solution through a Gooch crucible properly prepared with asbestos,¹ wash the insoluble matter five times with 10-cc. portions of *hot* kerosene, and finally wash the residual kerosene out thoroughly with petroleum ether. Dry the crucible and contents to constant weight as in the determination of moisture and volatile matter and report results as **INSOLUBLE IMPURITIES**.

SOLUBLE MINERAL MATTER

Place the combined kerosene filtrate and kerosene washings from the insoluble impurities determination in a platinum dish. Place in this an ashless filter paper folded in the form of a cone, apex up. Light the apex of the cone, whereupon the bulk of the kerosene burns quietly. Ash the residue in a muffle, to constant weight, taking care that the decomposition of carbonates is complete, and report the result as **SOLUBLE MINERAL MATTER**.²

FREE FATTY ACIDS

The **ALCOHOL**³ used shall be approximately 95 per cent ethyl alcohol, freshly distilled from sodium hydroxide, which with phenolphthalein gives a definite and distinct end-point.

DETERMINATION—Weigh 1 to 15 g. of the prepared sample into an Erlenmeyer flask, using the smaller quantity in the case of dark colored, high acid fats. Add 50 to 100 cc. hot, neutral alcohol, and titrate with $N/2$, $N/4$ or $N/10$ sodium hydroxide, depending on the fatty acid content, using phenolphthalein as indicator. Calculate to **OLEIC ACID**. In the case of palm oil the results may also be expressed in terms of **PALMITIC ACID**, clearly indicating the two methods of calculation in the report.

TITER

STANDARD THERMOMETER—The thermometer is graduated at zero and in tenths of a degree from 10 to 65°, with one auxiliary reservoir at the upper end and another between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark is at least 1 cm. below the 10° mark; the 10° mark is about 3 or 4 cm. above the bulb, the length of the thermometer being about 37 cm. over all. The thermometer has been annealed for 75 hours at 450° C. and the bulb is of Jena normal 16^{mm} glass, or its equivalent, moderately thin, so that the thermometer will be quick-acting. The bulb is about 3 cm. long and 6 mm. in diameter. The stem of the thermometer is 6 mm. in diameter and made of the best thermometer tubing, with scale etched on the stem; the graduation is clear cut and distinct, but quite fine. The thermometer must be certified by the U. S. Bureau of Standards.

GLYCEROL CAUSTIC SOLUTION—Dissolve 250 g. potassium hydroxide in 1000 cc. dynamite glycerin with the aid of heat.

DETERMINATION⁴—Heat 75 cc. of the glycerol-caustic solution to 150° C. and add 50 g. of the melted fat. Stir the mixture well and continue heating until the melt is homogeneous, at no time allowing the temperature to exceed 150° C. Allow to cool somewhat and carefully add 50 cc. of 50 per cent sulfuric acid. Now add hot water and heat until the fatty acids separate out perfectly clear. Draw off the acid water and wash the fatty acids with hot water until free from mineral acid, then

¹ For routine-control work, filter paper is sometimes more convenient than a prepared Gooch crucible. It must be very carefully washed to remove the last traces of fat, especially the rim.

² For routine work, an ash may be run on the original fat, and the soluble mineral matter obtained by deducting the ash on the insoluble impurities from this. In this case the Gooch crucible should be prepared with an ignited asbestos mat so that the impurities may be ashed directly after being weighed. In all cases ignition should be to constant weight so as to insure complete decomposition of carbonates.

³ For routine work methyl or denatured ethyl alcohol of approximately 95 per cent strength may be used. With these reagents the end-point is not sharp.

⁴ For routine work during period of high prices see p. 1069.

filter and heat to 130° C. as rapidly as possible, with stirring. Transfer the fatty acids, when cooled somewhat, to a 1 in. by 4 in. titer tube, placed in a 16-oz. salt-mouth bottle of clear glass, fitted with a cork which is perforated so as to hold the tube rigidly when in position. Suspend the titer thermometer so that it can be used as a stirrer and stir the fatty acids slowly (about 100 revolutions per minute) until the mercury remains stationary for 30 seconds. Allow the thermometer to hang quietly with the bulb in the center of the tube and report the highest point to which the mercury rises as the **TITER** of the fatty acids. The titer should be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

UNSAFONIFIABLE MATTER

EXTRACTION CYLINDER—The cylinder shall be glass stoppered, graduated at 40 cc., 80 cc. and 130 cc. and of the following dimensions; diameter about 1 $\frac{3}{8}$ in., height about 12 in.

PETROLEUM ETHER—Redistilled petroleum ether boiling under 75° C. shall be used. A blank must be made by evaporating 250 cc. with about 0.25 gram of stearin or other hard fat (previously brought to constant weight by heating) and drying as in the actual determination. The blank must not exceed a few milligrams.

DETERMINATION—Weigh 5 grams (± 0.20 gram) of the prepared sample into a 200 cc. Erlenmeyer flask, add 30 cc. of redistilled 95 per cent (approximately) ethyl alcohol and 5 cc. of 50 per cent aqueous potassium hydroxide, and boil the mixture for 1 hour under a reflux condenser. Transfer to the extraction cylinder and wash to the 40 cc. mark with redistilled 95 per cent ethyl alcohol. Complete the transfer, first with warm, then with cold water, till the total volume amounts to 80 cc. Cool the cylinder and contents to room temperature and add 50 cc. of petroleum ether. Shake vigorously for 1 minute and allow to settle until both layers are clear, when the volume of the upper layer should be about 40 cc. Draw off the petroleum ether layer as closely as possible by means of a slender glass siphon into a separatory funnel of 500 cc. capacity. Repeat extraction four more times, using 50 cc. of petroleum ether each time.¹

Wash the combined extracts in a separatory funnel three times with 25-cc. portions of 10 per cent alcohol, shaking vigorously each time. Transfer the petroleum ether extract to a wide-mouth tared flask or beaker, and evaporate the petroleum ether on a steam bath in an air current. Dry as in the method for **MOISTURE AND VOLATILE MATTER**. Any blank must be deducted from this weight before calculating unsaponifiable matter. Test the final residue for solubility in 50 cc. petroleum ether at room temperature. Filter and wash free from the insoluble residue, if any, evaporate and dry in the same manner as before.

NOTES ON THE ABOVE TENTATIVE METHODS

SAMPLING

The standard size sample adopted by the committee is at least 3 lbs. in weight. The committee realizes that this amount is larger than any samples furnished representing shipments of from 20,000 to 60,000 lbs., but it believes that the requirement of a larger sample is desirable and will work toward uniform and more concordant results in analysis. It will probably continue to be the custom of the trade to submit smaller buyers' samples than required by the committee, but these are to be considered only as samples for inspection and not for analysis. The standard analytical sample must consist of 3 lbs. or more.

The reasons for keeping samples in a dark, cool place are obvious. This is to prevent an increase in rancidity and any undue increase in fatty acids. In the case of many fats the committee has found in its cooperative analytical work that free acid tends to increase very rapidly. This tendency is minimized by low temperatures.

¹ When the unsaponifiable matter runs over 5 per cent, more extractions are recommended.

MOISTURE AND VOLATILE MATTER

After careful consideration the committee has decided that moisture is best determined in a vacuum oven of the design which accompanies the above report. Numerous results on check samples have confirmed the committee's conclusions. The oven recommended by the committee is constructed on the basis of well-known principles and it is hoped that this type will be adopted generally by chemists who are called upon to analyze fats and oils. The experiments of the committee indicate that it is a most difficult matter to design a vacuum oven which will produce uniform temperature throughout, and one of the principal ideas in the design adopted is uniformity of temperature over the entire single shelf. This idea has not quite been realized in practice, but, nevertheless, the present design approaches much closer to the ideal than other vacuum ovens commonly used. In the drawing above the essential dimensions are those between the heating units and the shelf and the length and breadth of the outer casting. The standard Fat Analysis Committee oven (F. A. C. oven) can be furnished by Messrs. E. H. Sargent & Company, 125 West Lake Street, Chicago.

The committee realizes that for routine work a quicker method is desirable and has added one such method and has also stated the conditions under which comparable results can be obtained by means of the ordinary well ventilated air oven held at 105 to 110° C. However, in accordance with a fundamental principle adopted by the committee at its first meeting, only one standard method is adopted and declared official for each determination.

The committee realizes that in the case of all methods for determining moisture by means of loss on heating that there may be a loss due to volatile matter (especially fatty acids) other than water. The title of the determination MOISTURE AND VOLATILE MATTER indicates this idea, but any considerable error from this source may occur only in the case of high acid fats and oils and particularly those containing lower fatty acids such as coconut and palm kernel oil, work on which is now in progress to be reported at a later date. In the case of extracted greases which have not been properly purified, some of the solvent may also be included in the moisture and volatile matter determination but inasmuch as the solvent, usually a petroleum product, can be considered only as foreign matter, for commercial purposes it is entirely proper to include it with the moisture. The committee has also considered the various distillation methods for the determination of moisture in fats and oils, but since, according to the fundamental principles which it was endeavoring to follow, it could standardize only one method, it was decided that the most desirable one on the whole was the vacuum oven method as given. There are cases wherein a chemist may find it desirable to check a moisture determination or investigate the moisture content of a fat or oil further by means of one of the distillation methods.

INSOLUBLE IMPURITIES

This determination, the title for which was adopted after careful consideration, determines the impurities which have generally been known as dirt, suspended matter, suspended solids, foreign solids, foreign matter, etc., in the past. The first solvent recommended by the committee is hot kerosene to be followed by petroleum ether kept at ordinary room temperature. Petroleum ether, cold or only slightly warm, is not a good fat and metallic soap solvent, whereas hot kerosene dissolves these substances readily, and for this reason the committee has recommended the double solvent method to exclude metallic soaps which are determined below as soluble mineral matter.

SOLUBLE MINERAL MATTER

Soluble mineral matter represents mineral matter combined with fatty acid in the form of soaps in solution in the fat or oil. Formerly, the mineral matter was often determined in combination by weighing the separated metallic soap or by weighing it

in conjunction with the insoluble impurities. Since the soaps present consist mostly of lime soap, it has been customary to calculate the lime present therein by taking one-tenth the weight of the total metallic soaps. The standard method as given above is direct and involves no calculation. The routine method given in the note has been placed among the methods, although not adopted as a standard method, for the reason that it is in use in some laboratories regularly. It should be pointed out, however, that the method cannot be considered accurate for the reason that insoluble impurities may vary from sample to sample to a considerable extent and the error due to the presence of large particles of insoluble impurities is thus transferred to the soluble mineral matter.

FREE FATTY ACID

The fatty acid method adopted is sufficiently accurate for commercial purposes. In many routine laboratories the fat or oil is measured and not weighed but the committee recommends weighing the sample in all cases. For scientific purposes the result is often expressed as "acid number," meaning the number of milligrams of KOH required to neutralize the free acids in one gram of fat, but the commercial practice has been, and is, to express the fatty acid as OLEIC ACID or, in the case of palm oil, as PALMITIC ACID, in some instances. The committee sees no objection to the continuation of this custom so long as the analytical report clearly indicates how the free acid is expressed. For a more exact expression of the free acid in a given fat, the committee recommends that the ratio of acid number to saponification number be used. This method of expressing results is subject to error when unsaponifiable fatty matter is present since the result expresses the ratio of free fatty acid to total saponifiable fatty matter present.

TITER

At the present time the prices of glycerol and caustic potash are abnormally high but the committee has considered that the methods adopted are for normal times and normal prices. For routine work during the period of high prices the following method may be used for preparing the fatty acids and is recommended by the committee:

Fifty grams of fat are saponified with 60 cc. of a solution of 2 parts of methyl alcohol to 1 of 50 per cent NaOH. The soap is dried, pulverized and dissolved in 1000 cc. of water in a porcelain dish and then decomposed with 25 cc. of 75 per cent sulfuric acid. The fatty acids are boiled until clear oil is formed and then collected and settled in a 150-cc. beaker and filtered into a 50-cc. beaker. They are then heated to 130° C. as rapidly as possible with stirring and transferred, after they have cooled somewhat, to the usual 1 in. x 4 in. titer tube.

The method of taking the titer, including handling the thermometer, to be followed is the same as that described in the standard method. Even at present high prices many laboratories are using the glycerol-caustic potash method for preparing the fatty acids, fearing that the saving of time more than compensates for the extra cost of the reagents.

UNSATURATED MATTER

The committee has considered unsaponifiable matter to include those substances frequently found dissolved in fats and oils which are not saponified by the caustic alkalies and which at the same time are soluble in the ordinary fat solvents. This term includes such substances as the higher alcohols such as cholesterol which is found in animal fats, phytosterol found in some vegetable fats, sterols and pseudosterols, etc. Unsaponifiable matter, however, should not be confused with the dry matter which is usually determined as soluble mineral matter. The method adopted by the committee has been among the simplest the most accurate combination of other methods such as the dry matter method and the wet method making use of the

separatory funnel. At first consideration the dry extraction process would seem to offer the best basis for an unsaponifiable matter method, but in practice it has been found absolutely impossible for different analysts to obtain agreeing results when using any of the dry extraction methods proposed. Therefore, this method had to be abandoned after numerous trials, although several members of the committee strongly favored it in the beginning. Again, at first glance, it would seem that the use of a siphon instead of a separatory funnel would be undesirable, but as a matter of fact in practice it is found to be more satisfactory than the separatory funnel, as well as much cheaper.

In carrying out the unsaponifiable determination in a routine way, the committee has found that the ordinary 250-cc. graduated and stoppered cylinder is reasonably satisfactory for the purpose.

One member of the committee, Mr. Ernst Twitchell of the Emery Candle Company, Cincinnati, Ohio, was an earnest advocate of another method devised by him for the determination of unsaponifiable matter as opposed to the method finally adopted by the committee. Mr. Twitchell's method is published in *THIS JOURNAL*, 7 (1915), 217, under the title, "Unsaponifiable Matter in Greases."

In brief, the Twitchell method consists in saponifying with alcoholic potash and evaporating to dryness. The soap is then dissolved in water containing 20 per cent alcohol approximately, and shaken out with ether in a separatory funnel. The combined ether extracts are shaken with dilute hydrochloric acid, washed with water, transferred to a weighed dish, evaporated, dried and weighed. The residue consists of unsaponifiable matter and fatty acids since the ether dissolves some soap which is afterward decomposed by the hydrochloric acid. The weighed residue is taken up with neutral alcohol and the fatty acids therein determined by titration with standard alkali solution. The fatty acids thus determined are calculated as oleic and deducted from the weight before obtained.

Under date of April 17, 1916, Mr. Twitchell wrote to the committee on the subject of his method which he recommended, as follows:

"At the last meeting I was requested to give in writing my arguments in favor of my method of determining unsaponifiable matter as published in *The Journal of Industrial and Engineering Chemistry*, March, 1915 (reprint enclosed herewith). I don't want to advocate this particular method or urge its adoption by the committee, but I do want to say that I consider that the work of the committee has proved that petroleum ether is not a suitable solvent for the extraction of unsaponifiable matter, for with one of the few samples examined (the yellow grease) the results obtained by, I believe, all the members of the committee, show that ether extracts from 25 to 30 per cent more than petroleum ether. Although with the other samples the two solvents gave about the same results, yet the fact that the petroleum ether failed with one should condemn it for all. I don't see how we can get away from this conclusion. I enclose a table of figures for unsaponifiable in the yellow grease, made with ether and with petroleum ether. I understand besides that the results obtained with ether by other members of the committee were nearly the same as mine.

"I should be obliged to you if, when turning over the proceedings of the committee to the new one which is to be formed, you would include what I have said above regarding *saponification and unsaponifiable* as a minority report.

"At the last meeting my method of determining unsaponifiable was criticized because of the varying corrections for soap in the ether. I hardly look at the determination of fatty acids as a correction, it being so easily, quickly and accurately made. It might almost be considered as the principal operation, and the washing out of the soap solution as a removal of the bulk of the fatty acids after which the remainder can be accurately titrated."

Mr. Twitchell's statements about a certain sample of yellow grease with which the committee experienced some difficulty are correct, but it was found afterward that this sample was abnormal in that it contained some wool grease or lanolin, and it is a question whether or not even Mr. Twitchell's results were high enough in consideration of this fact. In short, this sample

was considered by the committee so abnormal that results were not to be trusted and other samples were substituted for further cooperative work.

The committee, following its rule of adopting only one standard method, had to choose between Mr. Twitchell's method and the method finally adopted. One of the principal arguments against Mr. Twitchell's method is the correction for the fatty acids. This correction is variable and in many cases amounts to several times the amount of unsaponifiable matter determined, being usually from 0.5 to 2.5 times the amount of unsaponifiable matter in the hands of the average analyst. The committee did not feel that it could consistently adopt a method involving so large a correction, even though the final results were generally good.

The old argument in regard to ethyl ether vs. petroleum ether as a solvent for unsaponifiable was carefully considered by the committee. It is freely admitted that ethyl ether is a better solvent than petroleum ether, but in the opinion of the committee it is too universal a solvent for the purpose inasmuch as it absorbs soap from a water solution. On the other hand, petroleum ether is selective in its action and shows little or no tendency to dissolve soaps. Again, commercial ethyl ether is an impure product containing in solution both water and alcohol as well as organic impurities of various sorts including peroxides. It has been recommended chiefly perhaps for two reasons: (1) it is a chemical of definite composition, and (2) it is a very general solvent for unsaponifiable substances. Petroleum ether has been criticized because it is not of constant composition or boiling point. It consists of various hydrocarbons of various boiling points and varies again depending on the source of the crude petroleum from which it was distilled. The committee considered that its great recommendations were its selective solvent power, its immiscibility with water, its stability as regards decomposition on standing and its cheapness. Although it may vary slightly in solvent power when derived from different sources, even under the boiling point (75° C.) recommended by the committee, nevertheless, all samples have sufficient solvent power for the determination in question if the committee's directions are followed.

Taking everything into consideration, the committee decided in favor of petroleum ether as the solvent and finally adopted the method specified above, and it is believed that this method will be found quite satisfactory for the purpose.

AMERICAN ELECTROCHEMICAL SOCIETY 32ND GENERAL MEETING, PITTSBURGH OCTOBER 3 TO 6, 1917

The Thirty-Second General Meeting of the American Electrochemical Society was held at Pittsburgh, October 3 to 6, 1917, with headquarters at the William Penn Hotel. About 350 members and guests were registered.

PROGRAM OF PAPERS

- Hydroelectric Power. HENRY RANDALL
- Trend in Electric Furnace Design. W. H. COGGSWELL
- The Sub-Station Problem of the Electrochemical Plant. J. L. McK. VENABLE
- Electric Pig Iron in War Time. ROBERT TRUMBULL
- A Method of Procedure for the Commercial Analysis of Ferro-silicon. R. E. LOWE
- A Resistance Furnace. FRANK THORNTON, JR.
- The Electric Furnace in the Development of the Norwegian Iron Industry. HAARON STVRI
- Resistance Type Furnace for Melting Brass. T. F. BAILY
- Preparation of Pure Alloys for Magnetic Purposes. T. D. YENSEN
- The Influence of the Temperature of Measurement on the Electrical Resistivity and Thermo-Electromotive Potential of Solutes in Steel. E. D. CAMPBELL
- Calorized Iron as an Element for Thermocouples. O. L. KOWALEK
- Copper Castings for Electrical Use. W. M. CORSE AND G. F. COMSTOCK
- Silver Peroxide and the Valence of Silver. H. C. P. WEBER
- Suggested Reforms in Some Chemical Terms. CARL HERRING

Symposium on Electrochemical War Supplies

- The Application of Radium in Warfare. C. H. VIOL AND G. D. KAMMER.
 Chlorine as a War Factor. W. D. MARSHALL.
 Synthetic Gasoline by Electrochemical Means. L. B. CHERRY.
 The Spectroscopic Determination of Small Amounts of Lead in Copper. C. W. HILL AND G. P. LUCKEY.
 The Electrolytic Recovery of Copper and Sulfuric Acid from Copper Mill Pickling Solutions. J. L. JONES.
 Electrolytic Pickling Process and Its Effect on the Physical Properties of Metals. J. COULSON.
 The Corrosion of Fence Wire. O. W. STORRY.
 The Effect of Lithium Hydrate upon the Capacity of the Edison Storage Battery. L. C. TURNER.
 The Prevention of Brittleness in Electroplated Steel Springs. T. S. FULLER.
 A New Electro Analysis Apparatus. J. L. JONES.
 The Corrosion of Metals by Acids. O. P. WATTS AND N. D. WHIPPLE.
 The Poisoning of Catalytic Agents. W. D. BANCROFT.
 Fractional Combustion. W. D. BANCROFT.
 Theory of Contact Catalysis. W. D. BANCROFT.

REPORT OF THE COMMITTEE ON SAMPLING
FERTILIZER DIVISION, AMERICAN CHEMICAL SOCIETY

Boston, September 10 to 13, 1917

At the last meeting of this division a motion was made and passed appointing a committee to formulate methods for the sampling of fertilizers, to be presented to the Association of Official Agricultural Chemists, requesting that the Association adopt a standard method for sampling fertilizers, which would be official.

The members of your Committee did not deem it feasible to work out such methods before the annual meeting of the Association in November, 1916. However, the Chairman appeared before the members of the Executive Committee of the Association of Official Agricultural Chemists during their annual meeting, stated the action of the Fertilizer Division of the American Chemical Society, and requested the cooperation of the Association.

As a result of this conference the Chairman of the Association was instructed to appoint a Committee of three to cooperate with the American Chemical Society Committee to draw up satisfactory methods for the sampling of fertilizers, which might be adopted as official. This committee consists of Messrs. C. H. Jones, Vermont, Chairman; W. J. Jones, Jr., Indiana; and B. F. Robertson, South Carolina; the first two named being members of the American Chemical Society committee.

At an informal meeting of the members of the two committees present it was deemed advisable to make further tests of the different samplers, and arrangements were made to ship some carefully prepared fertilizers to distant points to determine what the effect of transit might be. A ton of fertilizer analyzing approximately 2 per cent ammonia, 8 per cent phosphoric acid, and 2 per cent potash was carefully mixed, and the entire ton quartered down to obtain a 5-lb. sample. The material was then bagged and samples taken from the bags by the Indiana sampler, the lard-tryer type sampler, and the Massachusetts sampler. The same procedure was gone through with a ton of fertilizer analyzing to per cent phosphoric acid and 8 per cent potash.

These two sets of bags were then placed in a car and shipped to Jeffersonville, Indiana from Chicago. At the same time a similar set was prepared and shipped to Atlanta, Georgia. Mr. W. J. Jones, Jr., of Indiana, arranged for his chief inspector, Mr. O. S. Roberts, to take all of these samples in Chicago and to proceed to Jeffersonville and to Atlanta and take samples of the goods on arrival, with the three types of samplers. In addition, at Atlanta, a sample was taken with a core from the top of the bags in the ton of 1982 which were standing on end to see if there might be any appreciable variation.

It is the intention that these various samples taken will be carefully "quartered down" in the laboratory of the State Chemist

of Indiana and portions of each sample sent to each member of the Committee for analysis. We hope to have some results to report by the time of this year's meeting of the A. O. A. C., but it will undoubtedly take a longer time before final recommendations can be made.

It is very encouraging to note that the interest aroused by the subject of sampling has been quite general. We learn that a large number of orders have been placed with the maker of the Indiana sampler, and that several additional states have adopted its use. We are also in receipt of a communication from the Chief Chemist of the Department of Agriculture and Stock, Queensland, Australia, outlining the sampling methods which were drawn up at that place by a Committee, and to learn that not only was the Indiana sampler adopted, but an entire set of regulations had been drawn up which can be subjected to very little criticism.

We feel that both the industry and state control will be greatly benefited by the agitation of this sampling question.

F. S. LODGE, Chairman

C. H. JONES

W. J. JONES, JR.

S. W. WILEY

F. B. CARPENTER

REPORT OF THE COMMITTEE ON RESEARCH AND
METHODS OF ANALYSIS
FERTILIZER DIVISION, AMERICAN CHEMICAL SOCIETY

Boston, September 12, 1917

The work on the determination of sulfur in pyrites has been carried forward by Mr. H. C. Moore, Armour Fertilizer Works, Atlanta, Georgia. Your Committee is advised by Mr. Moore that he is not yet ready to render a final report, owing to his failure to receive results from all collaborators and the hope of receiving the missing results later.

The results so far received have been tabulated as follows by Mr. Moore:

SUMMARY OF RESULTS REPORTED BY 45 ANALYSTS FROM 32
LABORATORIES ON PYRITES SAMPLE NO. 4

No. Analysts	ALLEN & BISHOP		MISCELLANEOUS MODIFICATIONS OF A. & B.		MISSOURI LABORATORY METHODS
	Modified 36	Original 16	A. & B. 3	LUDKE 12	
Maximum	42.03	41.18	41.66	42.14	41.34
Minimum	41.78	41.31	41.75	40.06	41.10
Average	41.75	41.24	41.69	41.30	41.88
Omitted from Average	5				

REMARKS

"The results are not quite all in and a further tabulation will follow later.

"Of the 35 results included in the average by the modified Allen & Bishop method are one between 41.50 and 41.75 per cent, 20 are between 41.60 and 41.80 per cent, 11 are between 41.65 and 41.85 per cent. This shows an improvement over former work.

"In our laboratory five analysts, working independently and at different times, each using a separate sample made 11 to 12 determinations. The maximum difference between any two results is 0.08 per cent, and the individual averages are from 41.60 per cent to 41.71 per cent. The standard deviation is between any two results from three determinations with the method is 0.01 per cent. The standard deviation using 41.68 per cent, 41.69 per cent and 41.70 per cent. These results prove satisfactory on samples used and show the precision of the method after a little experience."

The investigation of the modified West Analyst system method for the percentage assay of sulfate of soda has been previously covered by the laboratory reports of Dr. A. O. A. C., who will have further information as to how it can be used, containing a summary of the A. O. A. C.

Fertilizer Division, September

F. S. LODGE

A. J. FORT

C. H. JONES

F. B. CARPENTER

NOTES AND CORRESPONDENCE

A SOCIETY OF CHEMICAL INDUSTRY IN FRANCE

The following extract from a circular now being sent out is self-explanatory:

To the Chemists & Manufacturers of America:

There has been formed in France a French Society of Chemical Industry, the Société de Chimie Industrielle, whose objects are fully set forth in the attached letter (*not given here*) of Mr. Paul Kestner, President of the Society.

After consultation with Mr. René Engel, Secretary of the Society and a member of the French Scientific Mission in the United States, the undersigned committee believes that it would be most opportune to establish an American section of the Société de Chimie Industrielle and thus extend to our French fellow chemists and manufacturers, our moral and financial support and the right hand of good fellowship.

Furthermore, members of the American section will benefit by the closer relations which will naturally develop between American and French Chemical Industry.

Jerome Alexander
Leo H. Backlund
Raymond F. Bacon
Wildor D. Bancroft
Charles Baskerville
Albert Blum
Henri Blum
Marston T. Bogert
M. Ceresole
Arthur M. Comey

Charles A. Doremus
John V. N. Dorr
W. M. Grosvenor
Frank Heminway
Ellwood Hendrick
Chas. H. Hertz
J. B. F. Herreshoff
George F. Kunz
Parker C. McIlhenny
William H. Nichols
R. L. Orfila

Charles L. Parsons
Charles L. Reese
Allen Rogers
Samuel P. Sadler
Maximilian Toch
G. W. Thompson
G. E. Valabrigue
E. V. Verge
Henri Viteaux
C. B. Zabriskie

After the above introduction the circular contains the translation of a letter addressed by Mr. Paul Kestner, President of the Society, to the chemists of France, an extract of the By-Laws of the French Society, the list of officers of the Society, and a blank to be used as an application for membership in the American Section of the Society. Copies of this circular may be obtained by addressing the "Organization Committee of the American Section of the Société de Chimie Industrielle, c/o Chemists' Club, 50 East 41st St., New York City."

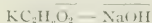
TWO LETTERS ON THE AVIDITY OF SOIL ACIDS

Editor of the Journal of Industrial and Engineering Chemistry:

In an article appearing in *THIS JOURNAL*, 8 (1916), 344, Truog describes a method which he has developed for the measurement of the avidity of the active soil acids. Briefly, his method is as follows:

To a weighed sample of soil is added an amount of potassium acetate solution which contains an amount of the salt equivalent to the active soil acids in the sample. The active soil acids are previously found by determining the amount of standard barium hydroxide it takes to neutralize the soil acids in a given length of time. Potassium acetate solution and soil are shaken together for two minutes when the mixture is filtered and an aliquot of the filtrate titrated with sodium hydroxide solution, using phenolphthalein indicator.

The avidity is calculated from the following formula, the chemical symbols standing for equivalents:



This factor times the avidity of acetic acid, taken arbitrarily as 1000, gives the avidity of the soil acids. Truog points out that since the soil acids are relatively insoluble, the avidity as found does not represent the strength of the soil acids, compared to acetic, but that the avidity figures for different soils are comparable with each other because the acids are all quite insoluble.

The purpose of this note is to point out that Truog does not in any sense of the word measure the avidity of the soil acids. In none of the text books of physical chemistry is any mention made of a titrimetric method for the measuring of the strength of acids. It is not the place here to go into a discussion of these methods. In the 4th English edition of Nernst's "Theoretical Chemistry" on pages 557 to 563 an outline of the theory of the

various methods is given, and, obviously, it is theoretically wrong when determining the *strength* of acids to titrate. Truog's method measures nothing more nor less than the amount of acids soluble in potassium acetate. Whether or not such a knowledge is of value we do not wish to discuss here.

IOWA STATE COLLEGE EXPERIMENT STATION R. S. POTTER
AMES, IOWA, September 12, 1917

Editor of the Journal of Industrial and Engineering Chemistry:

In reply to the criticisms of R. S. Potter regarding the method proposed for the determination of the avidity of the active soil acids, I wish to state as follows:

The avidity of an acid has reference to its relative strength, affinity or competing power for a base. Various methods have been proposed for the determination of the avidities of the common water-soluble acids. Thomsen's thermochemical method and Ostwald's volume method have been most widely used. Physical properties such as refractive indices, rotary powers, catalytic effects, electrical conductivities and biological effects have also been used to determine the relative strengths of acids. As the writer has indicated in the *Journal of Physical Chemistry*, 20 (1916), 473, soil acids are usually comparatively insoluble and hence the methods proposed for use with the common soluble acids cannot be used in the case of soil acids.

In the method proposed by the writer for the determination of avidity, the active soil acids are first determined quantitatively. By active soil acids is meant those acids which react with a soluble base almost instantly. Although these active soil acids are for the most part not in true solution, yet their physical condition is such (colloidal) that they react with surprising rapidity and some exhibit considerable avidity. After the amount of active soil acids has been determined, a known weight of soil is treated with a solution containing an amount of neutral potassium acetate which is chemically equivalent to the active soil acids present. The single addition of the potassium acetate is equivalent to adding separately, chemically equivalent amounts of acetic acid and potassium hydroxide. There results thus virtually the condition that chemically equivalent amounts of active soil acids, acetic acid and base in the form of potassium hydroxide are present in the mixture. The active soil acids are thus given an opportunity to compete with an equivalent amount of acetic acid for a definite and equivalent amount of base, as is done in Thomsen's thermochemical method and Ostwald's volume method. Obviously thermal effects or volume effects cannot be used to determine the distribution of the base between the active soil acids and acetic acid.

However, since the base that combines with the active soil acids forms salts which are comparatively insoluble in water and leaves in solution an amount of free acetic acid which is chemically equivalent to the base that the active soil acids have removed from solution, it is only necessary to filter the mixture and determine in the filtrate by titration the amount of acid present, in order to determine the amount of base which the active soil acids removed while in competition with an equivalent amount of acetic acid. By substitution in the formula comparative figures for different soils are obtained. The figures represent the collective, or better, average avidity of all the active acids in any particular soil sample.

As far as the writer is aware the method described in *THIS JOURNAL*, 8 (1916), 344, is the only method that has ever been proposed for use in case the acids are not in solution, and it is not at all surprising that Potter finds no mention of a titrimetric method in the text books of physical chemistry. Such methods as are mentioned, are for use under conditions in which the acids and salts formed are in true solution, and obviously

the method proposed for active soil acids could not be used in case all the acids and resulting salts formed a true solution.

Potter states that the method measures nothing more nor less than the amount of acids soluble in potassium acetate. There is absolutely no basis for this statement. In the case of the common acid upland mineral soils, it is usually impossible to wash out with water any considerable amount of the acids causing soil acidity, and usually the more these soils are washed with water the more acid do they become. If these soils are treated with a salt solution, the soil acids remove from the salt solution a certain amount of the base and thus liberate from the salt an equivalent amount of free acid in solution; or the soil acids may exchange wholly, or in part, iron and aluminum for the base of the salt, which again gives rise to an acid solution due to the ease of hydrolysis of iron and aluminum salts. The potassium acetate solution does not in any way dissolve any appreciable amounts of the active soil acids.

While it is perfectly evident that the avidity of an acid in colloidal solution is different than when in true solution, yet this does not affect the purposes of the method proposed. In the method proposed only such soil acids (active soil acids) as are free to react quickly with a base are considered. A method to be of any value in studying the effects of soil acidity on the fertility of these soils must measure the avidity of the soil acids in the condition that they actually exist in the soil. This is done as nearly as possible in the method proposed.

As the writer has pointed out in *Wisconsin Research Bull.* 41, p. 34, it is undoubtedly these active soil acids which limit the supply of calcium carbonate and bicarbonate in the soil solution to such an extent that the crop-producing capacity of some acid soils is affected. If this is the case it is evident that the avidity of the acids causing soil acidity may be of more importance than the total amount of acids present. The writer has found that soils may have a high total active acidity, but, because the avidity is low, the soils do not respond much to liming. Again soils having only a moderate active acidity but of high avidity respond decidedly to liming. The writer also has a considerable amount of data which indicate that the injurious effects of soil acidity are usually not due to a direct action of the soil acidity on the plants or biological processes, but that it is due to the too low rate at which the carbonic acid in competition with the soil acids is able to force out of the calcium compounds the calcium bicarbonate which is needed by plants and biological processes for maintaining the proper internal reaction.

Both from the theory involved and data secured from actual experiments, the writer is forced to disagree with the criticisms of Potter in every respect.

UNIVERSITY OF WISCONSIN
MADISON, October 3, 1917

EMIL TRUOG

THE WESTERN CHEMICAL MANUFACTURING COMPANY'S INDUSTRIAL COURSE

Editor of the Journal of Industrial and Engineering Chemistry:

The article in the July issue of your magazine entitled "An other Possible Form of Cooperation between Universities and the Chemical Industry," page 638, has come to our attention.

For a number of years it has been our custom to employ students from local colleges for odd jobs in and about our plant for the summer months. We also have adopted what we call an Industrial Course, in which we enter recent college graduates for any sort of work encountered in a plant such as ours is. The wages at the start are those of an ordinary workman. The men are asked to do any sort of work there in to do and are not confined to any one department but are shifted from place to place and thus are made familiar with all the detail of our various processes; these include the manufacture of sulfuric, nitric and muriatic acids (both commercial and chemically pure), com-

mercial and C. P. aqua ammonia, anhydrous ammonia, and the dressing of complex zinc-lead-iron sulfide ores.

From the men entered in this course we select those best qualified for taking charge of departments, laboratory men, etc. All of our present heads of departments have been through this course—in fact we would not consider employing outside professional men, except perhaps in the case of the installation of a process, the details of which are more or less unfamiliar to us.

In other words, we have found it more practical to train our men along lines to which we have given much careful thought and attention.

The 1917 vacation period is over, but there may be some who would consider entering our industrial course and we would be pleased to hear from such persons.

During the past summer we employed quite a few college men from the local colleges, more than the usual number for the summer months, and we were glad to do it, for we believe the benefit was mutual. You will understand, of course, that we can give such work to only a limited number.

Owing to the fact that our plant is so far from the Eastern colleges, we do not believe it will be practical for the men from such colleges to come so far west, considering the little time they will have, the railroad fare to and from Denver, and the fact that there are several colleges in and around Denver. Conditions, of course, would be different in the case of those men who would be permanent.

WESTERN CHEMICAL MFG. CO.

per PAUL C. SKINNER,

Treasurer and General Superintendent

DENVER, COLORADO
September 22, 1917

KILN DRYING OF WOOD

Editor of the Journal of Industrial and Engineering Chemistry:

I have just read your splendid editorial on "Aviation and the Chemist" in the September number of *THIS JOURNAL*. I am sure you will be interested in the progress being made along the lines you mention and was about to call our work on kiln drying to your attention when I received a letter from Dr. Hawley in which he states he has already mentioned this to you briefly.

This Laboratory has been giving a great deal of time to the study of kiln drying of wood, both from a theoretical and practical side. Conditions necessary to proper drying of wood have been explained theoretically and methods of drying developed accordingly. Several kilns are now in operation at this laboratory where these methods can be tried out experimentally, and it has been possible to dry various species and various forms with entirely satisfactory results. After tests in the experimental kilns it has been our policy to make demonstrations in commercial kilns to assist the industries in solving their drying problems.

In the present emergency the laboratory has been found well equipped with data already available to meet the problems in kiln drying wood, or to make further tests where necessary. It has been possible to kiln dry species grown from the saw and in a good, if not better, condition than air-dried stock for airplane construction. Tests on such are nearly completed and indications are that results will be satisfactory.

We are gradually developing specifications for drying all commercial species that will harmonize readily with any kiln in which the specified conditions can be maintained.

FOREST LABORATORY, BOSTON, MASS.
MASSACHUSETTS, WASHINGTON, D. C.

A. P. WILSON
Director

AVAILABLE OXYGEN IN PYROLUSITE CORRECTION

In the article by C. V. Tomlinson, *THIS JOURNAL*, 9 (1917) 1070, the formula for calculating the percentage available oxygen in pyrolusite is given as follows:

$$\text{Percentage available oxygen} = \frac{21.5}{100} \left(\frac{100}{\text{Molecular weight}} - 1 \right)$$

$$\text{Percentage available oxygen} = \frac{112.5}{100} \left(\frac{100}{\text{Molecular weight}} - 1 \right)$$

$$\text{Percentage available oxygen} = \frac{112.5}{100} \left(\frac{100}{\text{Molecular weight}} - 1 \right) \times 100$$

THE DETERMINATION OF IRON IN GLASS SAND— CORRECTION

Editor of the Journal of Industrial and Engineering Chemistry:

Referring to an article published in THIS JOURNAL, 9 (1917), 941, "The Determination of Iron in Glass Sand," the author quotes from the Geological Survey Bulletin 285 (1906), 454, by Ernest F. Burchard, analysis of sand submitted by the American Window Glass Company and the Pittsburgh Plate Glass Company which have no doubt been recorded incorrectly. In each

case the Iron content is stated one-tenth of the correct amount as found in any analysis we have ever made.

We have been aware of the error as stated in the Bulletin but did not think it necessary to draw attention to this as we considered that any one acquainted with glass manufacture would naturally take it as a clerical error and move the decimal point one place over to the right.

PITTSBURGH PLATE GLASS CO.
CREIGHTON, PA., October 16, 1917

F. GELSTHARP,
Chief Chemist

WASHINGTON LETTER

By PAUL WOOTON, Metropolitan Bank Building, Washington, D. C.

Location of the Government's nitrate plant on Muscle Shoals came as a surprise to nearly all here who are intimately interested in the matter. Even high officials, drawing their conclusions from the recent report of the Nitrate Board, had decided that Muscle Shoals had been eliminated. There is much speculation in official circles as to who is responsible for the selection of the site. Some are of the opinion that the selection was made by the President himself. It is known definitely, however, that army officers had combed southwestern Virginia carefully without finding a suitable site. The water is bad in that section of Virginia and that portion of the terrain which is not standing on edge is subject to overflow. With the elimination of southwestern Virginia, resort was had to the elastic "contiguous region" which had been specified by the Board in its report. Several officials were asked why Muscle Shoals was chosen, but, despite their rather determined attempts to point out a good reason for the selection of this site, none was established. One argument was that Muscle Shoals is near a supply of phosphate but in this connection attention is called to the fact that the location selected makes the obtaining of Florida phosphates much more difficult than would have been the case had the choice fallen to some of the other places which were considered. The announcement authorized by the Secretary of War is as follows:

The Secretary of War announces that the President has approved the location at Sheffield, Alabama, of the initial ammonia and nitric acid plants to be constructed with a portion of the \$20,000,000 appropriated for Nitrate Supply by the National Defense Act, providing a suitable site be there obtainable at a reasonable price. As satisfactory prices have now been agreed upon for the transfer of the several parcels of land involved, the location of these initial plants at Sheffield may now be regarded as assured.

Sheffield, Alabama, is located on the Tennessee River just below the Muscle Shoals and is near to the phosphate beds of central Tennessee. On the site selected there are several substantial steel buildings which can be utilized with a saving of expense and of time.

These initial plants were planned with a view to determining the best and most economical process of nitrogen fixation. Enough land is being acquired to permit of large expansion—by the same or by other processes—in case such expansion at the same place shall be decided upon. These plants will produce material of much value in the manufacture of munitions for the war. After the war, any excess of their product over the munitions requirements may be sold for use in fertilizer.

The Secretary of the Interior has not been advised of the selection of any scientist in connection with the Giragosian free energy generator. While it has been reported that Carabed T. K. Giragosian would go ahead with his plans informally, no word of it has come to the government scientists who were following the matter. The free energy generator bill passed both Houses of Congress but was not signed by the President. The fact that Congress was so willing to have the generator investigated led several of the government's mechanical specialists to look into the matter closely. It is their opinion that the generator is another Keeley motor fiasco. They point to the fact that those who have been convinced of the generator's merit are not specialists in the business of power generation. One government official who has followed the matter closely said: "Just because we laughed at Langley, it is no reason for throwing overboard all the knowledge we possess. The presentation of this seductive style of argumentation seems to have been employed very successfully in this case as Congress was willing to give large prestige to another perpetual motion machine under a different name."

Statements that the Burton process of producing gasoline has been freed from restriction for general use have been in circulation for the past ten days, but no official announcement concerning it has been made. As was announced some time ago at a Federal Trade Commission hearing, the Burton process has been available to any refiner not competing directly with the Standard Oil Company of Indiana, on payment of reasonable royalties. Since it is fairly well established that the Federal Trade Commission has requested those in control of this process to permit its more general use, it will not be surprising if the request is granted. Joseph F. Guffey, the government's adviser on oil purchases, has declined repeatedly to comment on the matter, which fact is taken to mean that there is a hitch in the plan.

A chemical division has been created as an integral part of Food Administration. Herbert Hoover, the food administrator, has summoned Charles Washington Merrill, of San Francisco, to Washington to take charge of the new division. Mr. Merrill, who is the president of the Merrill Metallurgical Co., the president of the Western Ore Purchasing Co., and a director on the board of the Union and the Caledonia Dredging Companies, is a chemist of national reputation. He took a notable part in establishing that the cyanide process of ore treatment could be used on a commercial scale. Under his direction one of the first cyanide plants in the country was erected on the property of the Standard Mining Co. at Bodie, Cal., in 1894. The new chemical division, which he will direct, will devote itself to the control and allocation of chemicals used in the production and conservation of foods. The importance, to the nation, of maintaining ample supplies of the chemicals used in insecticides, fertilizers, and in refrigeration and of stabilizing their prices is considered by Mr. Hoover as one of the highly important phases of his work. Mr. Merrill will serve on the dollar-a-year basis.

Henry Howard, chairman of the executive committee of the Manufacturing Chemists' Association of the United States, attended the hearing conducted Oct. 16 by Van H. Manning, the director of the Bureau of Mines, at which the regulations, which will accompany the explosives act, were discussed. While Mr. Howard objected to regulations attempting to define certain provisions of the law, the regulations as drafted are believed to meet the approval of the chemical industries. Changes now are being made in the regulations so as to conform with many of the suggestions made at the meeting, at which all industries affected were represented.

After an exhaustive investigation, the chemists appointed to report on the defective ammunition manufactured at the Frankfort arsenal, have their findings practically ready to submit to the War Department. The report probably will not be made public. The board consisted of C. L. Parsons, chief chemist of the Bureau of Mines; Col. Wirt Robinson, professor of chemistry at the United States Military Academy at West Point; and Wm. H. Walker, of the Massachusetts Institute of Technology.

All plans for the formation of the Chemical Alliance are at a standstill, awaiting action by the Department of Commerce. It is understood that the matter is being delayed while the State Department learns the attitude of the countries associated with us in the war. It is pointed out that under present conditions the activities of the Alliance would be international in its effects.

PERSONAL NOTES

Mr. Harry A. Curtis, First Lieutenant, commanding Troop K, Colorado National Guard, and formerly professor of physical chemistry in the University of Colorado, has been ordered to report to the Chief of Ordnance at Washington.

Among the distinguished visitors at the Chemical Exposition held recently in New York, were Lieutenant René Engel, chemical engineer and secretary of the Société de Chimie Industrielle of Paris, and Prof. Victor Grignard of the Institut de Chimie de Nancy. Both are members of the French Scientific Mission to the United States.

Mr. Otto I. Chormann, formerly chief chemist for the Pfaunder Company, Rochester, New York, has received the commission of Major, 1st Battalion, 3rd Infantry, N. G. N. Y.

Dr. H. B. North, associate professor of chemistry at Rutgers College, New Brunswick, N. J., has resigned to become connected with the York Metal and Alloy Company, York, Pa., in capacity of director of the research laboratories.

Dr. William B. Meldrum, of Vassar College, has been appointed assistant professor of chemistry at Haverford College, taking the place of Lyman B. Hall, professor of chemistry, who resigned at the retiring age after 37 years of service.

Dr. Reston Stevenson, assistant professor in charge of physical chemistry in the College of the City of New York, has been appointed captain of the Sanitary Corps of the National Army. His work at the College of the City of New York will be carried on by Paul Gross, graduate of City College and post-graduate of Columbia.

Milton W. Franklin, formerly engineer of the ozonator department of the General Electric Company, has severed connections with that company to go with E. F. Houghton & Co. as consulting engineer. Dr. Franklin becomes a member of the board of directors and chairman of the sales committee and assumes charge of plants and equipment and manufacturing processes.

Dr. Ralph H. McKee, head of the Research Department of the Tennessee Copper Company, has been appointed Associate Professor of chemical engineering, Columbia University. He will have charge of the work in industrial organic chemistry given by the Department of Chemical Engineering.

Prof. Chas. F. Chandler is reported recovering rapidly from his recent serious illness. On October 16th, he was able to be out-of-doors and to walk about town without feeling any ill effects from the exertion. Prof. Chandler expects to remain at his country place near New Hartford, Conn., for some time.

Dr. T. Dale Stewart of the University of Chicago has accepted a position as instructor in chemistry in the University of California. He has been in Pittsburgh for several weeks where he has been doing research work for the government.

Mr. H. N. Thomson has resigned his position as metallurgist for the United Verde Copper Co. and has entered consulting practice. His address is 918 S. Kingsley Drive, Los Angeles, Cal.

Mr. W. H. Ransom, who was formerly connected with the Technical Department of the Aetna Explosives Company, has been called into active service as Captain in the Ordnance Department, and assigned to duty as Inspector of Ordnance. Capt. Ransom is at present stationed at Wilmington, Del., where he is inspecting the smokeless powder and high explosives manufactured by the du Pont Company.

Mr. A. D. Shankland has been appointed chief chemist of the Sanson Laboratory of the Bethlehem Steel Company.

Dr. Max Kahn has resigned his position as biochemist to the Western Pennsylvania Hospital, Pittsburgh, Pa., to accept the appointment of director of the laboratories, Beth Israel Hospital, New York City.

Mr. L. E. Warren, for eight years associate chemist in the chemical laboratory of the American Medical Association, has resigned his position to take charge of the research laboratories of the New York plant of Wm. R. Warner & Co.

Dr. Alan Hirsch has sailed for Japan to continue his work as Consultant for the Japan Dyestuff Manufacturing Company, subsidized by the Japanese Government. Dr. Hirsch expects to be in the Orient three or four months.

Mr. Charles V. Bacon, consulting chemist on oils, of New York City, has been appointed head of a newly organized section on oils and liquid fire at the American University Experiment Station under the U. S. Bureau of Mines at Washington.

Dr. Minnie A. Graham has resigned her position as instructor in analytical chemistry at Wellesley College to act as abstractor for the research department of the General Chemical Company in New York.

Dr. W. A. Perlzweig, assistant professor in biochemistry in the Creighton University College of Medicine, has been appointed first lieutenant in the Sanitary Corps of the army.

Mr. Edward Booth, assistant professor of chemistry in the University of California, died at his home in Berkeley on August 23rd.

Mr. G. A. O'Reilly, Foreign Trade Representative of the Irving National Bank, made an address before the Philadelphia Section of the A. C. S. on October 18, entitled "The Banker and the Chemist."

Mr. W. H. Fegely, for several years instructor in chemistry and assistant director of the laboratories at Allegheny College, has resigned his position to take charge of the research laboratories of the Erie Malleable Iron Company, Erie, Pa.

Mr. L. M. Tolman, for 17 years connected with the U. S. Bureau of Chemistry and for the last 3 years Chief of the Central District for Food and Drug Inspection, has resigned to become Chief Chemist for Wilson & Co., Chicago, where he will have charge of their various control and research laboratories. E. M. Doolittle of the New York laboratories succeeds Mr. Tolman.

Dr. Frederic S. Mason announces his removal to new offices at 16 Fifth Avenue, New York.

Dr. J. H. Shrader, formerly laboratory director of the Gibbs Preserving Company, Baltimore, Md., is now in charge of the vegetable oil project of the Drug Plant Office, Bureau of Plant Industry, Washington, D. C. His former position has been filled by Mr. C. H. Campbell of the Puritan Food Products Co.

Nine Industrial Fellows of the Mellon Institute of Industrial Research have entered the service of the Government. They are Dr. Frank O. Amon, Dr. Harold S. Bennett, Mr. C. E. Howson, Dr. R. W. Miller, Mr. Ray V. Murphy, Mr. W. E. Vawter, Mr. C. L. Weirich, Mr. A. S. Crossfield and Mr. J. W. Harper. The first seven named have received commissions as first lieutenants. Three other Industrial Fellows, Messrs. C. O. Brown, G. F. Gray and R. P. Rose had previously been commissioned as captains; A. H. Stewart has entered the aviation service and C. N. Iry has been appointed a second lieutenant in the Engineer Corps.

Mr. Clarence Ebaugh, professor of chemistry in Dennison University, is on leave of absence for the year 1917-18, to serve as chairman of the Council of National Defense for the state of Utah.

Of the members of the instructing staff of the department of chemistry at the Massachusetts Institute of Technology, Professors W. H. Walker and J. F. Norris, Dr. F. H. Smyth and Mr. R. E. Wilson are on leave of absence, and Professor W. K. Lewis devotes only part of his time to the institute during the present year. All these men are actively engaged in gas-defense problems, and are holding responsible positions in the organization which is dealing with these problems at Washington and elsewhere. Professor A. A. Noyes spends a part of his time in Washington, in connection with the work of the National Research Council and the Nitrate Committee. Professors Mulliken, Spear and Mueller have also been engaged at the institute on investigations relating to gas-defense. Professors F. J. Moore and H. P. Talbot gave, during a portion at the summer, courses of instruction to students who were expecting to apply for commissions in the Reserve Officers Training Corps.

Honorary membership in the Chemists' Club, New York City, was conferred upon Prof. Grignard of the French Mission, at a joint meeting of the New York Section of the Society of Chemical Industry, American Chemical Society and the American Electrochemical Society, on Friday evening, October 19. The thoughtful address of Prof. Grignard in acknowledging the honor will be printed in the next issue of THIS JOURNAL.

INDUSTRIAL NOTES

We learn from *The Journal of Commerce and Commercial Bulletin* that in July nearly \$500,000 worth of aniline dyes were shipped abroad, according to figures published by the Bureau of Foreign and Domestic Commerce. This is the first time that separate statistics for aniline exports have ever been issued, the innovation resulting from the recent striking growth of the trade. The industry has developed until now it not only supplies the domestic demand for colors but has even invaded the foreign markets in European neutral and allied countries, Canada, Mexico, Argentina, Brazil, British India and Japan.

The American Writing Paper Company, Holyoke, Mass., has established a school for paper making in the Department of Tests, for the benefit of employees. John W. Brassington, chief engineer for the company, will direct the classes in engineering and Henry P. Carruth will teach the classes in chemistry.

In the suit of Procter and Gamble Company, Complainant, against Berlin Mills Company, Defendant, for infringement of patent No. 1,135,351, assigned to the Complainant by John J. Burchenal, Judge Augustus N. Hand of the United States District Court, Southern District of New York, rendered an opinion on October 3, 1917, which concludes as follows: "The bill should be dismissed with costs because the patent is void for lack of invention and for the further reason that claims 1 and 2 if properly construed are not infringed by the defendant."

The Panama Canal Record reports that arrangements have been made at the Miraflores purification plant for a central laboratory to handle the inspection and testing of paints used on Panama Canal structures and equipment. A laboratory is being installed at the purification plant, and a chemist who has specialized in paints will go from the United States to conduct the work. The purpose is to make a study of formulas and methods of application and determine the best processes of protecting woods and metals in varying circumstances. Expenditures by the Canal for paint materials amounted to \$127,173 in 1914; \$255,366 in 1915; and \$229,463 in 1916. There are five paint-grinding machines at Balboa Shops for general Canal needs and one at Pedro Miguel Lock, which does work for all locks. The problem of painting has never been solved, although practically every kind of paint that is mixed has been tried on the Isthmus, and tests have been made in coating with concrete and metal sprays. There are now between 15 and 20 steel plates, coated with various mixtures, exposed at the lower end of Miraflores Locks for tests. Geo. C. Bunker, Balboa Heights, C. Z., in charge of Water Purification, will supervise the operation of this laboratory.

The British-American Chemical Company of College Point, Long Island, New York, was damaged to the amount of more than \$250,000 by fire on October 13, the greater part of the loss being in machinery and chemicals. The fire also did damage to the extent of several thousand dollars to the aviation plant of the L. W. F. Manufacturing Company, where airplanes are being manufactured for the Government. Federal authorities as well as the police and fire marshal are conducting an investigation. Following the start of the fire in the chemical plant there was an explosion, which according to one of the employees was caused by spontaneous combustion of chemicals in a vat in the mixing room. This employee declared that alien enemies would have no reason to blow up the plant as it was not engaged in making war supplies, its products being chemicals used as preservatives for canned goods and in manufacturing medicines for rheumatism.

The Federal Chemical Company of Louisville, manufacturers of commercial fertilizers, has announced that the company will shortly erect a large sulfuric acid plant at Columbus, Ohio, adjoining the present mixing plant, which was started last spring and just completed at a cost of \$200,000. The new plant will cost in the neighborhood of \$30,000.

Charles Engelhard, 30 Church St., New York, announces the perfection of "Impervite" tubes for protecting thermo-couples: these tubes possess qualities practically identical and in many ways superior to the imported Marquardt tubes formerly used for the same purpose.

We learn from *Science* that the Pacific Coast Gas Association has given \$4,415 to the University of California to further investigation and research in gas engineering.

It is reported from London that the Minister of Munitions has taken possession of all calcium carbide in stocks exceeding 56 pounds. Further dealings are prohibited except in execution of written contract, save under license from the Ministry of Munitions.

The Department of Agriculture's Experimental Kelp-Potash Plant at Summerland, California, is now in operation. The apparatus now in use permits the production of only crude potash. By the time the balance of the equipment is installed, it is expected that considerable skill in the operation of the present equipment will have been developed. The capacity is small, the theoretical capacity being not more than two hundred tons of wet kelp per day; still it is expected that the plant will be able to turn out the product in ton lots, which should permit of their securing data of a commercial nature.

It is reported that arrangements are under way at Ottawa for testing the possibilities of developing motor and other fuel from the lignite deposits of Saskatchewan. There are extensive deposits of lignite in that province and in other parts of the West. It was proposed earlier in the year that the Dominion Government purchase a complete plant for this purpose, but it has been decided by the Scientific and Industrial Research Committee at Ottawa, which has the undertaking in charge, to start work with a rented plant from the United States. The lignite will, it is thought, prove a source of fuel oil, and possibly motor fuel, in addition to briquetted fuel and by-products.

The Southern Sulfur Company of Houston, Texas, has been organized to develop sulfur deposits, with a capital of \$300,000, by John H. Kirby, B. F. Bonner and H. L. Fagin.

Owing to the general shortage of the coal supply, complete stoppage of the Netherlands glass industry is threatened. The government coal distribution bureau has informed the factories that no more coal can be supplied; in consequence, at least some of the ovens must cease working very soon.

A temporary embargo has been laid on all exports of sulfur to Canada pending an investigation by this government of the sulfur requirements of the American Military Establishment. Canada has been asked to submit an estimate of what sulfur she will need for the manufacture of explosives and for industrial uses, especially the manufacture of news-print paper. After both American and Canadian military requirements are met it is expected that some sulfur will be exported to Canada under special license for non-military use.

Three prominent Japanese scientists have been sent to this country by the Japanese Government for the prosecution of scientific studies to contribute to the development of chemical and other industries in Japan. The mission is made up of Dr. Masaharu Nishikawa, lecturer of the college of science of the Imperial Tokyo University, Genshichi Asahara, graduate of the same university and Dr. Kikumae Ikeda, also professor of the college of science. Dr. Ikeda, who is senior professor and an authority on chemistry, is commissioned with the investigation and inspection of the development of scientific studies and industries, both theoretical and practical.

The Court has appointed temporary receivers for the Federal Dyestuff and Chemical Corporation. Charles W. Holloway, president of the corporation, consented to the appointment of the receivers. The corporation was promoted by Archibald S. White, who conducted a wide-spread advertising campaign for the sale of the stock at \$50 a share. Mr. White announced his retirement from the banking business last March. A statement issued said that the credit of the corporation was seriously impaired, and that new working capital, according to the Directors, was indispensable.

A Chemical Industries Bureau is in course of formation in Sweden, the object of which will be to bring together the Swedish chemical industrial interests.

The Pfaunder Company of Rochester, N. Y., has opened two new branch offices, one at 1502 Oliver Building, Pittsburgh, Pa., and one at 1946 Penobscot Building, Detroit, Michigan.

On Friday, October 19th, the Government commandeered approximately 7000 tons of caustic soda, to be used in the manufacture of picric acid. The price paid was considerably lower than the market price but was considered fair in all ways. It is understood that during the next 15 months the Federal authorities will requisition more than four times the above amount. This action will automatically reduce, pro rata, the contracts of customers.

The business of the Brown Instrument Company of Philadelphia has increased to such an extent that they have found it necessary to purchase a large piece of ground located on the south side of their factory, which will permit such extensions to their plant as may be required from time to time.

GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

COUNCIL OF NATIONAL DEFENSE

X-Ray Apparatus and Supplies. ANONYMOUS. Part 4 of the list of staple medical and surgical supplies selected to meet war conditions by the Committee on Standardization of the Council of National Defense. 14 pp. Issued July, 1917.

PUBLIC HEALTH SERVICE

Rodent Destruction on Ships. R. H. CREEL AND F. SIMPSON. Public Health Reports, 32, 1445-50 (September 7). This is a report on the relative efficiency of fumigants as determined by subsequent intensive trapping over a period of one year.

A New Water Sample Shipping Case. R. R. SPENCER AND H. P. LETTON. Public Health Reports, 32, 1476-83 (September 14). This report includes a few observations on the changes that take place in stored samples of water.

GEOLOGICAL SURVEY

Fluorspar. E. F. BURCHARD. Bulletin 666-CC. 8 pp. Prior to 1905 the production of fluorspar was less than 50,000 short tons annually; up to 1908 it fluctuated considerably, but in 1909 it began to increase rapidly, owing to the more general recognition of the value of fluorspar in the manufacture of open-hearth steel and to the expansions in facilities for mining and milling the mineral in Illinois and Kentucky. There was a steady increase in production from 1908 to 1912, but in 1913 and 1914 there were decreases coincident with depression in the steel industry. In 1915 and 1916 the production largely increased, owing to the revival of the steel and chemical industries, the output for both of these years exceeding all previous records. During the period 1910 to 1916, for which complete records are available, there has been an almost steady decrease in imports, but the considerable falling off during the war years may be attributed to the interruption to commerce as well as to depression in the mining industry in England caused by the scarcity of available miners.

It is apparent that American fluorspar deposits have proved ample to supply more than the additional fluorspar needed to make up for the decrease in imports. There are no considerable exports of fluorspar at present, so that the consumption is represented practically by the domestic production plus the imports.

The average price of domestic fluorspar at mines or local shipping points, for all localities and all grades of spar, has ranged between \$5.50 and \$6.50 a short ton during the last four years. The price decreased from 1913 to 1915 but increased more than 50 cents a ton in 1916. Ground spar has commanded the highest price—from \$10.75 to \$13.15 in recent years; lump spar has brought from \$6.00 to \$13, and gravel spar from \$4.85 to \$10, a ton, the price depending on quality, locality, and condition of the market.

Petroleum. J. D. NORRIS. Bulletin 666-DD. 13 pp. A full statistical report.

Potash in 1916. H. S. GALE. Mineral Resources of the United States, 1916, Part II. 98 pp. Published September 10, 1917.

The manufacturers of potash salts and potash products in the United States reported a production in 1916 of 35,739 short tons, having a mean content of about 27 per cent potash (K_2O) and a total content of 9,720 short tons of potash (K_2O). This is almost exactly ten times the production reported for 1915.

Practically all the predicted possibilities as to potash found some fulfillment in 1916. The almost entire stoppage of supplies from abroad and in small stocks on hand with which to meet the requirements have at times carried the price of potash to a high figure. Much potash has been used as fertilizer, even under these conditions, and a quantity of high-grade sulfate produced in this country has been exported to Cuba to meet a special agricultural demand there.

The forms in which potash has been produced and marketed are so diverse that it is difficult to make a summation of the production that will have any real significance. Therefore, the reports for all forms have been reduced to terms of tons of actual available or water-soluble potash (K_2O), the standard commercial unit by which the potash value of these products is usually expressed.

SUMMARY OF POTASH PRODUCED IN 1916

SOURCE	AVAILABLE POTASH (K_2O)	
	Quantity (short tons)	Value at Point of shipment
Natural salts or brines.....	3,994	\$1,937,600
Alunite and silicate rocks, including recoveries through furnace dust.....	1,850	715,000
Kelp.....	1,556	781,100
Wood ashes (potashes, pearlash).....	412(a)	270,000
Distillery waste (molasses).....	1,845	500,900
Miscellaneous organic sources.....	63	38,130
	9,720	\$4,242,730

(a) The reported production from wood ashes amounted to 825 tons of salts of varying grades, containing, by a moderate estimate, 50 per cent of potash.

Strontium in 1916. J. M. HILL. Mineral Resources of the United States, 1916, Part II. 10 pp. Published September 6, 1917.

From the best information available to the United States Geological Survey it would seem that approximately 250 short tons of strontium ore, of which about 4 per cent was strontianite (strontium carbonate) and the remainder celestite (strontium sulfate), was mined in the United States during 1916. This ore was mined in Arizona, California, and Washington, but not all the ore mined was sold.

As stated in the report for 1914, the apparent demand for strontium ore was then about 2500 short tons. Apparently the demand in 1916 was somewhat larger.

It is not possible to publish exact figures of production of strontium salts without divulging confidential information furnished the Geological Survey. Strontium nitrate was the principal salt produced, but a small output each of sodium carbonate and bromide was reported. Quotations on strontium nitrate during 1916 ranged from 22 to 30 cents and averaged about 33 cents a pound. Quotations for strontium carbonate did not fluctuate so did those for the nitrate, technical carbonate being quoted in 1916 at from 16 to 18½ cents and chemically pure carbonate at 45 to 50 cents a pound.

The total value of strontium salts, both imported and of domestic manufacture, consumed in the United States in 1916 was approximately \$250,000, a considerable increase in value, due in part to increased price received for the product and in part to increase in quantity consumed. There can be little question that the heavy freight traffic in 1916 must have demonstrated a large increase in the use of signal flares and it seems

equally certain that the use of signal lights in which strontium is employed has increased in Europe and on the high seas.

Abrasive Materials in 1916. F. J. KATZ. Mineral Resources of the United States, 1916, Part II. 15 pp. Published September 15, 1917.

The total value of the abrasive materials which are considered in this report and which entered trade in 1916 was \$5,156,098. This was an increase of \$1,148,029, or 29 per cent, compared with 1915. There was increase in value of domestic production of natural and artificial abrasives amounting to 27 and 31 per cent, and imports increased about 3 per cent in value.

Among the natural abrasives a gain was shown in production of grindstones and pulpstones, oilstones and scythestones, emery, garnet, pumice, tripoli and rottenstone, and tube mill linings, and in 1916 the first marketing of domestic pebbles for grinding was recorded. The reported value of diatomaceous earth sold was less than in 1915.

Thorium Minerals in 1916. W. T. SCHALLER. Mineral Resources of the United States, 1916, Part II. 14 pp. Published September 13, 1917.

This report states the conditions of the monazite sand industry throughout the world in a quantitative way rather than in a descriptive way, so that the intending producer of domestic sand can see what he would have to compete with and, from the qualities of his own, can judge for himself whether he can profitably undertake the production of his particular lot of sand. The monazite sand industry in the United States was prosperous at the beginning of this century and continued so until about 1910, after which the production ceased entirely for several years. Some sand has been mined and marketed since 1914, but the industry has in no way regained its prosperity of a decade or two ago.

Barytes and Strontium in 1915. J. M. HILL. Mineral Resources of the United States, 1915, Part II. 26 pp. Published October 6, 1916.

The marketed production of crude barytes in the United States in 1915 was 108,547 short tons, valued at \$381,032. This is a notable increase over the production in 1914, which was 52,747 short tons valued at \$155,647. The increase was in large part due to the activity of the mines in Georgia, Kentucky, and Tennessee. The Missouri mines, as will be seen from the following table, made an increase of approximately 6,000 tons,

MARKETED PRODUCTION OF BARIUM PRODUCTS IN 1915

	Quantity (short tons)	Average price per ton	TOTAL VALUE
Ground barytes	51,557	\$12.32	\$ 635,318
Lithopone	46,494	80.88	3,760,472
Barium chemicals(a)	8,823	(b)	(b)

(a) Barium chemicals include the binoxide, carbonate, chloride, hydroxide, nitrate, sulfate (blanc-fixé), and sulfide.

(b) Value cannot be reported.

but that is much below the increase in Georgia and Tennessee, which amounted to more than 15,000 tons in each State; the increase in Kentucky from a nominal quantity in 1914 to 7,753 tons in 1915 is remarkable. It is interesting to note that Alaska has entered the list of producers of barytes.

The prices paid for crude barytes in 1915 varied considerably in different States; thus, in Georgia the average price was \$3.31 a short ton; in Missouri the price was \$4.05 a short ton f. o. b. cars. These prices are higher than in 1914, but the average price did not advance as much as might have been expected, one factor in keeping it down appearing to be the opening of many deposits which have been idle for some time and whose output increased the supply in 1915.

Reports received by the Survey from 9 grinders, 8 makers of lithopone, and 4 barium chemical plants, producers in 1915, show that during the year 51,557 short tons of ground barytes, 46,494 short tons of lithopone, and 8,823 short tons of barium chemicals, made in the United States, were marketed.

The average price of ground barytes was \$12.95 a ton in 1914, and \$12.32 in 1915. This reduction in average price is believed to be due to the sales of unbleached ground barytes from some plants at prices considerably below the average for bleached ground barytes.

The average price of lithopone rose from \$75.89 a ton in 1914 to \$80.88 in 1915, but the prices reported by different companies varied considerably.

According to statistics collected by the Bureau of Foreign and Domestic Commerce, Department of Commerce, the imports of barium chemicals in 1915 were valued at 282,094; this is a decrease of nearly 43 per cent from the 1914 imports and is less than the 1913 imports by 32 per cent. It is not entirely clear that manufactured barytes refers to what is known in the United States as ground barytes, but it is believed that this is the case.

The principal barium chemicals made in the United States are the binoxide, carbonate, chloride, hydroxide, nitrate, and sulfate or blanc-fixé. Some crude barium sulfide ("Black Ash") is sold to makers of lithopone and manufacturers of chemicals who are not equipped to roast sufficient barytes to meet their needs.

No strontium-bearing ores of domestic origin were reported sold during the year 1915, and so far as the Survey has learned none of the American deposits were exploited. Commercial strontium ores should contain at least 95 per cent strontium sulfate. At present English celestite is largely used on the eastern seaboard, where the strontium salts are made, and is laid down at the works at approximately \$12 a ton.

According to the reports of the Bureau of Foreign and Domestic Commerce, Department of Commerce, the imports of strontium oxide, protoxide of strontium, and strontianite or mineral carbonate of strontium were valued at \$1,016 in 1914 and at \$6,411 in 1915. Imports of the strontium salts are free from duty. No figures are available for imports of celestite, strontium sulfate, used by manufacturers of strontium salts, this material being classed with all other chemicals not specially provided for in the present tariff.

Asphalt, Related Bitumens, and Bituminous Rock in 1916. J. D. NORTROP. Mineral Resources of the United States, 1916, Part II. 18 pp. Published September 22, 1917.

The year 1916 was one of prosperity for the asphalt industry in the United States. The quantity of natural asphalt produced and sold at mines and quarries in that year exceeded the quantity marketed in any preceding year except 1909 and 1910, and the value of the output exceeded that in any preceding year except 1907. The combined production in the United States of manufactured asphalt derived from domestic and from Mexican petroleum was 20 per cent greater than in any preceding year. All branches of the industry shared in the general prosperity, and gains in output included, expect for grahamite, each of the principal varieties of asphaltic materials produced in the country. Ozokerite from domestic sources reappeared in the statistics of production for the first time since 1907.

The quantity of natural asphalt, including bituminous rock, grahamite, gilsonite, wurtzilite, and the native paraffin, ozokerite, produced and sold at mines and quarries in the United States in 1916 was 98,477 short tons. This quantity was greater by 22,726 tons, or 30 per cent, than the output in 1915, and was less by only 584 tons, or about 0.6 per cent, than the record output of 99,061 tons in 1909.

The average price received for this material at the sources of production was \$9.37 a ton, and the gross market value was \$923,281, a gain of \$2.42 in average price per ton and of \$396,791, or 75 per cent, in gross market value, compared with 1915.

An analysis of the statistics of production in 1915 and 1916 shows gains in 1916 of 42.5 per cent in the output of bituminous rock and of 31 per cent in the combined output of gilsonite and

wurtzilit, but a loss of 22 per cent in the output of grahamite. With regard to the market value of these products, the statistics for 1916 show gains of 26 per cent for bituminous rock and of 129 per cent for gilsonite and wurtzilit combined, but a loss of a little less than 2 per cent for grahamite.

The large gain in market value of gilsonite is chiefly due to the inability of the producers of this mineral to supply the demand for it, an inability resulting solely from the lack of railway facilities in proximity to the mines. The moderate decline in the production of grahamite in 1916 is believed to be accounted for by the increased use of manufactured asphalt in the preparation of ready roofing, for which practically all the grahamite produced in the country is used.

The sales in 1916 of manufactured asphalt derived from crude petroleum of domestic origin, as reported to the Geological Survey, amounted at the sources of production to 688,334 short tons. Compared with the production marketed in 1915, this quantity is greater by 23,831 tons, or 3.6 per cent.

The average price received for the material sold in 1916 was \$8.98 a ton, a gain of \$1.88 a ton over the average price received in 1915. This gain was sufficient to make the total market value of the production in 1916, amounting to \$6,178,851, exceed the value of the output in 1915 by more than a million dollars.

Manufactured asphalt includes asphaltic oils used either for road sprinkling to allay dust or as a flux for softening harder bitumens and also semisolid products and residual pitches used in paving or in the roofing trade. The quantity of road oil and flux obtained from domestic petroleum and sold in 1916 was 404,009 short tons, market value \$3,158,603, an average of \$7.82 a ton. Compared with 1915, this output shows loss of 13,800 short tons in quantity but gain of \$2.09 in average price per ton. The quantity of paving asphalt and residuals was 284,325 short tons, market value \$3,020,248, an average of \$10.62 a ton. Compared with 1915 this output shows a gain of 37,681 tons in quantity and of \$1.20 a ton in average price.

Silica in 1916. F. J. KATZ. Mineral Resources of the United States, 1916, Part II. 5 pp. Published September 24, 1917.

So far as can be learned no true flint or chert has been produced for consumption as crushed or ground silica or for use as pebbles in grinding mills in the United States. The manufacture of flint, chert, and quartzite blocks for tube mill lining is reported in the chapter on abrasive materials.

Quartz from quartz veins, pegmatite, and quartzite amounting to 88,514 short tons, valued at \$242,786, was sold in 1916. This was a decrease of 21 per cent in quantity and 11 per cent in value as compared with 1915. The decrease was for both crude and ground material but greater for the former.

The prices of crude quartz in 1916 ranged from about \$1 to \$4.50 and (exclusive of large quantities used in copper smelting, valued at 50 cents to \$2 a ton) averaged \$2.37 as compared with \$3.30 in 1915 and \$2.44 in 1914. Prices of ground quartz ranged from \$6 to \$18 and averaged \$9.09, as compared with \$10.56 in 1915 and \$9.09 in 1914.

Pottery in 1916. J. MIDDLETON. Mineral Resources of the United States, 1916, Part II. 10 pp. Published September 13, 1917.

The value of all domestic pottery marketed in 1916 was \$48,217,242, an increase of \$10,891,884, or nearly 30 per cent over 1915, and of \$10,334,807, or 27 per cent over 1914, the previous year of highest value. The pottery imports decreased \$1,027,501, or 16 per cent, and the ratio of production to consumption, 92 per cent, was the highest recorded.

Every variety of ware as classified in this report showed an increase in 1916 as compared with 1915, where comparison can be made, and reached its maximum value in 1916. No comparison can be made with regard to the production of chemical pottery,

as it has not been reported separately before 1916. Sanitary ware showed the largest increase, \$3,118,201, or 39 per cent; white ware increased \$2,867,148; and china, the highest grade of pottery, increased \$1,148,216, or nearly 50 per cent.

The value of white ware and china, which comprise the general household wares and constitute nearly 50 per cent of all pottery products, was \$21,669,762 in 1916, an increase of \$4,015,364 over 1915. If to this sum is added the value of sanitary ware and porcelain electrical supplies the total value in 1916 was \$39,815,599, or \$9,496,783 more than in 1915.

This increase was due primarily to a larger volume of business, but some of it was due to higher prices for the wares. It should be said, however, to the credit of the operating potteries, that they refused to increase the price of their wares until it was made necessary by the greatly increased cost of labor and raw materials, the advances in prices of domestic pottery coming a year after foreign wares had been advanced.

The total value of imports of all clay products decreased \$1,034,222, or 15 per cent in 1916; in 1915 there was a decrease of \$1,806,350, or nearly 21 per cent. The total value of imports for 1916 was the lowest in 30 years, except in 1890, and was less than that of 1907, the year of maximum value, by \$8,045,267, or 58 per cent. Of the imports for 1916, about 97 per cent was pottery and about 3 per cent was brick and tile. The value of imports of pottery in 1916 decreased \$1,027,501, or 16 per cent, from 1915, and was considerably less than half of the value of the pottery imported in 1907. In 1916 the imports of the higher grades of pottery constituted 95 per cent of the total. Brick and tile imports decreased \$6,721, or 4 per cent, in 1916.

The value of exports of domestic clay products in 1916 increased \$2,150,290, or 79 per cent, over 1915. In 1915 there was a decrease of \$872,765, or 24 per cent from 1914. Of the exports in 1916, 62 per cent was brick and tile, 22 per cent pottery, and 16 per cent unclassified.

Each of these classes of ware increased in 1916 compared with 1915. Brick and tile showed the largest increase, \$1,467,826, or 95 per cent; pottery exports increased \$513,120, or 90 per cent; and all other clay products increased \$169,344, or 27 per cent. Exports of fire brick and china reached their maximum value in 1916.

BUREAU OF THE CENSUS

Butter, Cheese, and Condensed Milk. Separate from Census of Manufactures, 1914. 23 pp. Issued August, 1917. This is one of a large number of bulletins presenting statistics of industries as developed from the 1914 data. Information is given regarding raw materials, products, and methods of manufacture, both for the industry as a whole and for various states and subdivisions.

Glucose and Starch Industry. Separate from Census of Manufactures, 1914. 9 pp. Issued August, 1917.

Oilcloth and Linoleum. Separate from Census of Manufactures, 1914. 8 pp. Issued August, 1917.

INDIAN AFFAIRS OFFICE

Regulations to Govern Utilization of Casing-head Gas Produced from Oil Wells on Restricted Indian Lands. Unnumbered leaflet. 6 pp.

COMMERCE REPORTS AUGUST 1917

Details of the combination of seven of the largest German chemical and dyestuff manufacturers are discussed. The ammonia output of the *Baseler Anilin- und Soda-Fabrik* by the *Hoechst* process increased from 50,000 tons in 1914 to 60,000 tons in 1916. All the plants are at present making war supplies. P. 38.

Commercial deposits of tin, tungsten and antimony ores are found in South Africa. P. 41.

Experiments were conducted in England to determine the cause of superior decolorizing power of the German and Dutch decolorizing carbons known as "eponite" and "norite." It was found that by treating any porous wood, *e. g.*, pine, willow or cedar, with milk of lime (or with calcium acetate) and calcining at a white heat, charcoal is obtained, which after extraction with hydrochloric acid is a more active decolorizer than eponite or norite. (P. 443)

Efforts are being made in this country to facilitate the collection and utilization of tin cans. The supply of tin tetrachloride now exceeds the demand, so that increased recovery of tin must be made in other forms. (P. 304)

Production of peat in Norway and Denmark is now several times as great as in 1916. (P. 505)

Electric motors are being built in Switzerland up to 800 horse power, in which aluminum practically replaces copper. (P. 510)

A plant is to be erected in Venezuela for the production of tanning extract from divi-divi, since divi-divi is so bulky to transport. (P. 517)

Oil of *petitgrain*, an extract obtained from bitter orange leaves, and used for perfumes and perfumed soaps, is the principal article of export from Paraguay to the United States. (P. 611)

There is an increased demand in the United States for Brazilian zircon for use as a refractory. (P. 617)

Experiments are being conducted in England to determine possible uses for the oil of rubber-seed, large quantities of which are now wasted in the Malay states. (P. 650)

The Italian government has taken over the control of all tanning materials. (P. 663)

A census of all stocks of sulfur is being taken in Italy. (P. 794)

The annual production of *margarine* in Holland is about 180,000 metric tons, with a domestic consumption of 30,000 tons. In addition to animal fats, the following vegetable oils are used, *viz.*, cottonseed, peanut, sesame, soy bean, palm kernel, rapeseed, linseed, kapok seed and cocoanut. (P. 612)

SPECIAL SUPPLEMENTS ISSUED DURING THE MONTH

NORWAY—10a	SPAIN—15c	CHINA—52c, d, e
PORTUGAL—11a	BRITISH HONDURAS—	BRITISH EAST AFRICA
RUSSIA—13a	21a	65b
	COLOMBIA—42a	BRITISH SOUTH AFRICA
		66a

EXPORTS TO THE UNITED STATES

GLASGOW—710	RUSSIA—Sup. 13a	SPAIN—Sup. 15c
Acids	Ergot	Fertilizer
Ammonium sulfate	Lycopodium	Licorice
Corundum	Pine needle oil	Kags
Cresosote	Santonin	Olive oil
Sodium cyanide	Birch tar	Glycerin
Fertilizers	Fusel oil	Copper ore
Hides		Pyrites
Magnesite	BRITISH SOUTH AFRICA	
Paper stock	—Sup. 66a	
	Asbestos	COLOMBIA—Sup. 42a
	Buchu leaves	Gold
BRITISH HONDURAS—	Hides	Hides
Sup. 21a	Wattle bark	Ipecac
Cbicle	Diamonds	Ivory nuts
Copra	Chrome ore	Platinum
Hides	Corundum ore	Rubber
Logwood	Magnesite	Sugar
Mangrove bark	Scheelite	Tanning extract

COMMERCE REPORTS—SEPTEMBER, 1917

The annual output of natural indigo in Honduras has increased to 100,000 pounds. (P. 861)

Deposits of monazite and samarskite have been discovered in Mysore, India. (P. 894)

The British glass industry has shown a remarkable growth. Production of optical glass is about 300 tons annually. (P. 934)

Large deposits of sheet mica are being operated in Argentina. (P. 970)

The true citronella oil is obtained in Burma, India, by steam distillation of citronella grass, "cymbopogon nardus," the oil of which is superior to that of the lemon grass. (P. 794)

The list of articles, export of which is prohibited except upon grant of special licenses consists principally of chemical products including: acetone, alcohol, aluminum, arsenates, iron and steel, phenol, castor oil, cyanides, ferro-alloys, glycerine, mercury salts, nitric acid and nitrates, phosphorous, phosphoric acid, potassium salts, sulfites, spiegeleisen, sugar, sulfur, sulfuric acid, superphosphate, tin plate, toluol, and tungsten. (P. 1032)

Italy has fixed a maximum price for sulfur. (P. 1045)

The output of iron ore in Russia is greatly in excess of the consumption, owing to shutting down of metallurgical plants. (P. 1086)

Examination in Canada of 55 samples of borax showed that 19 contained excessive amounts of arsenic, some as much as 50 to 100 parts per million. (P. 1106)

A new factory is being erected in Norway for the manufacture annually of 4000 tons carbon and 1000 tons graphite electrodes. (P. 1124)

Production of potassium chlorate in Japan now greatly exceeds consumption, permitting large exports. Chemicals now imported into Japan from the United States include: Soda ash, borax, potassium dichromate, caustic soda, glycerine, and carboic acid. (P. 1129)

A plant for the production of potash from kelp and of fertilizer from fish is being installed near Prince Rupert, British Columbia. (P. 1166)

In the second annual report of the British Advisory Council for Scientific and Industrial Research, it is recommended that the £1,000,000 appropriated by Parliament, be used for the establishment in the various industries of associations for research. Among those organized or in prospect are those for the following industries, *viz.*, cotton, wool, shale oil, photographic supplies, electrical supplies, aircraft and shipbuilding steel, non-ferrous alloys, Diesel engines, coal mining, printing, cocoa, paper, etc. The National Physical Laboratory has been transferred from the Royal Society to the Advisory Council. A special Fuel Research Board is proposed to study methods of domestic heating, heat transmission, ventilation, etc. Researches being conducted include those on mine rescue apparatus, fire-resisting properties of materials, concrete, optical glass and optical instruments. Surveys of the literature of various industries are in preparation (P. 1172-4)

Production of sulfuric acid in Japan has increased so greatly that at the end of the war a great over-production is feared. (P. 1208)

SPECIAL SUPPLEMENTS FOR SEPTEMBER

GREECE—7a	PANAMA—35b	JAPAN—55a and b
SWITZERLAND—17b	NICARAGUA—34a	FRENCH WEST AFRICA
HONDURAS—31b		—69a

EXPORTS TO THE UNITED STATES

LONDON—1017	Glycerine	Silver
Rubber	Synthetic perfumes	Sugar
Tin		
Hides	HONDURAS—Sup. 31b	JAPAN—Sup. 55a
Indigo	Chicle	Camphor
GREECE—Sup. 7a	Antimony ore	Coal
Gum mastic	Copra	Copper
Licorice	Dyewoods	Vegetable isinglass
Olive oil	Gold	Menthol
Opium	Hides	Porcelain
Chrome ore	Indigo	Sulfur
Emery	Mangrove bark	
Magnesite	Rubber	PANAMA—Sup. 35b
Hides	Silver	Copra
Amyl alcohol	Sugar	Gold
SWITZERLAND—Sup. 17b	Zinc	Hides
	Fustic	Ipecac
		Ivory nuts
Aniline dyes	NICARAGUA—Sup. 34a	Manganese ore
Indigo	Dyewoods	Rubber
Artificial silk	Gold	Balsam
Hides	Hides	Tallow
Saccharine	Rubber	

NEW PUBLICATIONS

By IRVING DE MATTEY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

Agriculture in Some of Its Relations to Chemistry. Vol. 3. F. H. STORER. 7th Ed. 8vo. Price, 30s. Sampson, Low, Marston & Co., London.

Apparatus: Theory and Calculations of Electrical Apparatus. C. P. STEINMETZ. 8vo. 480 pp. Price, \$4.00. McGraw-Hill Book Co., New York.

Bacteria, Yeasts and Molds. H. W. CONN. 2nd Ed. 12mo. 295 pp. Price, \$1.00. Ginn & Co., Boston.

Biology of Waterworks. R. KIRKPATRICK. 8vo. 58 pp. Price, 1s. British Museum of Natural History, London.

By-Product Coking. G. S. COOPER. 8vo. 174 pp. Price, 7s. 6d. Benn & Cronin, London.

Chemical Patents and Allied Patent Problems. EDWARD THOMAS. 8vo. Price, \$2.50. John Byrne & Co., Washington, D. C.

Chemistry: A Laboratory Manual of General Chemistry. W. J. HALE. 12mo. 474 pp. Price, \$1.50. The Macmillan Co., New York.

Electrical Measurements. F. A. LAWS. 8vo. 719 pp. Price, \$5.00. McGraw-Hill Book Co., New York.

Electrical Motors. C. M. JANSKY. 8vo. 416 pp. Price, \$3.00. McGraw-Hill Book Co., New York.

Electrochemistry: Applied Electrochemistry and Welding. C. F. BURGESS and G. W. CRAVENS. 8vo. 132 pp. Price, \$1.50. American Technical Society, Chicago.

Engineering: A Text-Book of Mechanical Engineering. Vol. 2. W. J. LINEHAM. 11th Ed. 8vo. 1265 pp. Price, 15s. Chapman & Hall, London.

Engineering for Masonry Dams. W. P. CREAGER. 8vo. 237 pp. Price, \$2.50. John Wiley & Sons, New York.

Engineers: Kelly's Directory of the Engineers and Iron, Metal and Electrical Trades for 1917. 2072 pp. Price, 36s. Kelly's Directories, Ltd., London.

Explosives. Vol. 2. ARTHUR MARSHALL. 2nd Ed. 8vo. 795 pp. Price, \$16.00. P. Blakiston's Son & Co., Philadelphia.

Exporters' Encyclopedia, 1917. 13th Ed. 8vo. 1330 pp. Price, \$7.50. Exporters' Encyclopedia Co., New York.

Flotation. T. A. RICKARD and O. C. RALSTON. 8vo. 400 pp. Price, \$3.00. Mining and Scientific Press, San Francisco.

Food: How Food Poisons Us. C. H. COLLINGS. 12mo. 60 pp. Price, 1s. E. Miles, London.

Gold Deposits in the Rand. C. B. HORWOOD. 8vo. 436 pp. Price, 15s. C. Griffin & Co., London.

Illuminating Engineering Practice. Lectures Delivered at the University of Pennsylvania. 8vo. 578 pp. Price, \$5.00. McGraw-Hill Book Co., New York.

Illumination: Practical Electric Illumination. T. W. CROFT. 8vo. 225 pp. Price, \$2.00. McGraw-Hill Book Co., New York.

Indicators: The Theory and Use of Indicators; an Account of the Chemical Equilibria of Acids, Alkalis and Indicators. E. B. R. FRIDHAUX. 8vo. 382 pp. Price, 12s. 6d. A Constable & Co., London.

Inorganic Chemistry: A Textbook of Inorganic Chemistry. Vol. 4. H. F. V. LITTLE. 8vo. 505 pp. Price, 15s. C. Griffin & Co., London.

Irrigation: Operation and Maintenance of Irrigation Systems. S. T. HARDING. 8vo. 271 pp. Price, \$2.50. McGraw-Hill Book Co., New York.

Metallurgy: La Métallurgie française. C. CAVALIER. 8vo. 30 pp. Price, 3 fr. Chaix, Paris.

Microscopic Analysis of Cattle Foods. T. N. MORRIS. 8vo. Price, 2s. Cambridge University Press.

Mineralogy: Descriptive Mineralogy. W. D. BAYLEY. 8vo. 542 pp. Price, \$3.50. D. Appleton & Co., New York.

Mining: The Elements of Coal Mining. DANIEL BURNS. 8vo. 232 pp. Price, \$1.10. Longmans, Green & Co., New York.

Mycology: A Textbook of Mycology and Plant Pathology. J. W. HARRISON. 12mo. 779 pp. Price, \$3.00. P. Blakiston's Son & Co., Philadelphia.

Physiological Chemistry. A. F. MATTHEWS. 2nd Ed. 8vo. 1055 pp. Price, 21s. Baillière, Tindall & Cox, London.

Power: The Cost of Power. G. B. GOULD and C. W. HUBBARD. 16mo. 125 pp. Price, \$2.00. Ford Engineering Co., New York.

Roads: Practical Road Building. C. E. FOOTE. 12mo. 295 pp. Price, \$1.25. David McKay, Philadelphia.

Soil Conditions and Plant Growth. H. J. RUSSELL. 3rd Ed. 8vo. Price, \$2.00. Longmans, Green & Co., New York.

Standard Table of Electrochemical Equivalents and Their Derivatives. C.

HERING and F. H. GETMAN. 12mo. 130 pp. Price, \$2.00. D. Van Nostrand Co., New York.

Steam Boilers. R. H. KUSS. 8vo. 138 pp. Price, \$1.00. American Technical Society, Chicago.

Steam Charts and Special Tables for Turbine Calculations. F. O. ELLENWOOD. 4to. 43 pp. Price, \$1.00. John Wiley & Sons, New York.

Sugar: Calculations Used in Cane-Sugar Factories. I. H. MORSE. 2nd Ed. 189 pp. Price, \$2.00. John Wiley & Sons, New York.

Welding: A Practical Manual of Autogenous Welding. R. GRANJON and P. ROSENBERG. 8vo. 266 pp. Price, 5s. C. Griffin & Co., London.

Wiring for Light and Power. T. W. CROFT. 12mo. 426 pp. Price, \$2.00. McGraw-Hill Book Co., New York.

Worm Gearing. H. K. THOMAS. 2nd Ed. 8vo. 96 pp. Price, \$1.50. McGraw-Hill Book Co., New York.

X-Rays: Bibliography of Titles on Röntgen Rays. AMERICAN RESEARCH INSTITUTE. 4to. Price, \$2.50. The American Research Institute, Washington, D. C.

RECENT JOURNAL ARTICLES

Boiler Standardization. J. A. STEVENS. *Power*, Vol. 46 (1917), No. 13, pp. 413-415.

Chemical Exposition in Relation to the South and the Development of American Chemical Industries. W. H. STONE. *Manufacturers Record*, Vol. 72 (1917), No. 12, pp. 52-53.

Chemical Progress in the United States. ELLWOOD HENDRICK. *Manufacturers Record*, Vol. 72 (1917), No. 12, pp. 54-56.

Coal: Dealing with the High Cost of Coal. A. T. BALDWIN. *Textile World Journal*, Vol. 53 (1917), No. 14, p. 45.

Crystallization of Steel Ingots. J. F. KELLER. *The Blast Furnace and Steel Plant*, Vol. 5 (1917), No. 10, pp. 455-456.

Dyestuffs: American Dyestuffs for the American Army. L. J. MATOS. *Textile World Journal*, Vol. 53 (1917), No. 13, pp. 29-31.

Electricity for Japanning Ovens. C. D. CARLSON. *The Iron Trade Review*, Vol. 61 (1917), No. 11, pp. 541-542.

Electricity in the Pulp and Paper Industry. W. W. CRONKHITE. *Pulp and Paper Magazine*, Vol. 15 (1917), No. 38, pp. 898-900.

Felts: The Manufacture of Press Felts. E. S. BATES. *Pulp and Paper Magazine*, Vol. 15 (1917), No. 39, pp. 915-916.

Gasoline: The Supply of Gasoline. M. A. ALLEN. *Mining and Scientific Press*, Vol. 115 (1917), No. 14, pp. 511-512.

Hydro-Electric Plant: A Flexible Hydro-Electric Plant. C. V. JOHNSON. *Power*, Vol. 46 (1917), No. 13, pp. 424-425.

Iron: Structure of Iron Cast in Metal Molds. E. F. CONE. *The Iron Age*, Vol. 100 (1917), No. 12, pp. 656-658.

Magnesite: Washington Magnesite Industry. C. D. HUDSON. *Engineering and Mining Journal*, Vol. 104 (1917), No. 13, pp. 549-550.

Niagara Power Situation. F. J. TONE. *Metallurgical and Chemical Engineering*, Vol. 17 (1917), No. 6, pp. 257-259.

Nickel: Canada's Share in the World's Supply. E. B. BIGGAR. *Chemical News*, Vol. 116 (1917), No. 3016, pp. 133-134.

Nitrate: Domestic Nitrate Possibility. M. R. LAMB. *Engineering and Mining Journal*, Vol. 104 (1917), No. 11, p. 461.

Paper: Manufacture of Coated Paper. ALEXANDER THOMSON. *Paper*, Vol. 21 (1917), No. 1, pp. 11-13.

Paper and Allied Materials Imported into Canada and Exports of Pulp, Paper, Etc., of Canadian Origin. *Pulp and Paper Magazine*, Vol. 15 (1917), No. 38, pp. 894-897.

Pulverized Coal for Air Furnaces. W. R. BEAN. *The Iron Trade Review*, Vol. 61 (1917), No. 13, pp. 660-661.

Refractory Magnesite. R. C. GOSBOW. *Metallurgical and Chemical Engineering*, Vol. 17 (1917), No. 7, pp. 415-416.

Sand-Blast Operation. DAVID EVANS. *The Iron Age*, Vol. 100 (1917), No. 12, pp. 651-659.

Science: Applications of Science to Warfare in France. G. K. BURGESS. *The Scientist Monthly*, Vol. 5 (1917), No. 4, pp. 297-297.

Salable Frothing Agents. C. I. FERRIS. *Mining and Scientific Press*, Vol. 115 (1917), No. 12, pp. 380-382.

Steel, Its Selection and Treatment. J. F. KELLER. *The American Drop Forge*, Vol. 4 (1917), No. 3, pp. 23-29.

Sulfate Acid Situation. HENRY HEDGECOCK. *Metallurgical and Chemical Engineering*, Vol. 17 (1917), No. 8, p. 394.

Textiles: Notes on Textile Chemistry and Dyeing. W. H. BROWN. *Textile World Journal*, Vol. 53 (1917), No. 12, pp. 11-13.

Wastes: Utilization of Factory Wastes. C. B. ADAMS. *Industrial Management*, Vol. 14 (1917), No. 1, pp. 7-9.

Wire: An Investigation of Wire Degradation. A. D. HITCHCOCK. *Paper*, Vol. 21 (1917), No. 1, pp. 12-13.

Zinc Dust as a Precipitant on Oxidation. W. J. HEDGECOCK. *Mining and Scientific Press*, Vol. 115 (1917), No. 1, pp. 408-411.

INORGANIC CHEMICALS

Acetate of Lime.....	100 Lbs.	6.00	@	6.05
Alum. Ammonia, lump.....	100 Lbs.	4.25	@	4.50
Aluminum Sulfate, high-grade.....	Ton	70.00	@	75.00
Ammonium Carbonate, domestic.....	Lb.	11 1/2	@	12 1/2
Ammonium Chloride, white.....	Lb.	16	@	17
Aqua Ammonia, 26°, drums.....	Lb.	13 1/2	@	14
Arsenic, white.....	Lb.	16	@	16 1/2
Barium Chloride.....	Ton	70	@	85
Barium Nitrate.....	Lb.	8 1/2	@	11
Barytes, prime white, domestic.....	Ton	30.00	@	40.00
Bleaching Powder, 35 per cent.....	100 Lbs.	1.25	@	2.00
Blue Vitriol.....	Lb.	9 1/4	@	9 1/2
Borax, crystals, in bags.....	Lb.	7 1/4	@	7 1/2
Boric Acid, powdered crystals.....	Lb.	12 1/2	@	13 1/4
Bristolstone, crude, domestic.....	Long Ton	45.00	@	—
Bromine, technical, bulk.....	Lb.	55	@	60
Calcium Chloride, lump, 70 to 75% fused.....	Ton	30.00	@	35.00
Caustic Soda, 76 per cent.....	100 Lbs.	7.70	@	8.00
Chalk, light precipitated.....	Lb.	4 1/2	@	5 1/2
China Clay, imported.....	Ton	18.00	@	30.00
Feldspar.....	Ton	8.00	@	15.00
Fuller's Earth, foreign, powdered.....	Ton	—	@	35.00
Fuller's Earth, domestic.....	Ton	8.50	@	15.00
Glauber's Salt, in bbls.....	100 Lbs.	80	@	85
Green Vitriol, bulk.....	100 Lbs.	1.00	@	1.05
Hydrochloric Acid, commercial, 18°.....	Lb.	17 1/2	@	—
Hydrochloric Acid, C. P., conc., 22°.....	Lb.	2	@	2 1/4
Iodine, resublimed.....	Lb.	3.50	@	3.75
Lead Acetate, white crystals.....	Lb.	16	@	16 1/2
Lead Nitrate.....	Lb.	15 1/4	@	16
Litharge, American.....	Lb.	11	@	11 1/4
Lithium Carbonate.....	Lb.	1.25	@	—
Magnesium Carbonate, U. S. P.....	Lb.	18	@	22
Magnesite, "Calcined".....	Ton	60.00	@	65.00
Nitric Acid, 36°.....	Lb.	7 1/4	@	8
Nitric Acid, 42°.....	Lb.	8 1/2	@	9
Phosphoric Acid, U. S. P.....	Lb.	55	@	—
Phosphorus, yellow.....	Lb.	2.20	@	2.25
Plaster of Paris.....	Bbl.	2.00	@	2.50
Potassium Bichromate, casks.....	Lb.	44	@	45
Potassium Bromide, granular.....	Lb.	1.35	@	1.36
Potassium Carbonate, calcined, 80 @ 85%.....	Lb.	75	@	80
Potassium Chlorate, crystals, spot.....	Lb.	50	@	—
Potassium Cyanide, bulk, 98-99 per cent.....	Lb.	2.30	@	2.40
Potassium Hydroxide, 88 @ 92%.....	Lb.	83	@	85
Potassium Iodide, bulk.....	Lb.	2.90	@	—
Potassium Nitrate.....	Lb.	28	@	30
Potassium Permanganate, bulk.....	Lb.	3.80	@	3.85
Quicksilver, flask.....	75 Lbs.	100.00	@	—
Red Lead, American, dry.....	Lb.	11	@	12 1/4
Salt Cake, glass makers'.....	Ton	25.00	@	30.00
Silver Nitrate.....	Oz.	56	@	58
Soapstone, in bags.....	Ton	10.00	@	12.50
Soda Ash, 58%, in bags.....	100 Lbs.	3.10	@	3.15
Sodium Acetate.....	Lb.	11 1/2	@	12
Sodium Bicarbonate, domestic.....	100 Lbs.	2.30	@	2.60
Sodium Bichromate.....	Lb.	23 1/2	@	24
Sodium Chlorate.....	Lb.	23	@	24
Sodium Fluoride, commercial.....	Lb.	18	@	19
Sodium Hyposulfite.....	100 Lbs.	1.75	@	2.00
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	4.95	@	5.00
Sodium Silicate, liquid, 40° Bé.....	100 Lbs.	2.00	@	2.10
Sodium Sulfide, 60%, crystals, in bbls.....	Lb.	3 1/4	@	4
Sodium Bisulfide, powdered.....	Lb.	6 1/4	@	7
Strontium Nitrate.....	Lb.	25	@	—
Sulfur, flowers, sublimed.....	100 Lbs.	4.05	@	—
Sulfur, roll.....	100 Lbs.	3.70	@	4.15
Sulfuric Acid, chamber, 66° Bé.....	Ton	35.00	@	36.00
Sulfuric Acid, oleum (fuming).....	Ton	50.00	@	—
Talc, American white.....	Ton	15.00	@	18.00
Terra Alba, American, No. 1.....	100 Lbs.	85	@	90
Tin Bichloride, 50°.....	100 Lbs.	19.75	@	20.25
Tin Oxide.....	Lb.	64 1/2	@	65
White Lead, American, dry.....	Lb.	10	@	11
Zinc Carbonate.....	Lb.	23	@	25
Zinc Chloride, commercial.....	Lb.	16	@	17
Zinc Oxide, American process XX.....	Lb.	15 1/2	@	16

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	65	@	70
Acetic Acid, 56 per cent, in bbls.....	Lb.	11	@	11 1/4
Acetic Acid, glacial, 99 1/4%, in carboys.....	Lb.	35	@	37
Acetone, drums.....	Lb.	35	@	36
Alcohol, denatured, 180 proof.....	Gal.	1.00	@	1.01

Alcohol, grain, 188 proof.....	Gal.	5.60	@	6.00
Alcohol, wood, 95 per cent, refined.....	Gal.	1.10	@	1.12
Amyl Acetate.....	Gal.	5.00	@	5.25
Aniline Oil.....	Lb.	26	@	27
Benzoic Acid, ex-toluol.....	Lb.	1.75	@	2.00
Benzol, 90 per cent.....	Gal.	48	@	50
Camphor, refined in bulk, bbls.....	Lb.	75	@	80
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	49	@	50
Carbonyl Bisulfide.....	Lb.	7	@	7 1/2
Carbon Tetrachloride, drums, 100 gals.....	Lb.	17	@	17 1/2
Chloroform.....	Lb.	62	@	65
Citric Acid, domestic, crystals.....	Lb.	72	@	75
Cresote, beechwood.....	Lb.	1.90	@	2.00
Cresol, U. S. P.....	Lb.	18	@	19
Dextrine, corn (carloads, bags).....	100 Lbs.	7.60	@	7.65
Dextrine, imported potato.....	Lb.	—	@	—
Ether, U. S. P. 1900.....	Lb.	31	@	39
Formaldehyde, 40 per cent.....	Lb.	16 1/2	@	17
Glycerine, dynamite, drums included.....	Lb.	70	@	72
Oxalic Acid, in casks.....	Lb.	44	@	45
Pyrogallol Acid, resublimed, bulk.....	Lb.	3.10	@	3.25
Salicylic Acid.....	Lb.	1.30	@	1.40
Starch, cassava.....	Lb.	—	@	—
Starch, corn (carloads, bags) pearl.....	100 Lbs.	6.30	@	6.50
Starch, potato.....	Lb.	13	@	14
Starch, rice.....	Lb.	9	@	11
Starch : sago flour.....	Lb.	5	@	6
Starch, wheat.....	Lb.	5 1/2	@	6
Tannic Acid, commercial.....	Lb.	60	@	70
Tartaric Acid, crystals.....	Lb.	79	@	80

OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	57	@	65
Black Mineral Oil, 29 gravity.....	Gal.	13 1/4	@	14
Castor Oil, No. 3.....	Lb.	25	@	26
Ceresin, yellow.....	Lb.	16	@	17
Corn Oil, crude.....	Lb.	—	@	—
Cottonseed Oil, crude, f. o. b. midl.....	Gal.	1.18	@	1.20
Cottonseed Oil, p. s. g.....	Lb.	16 1/2	@	16 1/4
Menhaden Oil, crude (southern).....	Gal.	—	@	—
Neat's-foot Oil, 20°.....	Gal.	1.90	@	2.00
Paraffin, crude, 118 to 120 m. p.....	Lb.	7 1/4	@	8
Paraffin Oil, high viscosity.....	Gal.	29 1/2	@	30
Rosin, "F" Grade, 280 lbs.....	Bbl.	6.75	@	6.80
Rosin Oil, first run.....	Gal.	35	@	—
Shellac, T. N.....	Lb.	46	@	48
Spermaceti, cake.....	Lb.	25	@	—
Sperm Oil, bleached winter, 38°.....	Gal.	1.70	@	—
Spindle Oil, No. 200.....	Gal.	24	@	25
Stearic Acid, double-pressed.....	Lb.	23	@	24
Tallow, acidless.....	Gal.	1.50	@	—
Tar Oil, distilled.....	Gal.	33	@	34
Turpentine, spirits of.....	Gal.	52	@	53

METALS

Aluminum, No. 1, ingots.....	Lb.	37	@	39
Antimony, ordinary.....	Lb.	14 1/4	@	15
Bismuth, N. Y.....	Lb.	2.85	@	2.90
Copper, electrolytic.....	Lb.	23 1/2	@	—
Copper, lake.....	Lb.	23 1/2	@	—
Lead, N. Y.....	Lb.	65	@	7
Nickel, electrolytic.....	Lb.	55	@	56
Platinum, refined, soft.....	Oz.	105.00	@	—
Silver.....	Oz.	84 1/2	@	—
Tin, Straits.....	Lb.	61 1/4	@	—
Tungsten (Wo).....	Per Unit	23.00	@	25.00
Zinc, N. Y.....	Lb.	8 1/4	@	8 1/2

FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	7.00	@	7.10
Blood, dried, f. o. b. Chicago.....	Unit	6.05	@	6.10
Bone, 4 and 50, ground, raw.....	Ton	35.00	@	40.00
Calcium Cyanamid.....	Unit of Ammonia	—	@	4.00
Calcium Nitrate, Norwegian.....	100 Lbs.	—	@	—
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	6.50	@	10
Phosphate, acid, 16 per cent.....	Ton	16.00	@	18.00
Phosphate rock, f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	3.15	@	3.25
Tennessee, 78-80 per cent.....	Ton	5.50	@	6.00
Potassium "muriate," basis 80 per cent.....	Ton	350.00	@	—
Pyrites, furnace size, imported.....	Unit	—	@	nominal
Tankage, high-grade, f. o. b. Chicago.....	Unit	5.80	@	5.85 & 10

The Journal of Industrial and Engineering Chemistry

Published by THE AMERICAN CHEMICAL SOCIETY

AT EASTON, PA.

Volume IX

DECEMBER 1, 1917

No. 12

Editor: CHARLES H. HERTY

Assistant Editor: LEOLA E. MARRS

Advertising Manager: G. W. NOTT

ADVISORY BOARD

H. E. BARNARD, H. K. BENSON, F. K. CAMERON, B. C. HESSE, A. D. LITTLE, A. V. H. MORY, M. C. WHITAKER

Published monthly. Subscription price to non-members of the American Chemical Society, \$6.00 yearly; single copy, 60 cents
Price per single copy to American Chemical Society members, 50 cents. Foreign postage, seventy-five cents, Canada, Cuba and Mexico excepted
Entered as Second-class Matter December 19, 1908, at the Post-Office at Easton, Pa., under the Act of March 3, 1879

All communications should be sent to The Journal of Industrial and Engineering Chemistry,

Telephone : Vanderbilt 1930

35 East 41st Street, New York City

Subscriptions and claims for lost copies should be referred to Charles L. Parsons, Box 505, Washington, D. C.

ESCHENBACH PRINTING COMPANY, EASTON, PA.

TABLE OF CONTENTS

EDITORIALS:

Useless Work for the Tariff Commission.....	1084
Expanding Nitrate Plans.....	1084
The Platinum Situation.....	1085
The Chemist, the Draft, and Patriotism.....	1085
An Appeal to the National Association of Retail Druggists.....	1085
Wonders Will Never Cease.....	1086
An A. C. S. Pin for Every Member.....	1086

THE SCHOOL OF CHEMICAL ENGINEERING PRACTICE— A YEAR'S EXPERIENCE.....

1087

ORIGINAL PAPERS:

Comparative Tests of Chemical Glassware. Percy H. Walker and F. W. Smither.....	1090
Effect of Copper on Crude Rubber. Chas. P. Fox. Copper in Sewage at the New Haven Sewage Experi- ment Station. F. W. Mohlman.....	1092
Tannin Content of Pacific Coast Trees. H. K. Benson and Frank M. Jones.....	1096
Saturated Hydrocarbons in Basking-Shark Liver Oil. Mitsumaru Tsubimoto.....	1098
Some Data on Sperm Oils Used for Burning Purposes. Abraham G. Blakeley and Edmund A. Reilly.....	1099
Some Effects of Certain Solvents on Tars in the "Free Carbon" Determination. G. S. Monroe and H. J. Broderson.....	1100
The Estimation of Phenol in Crude Carbohic Acid and in Coal-Tar Oils. F. W. Skirrow.....	1102
Analytical Control of the Ammonia Oxidation Process. Guy B. Taylor and Joe D. Davis.....	1106
A Volumetric Method for the Determination of Formic Acid or Formates in the Presence of Hydroxides, Carbonates, Oxalates and Acetates. F. Tsubokawa.....	1110
A Study of the Estimation of Fat in Condensed Milk and Milk Powders. C. H. Biesterfeld and O. L. Evenson.....	1111
A Rapid Method for the Determination of Lime as Calcium Sulfate. L. G. Willis and W. H. Mac- Intire.....	1114
A Modified Method for the Determination of Fluorine with Special Application to the Analysis of Phos- phates. Cary R. Wagner and William H. Ross.....	1116

A Wool Fat (Lanolin) Substitute and the Preparation of Cetyl Alcohol. Sol. Axelrad.....	1123
The Rennetic Properties of Pepsin. Howard T. Graber.....	1125
A Method for the Determination of Alcohol. C. J. Haines and J. W. Marden.....	1126

ADDRESSES:

"Doing Our Bit." Bernhard C. Hesse.....	1128
Merchandise Control Laboratories. Ellwood Hendrick The Production of Scientific Knowledge. C. E. Ken- neth Mees.....	1133
France and America in Scientific Union. Prof. Victor Grignard.....	1137

CURRENT INDUSTRIAL NEWS

Estimation of Tin in Low-Grade Stuff; Coconut In- dustry; Starch Substitutes in Germany; Saltpeter Production in India; Ceramics; British Board of Trade; Manganese Steel; Hardening of Aluminum Bronze; Potash from Flue Dust; A New Test Paper; Ferro-Concrete Ships; Russian Cottonseed Oil In- dustry; Japanese Paper-Making Industry; Appli- cation of Radio-Active Substances for Batteries; Lining White Metal Bearings; Artificial Wood; Paints and Varnishes for Siam; Cotton Trade in Japan.....	1143
--	------

NOTES AND CORRESPONDENCE

Hydrogenation of Oil, The American Coal-Tar Products Industry. Production to be Ascertained by the United States Tariff Commission. Sampling Fats and Oils. Correction. Concerning the Manufacture of Phthalic Acid and Phthalic Anhydride. Chicago Chemical Exposition. Fats. Aromatic. Nitric Acid. Saponification. Correction. The Determina- tion of Sulfur Dioxide. Correction.....	1146
---	------

WASHINGTON LETTER

1149

PERSONAL NOTES

1150

INDUSTRIAL NOTES

1151

GOVERNMENT PUBLICATIONS

1153

BOOK REVIEWS

1155

NEW PUBLICATIONS

1159

MARKET REPORT

1160

INDEX

1161

EDITORIALS

USELESS WORK FOR THE TARIFF COMMISSION

At the request of the Chairman of the Tariff Commission there is printed on page 1148 of this issue a statement from the Commission concerning the information it is now seeking from manufacturers of crudes, intermediates and finished dyestuffs as to production of these materials within the United States during the year 1917.

This action is evidently a tuning up of the extensive machinery which will be necessary to determine whether or no at the end of the five-year period following the enactment in September 1916 of the Dyestuff Section of the General Revenue Act there is being produced in this country sixty per cent of the values of domestic consumption of these products. Failing such a development within that five-year period the special, but not the ad valorem, duties, are, by the terms of the Act, to be at once removed by Presidential proclamation rather than by the sliding scale of a twenty per cent annual reduction during the following five-year period.

The early beginning of this work of compilation is clearly indicative of the technical difficulties the Commission foresees. It is equally evident that the dyestuff manufacturers, at present about the busiest set of men in America, are to have another annual burden imposed upon their present overtaxed forces. Stronger and stronger is growing the appeal for a concentration of the nation's energies on necessary industries at the sacrifice, if need be, of unnecessary industries. Let the movement apply also to matters of legislation.

The sixty per cent clause of the Revenue Act admits of only one interpretation—doubt as to the good faith or ability of American manufacturers of dyestuffs.

Is there any fair-minded person in this country who is not proud of the accomplishments in this line during the brief period of scarcely more than one year since the legislation was enacted? Consumers have been supplied with the full tonnage of pre-war days and the variety of dyestuffs is constantly increasing. The progress made is the talk of the street.

Highest endorsement of these achievements has been given by a distinguished member of the Tariff Commission itself, the Hon. William S. Culbertson. In an address at the recent National Exposition of Chemical Industries [THIS JOURNAL, 9 (1917), 1015], Mr. Culbertson said of the dyestuff industry:

"The rapidity of its progress has amazed the world. The record of its achievement reads like a fairy tale and will prove an imperishable monument to American chemists and business men."

In view of such generally acknowledged progress and in the interest of economy of effort, we appeal to the Tariff Commission to recommend to the Congress, about to convene, the removal of this sixty per cent clause from our statutes.

EXPANDING NITRATE PLANS

The successful offense along the Flanders front within the last two months, resulting from the use of seemingly unlimited amounts of high explosives, has revolutionized prevailing views concerning the stalemate results of trench warfare.

During this same period we have become aware that while T. N. T. is the preferred high explosive, nevertheless our army must depend upon the gas works for toluol, the basis of this explosive, and this source, at its maximum output, is sufficient for only one half of the toluol needed for an army of one million men. In such a situation the officials of the War Department have naturally turned to ammonium nitrate, for use with T. N. T. Abundant confirmation of the high value of such a mixed explosive has been given by British experts recently visiting America.

The plans of our Government for independence in nitrate supply have necessarily undergone a rapid expansion, for in addition to nitric acid for explosives and ammonia salts for fertilizers, there must now be quickly available still larger quantities of ammonia for the explosive ammonium nitrate.

The immediate need of ammonia can be met by drawing temporarily upon the supplies of coke-oven ammonia without serious detriment to agriculture. We are informed by officials of the War Department that good progress is being made at Muscle Shoals in the installation of the synthetic method for manufacture of ammonia from air nitrogen. Much of the machinery is completed and the remainder is ordered and will be delivered as rapidly as completed. Materials for the buildings have been contracted for and three hundred and fifty laborers are engaged in the work of construction.

It is sincerely to be hoped that this synthetic plant will soon be greatly enlarged. The investigation of this method on April 20 by Col. C. B. Wheeler and Col. C. C. Keller of the War Department, Dr. Charles L. Parsons of the Bureau of Mines and Dr. A. A. Noyes of the Nitrate Supply Committee, showed clearly that a decided improvement had been made over the Haber process, now so largely employed in Germany, that the method had passed the experimental stage, and was capable of producing ammonia at lower cost than any other known method. As the process was immediately available for use without recompense by the Government it was recommended by the Nitrate Supply Committee to the Secretary of War as most adequately meeting the terms of the National Defense Act, namely, "the best, cheapest and most available means for the production of nitrates," etc.

The situation has become suddenly so acute, however, that the officials have wisely decided that all possible sources of ammonia should be utilized, regardless of the relative merits of the individual processes or of cost of the product. They have naturally turned therefore to the cyanamide process, the only other

available source of ammonia through nitrogen fixation. At this writing no official statement of plans has been published by the War Department, but it is understood that a cyanamide plant will also be located at Muscle Shoals, utilizing surplus power of adjacent hydro-electric developments and supplementing this by a steam plant.

We are confident that the entire Nation will support the policy of the War Department in leaving no stone unturned to secure ammonia from every possible source. Meanwhile, the operation of the two methods, the synthetic and the cyanamide, side by side at Muscle Shoals, will furnish abundant facts as to the relative merits of each for nitrogen fixation under American conditions.

THE PLATINUM SITUATION

From one who is in close touch with all phases of the platinum situation we have learned that a decrease of about forty per cent in the use of platinum for certain lines of bulky jewelry has resulted from the patriotic stand taken last spring by the jewelers. That is fine as far as it goes.

Our Washington correspondent points out in this issue that there is a possibility of complications in shipments of platinum from Colombia. This gives rise to apprehensions.

Platinum jewelry is now being extensively advertised in many periodicals. Without any attempt at a systematic survey we have read recently the advertisements of the Charles L. Trout Company in the *New York Times* of November 18, 1917, Daniel Low and Company in *Scribner's Magazine* for November, 1917, Sallan's touchingly illustrated advertisements of platinum engagement rings in the illustrated section of the *Detroit Free Press* of November 11, 1917, the James R. Armiger Company's well displayed advertisement of "Fine Platinum Jewelry" in the *Baltimore Sun* of November 6, 1917, etc. These advertisements seem to indicate an aggressive sale of platinum jewelry.

Meanwhile war developments of the last two months point clearly to the fact that chemical activities involving the use of platinum, both within and without Government circles, must be enormously expanded if the great army we are now beginning to raise is to be thoroughly supplied with essential war materials. In spite of all efforts to remedy the situation, platinum is bringing to-day (November 19, 1917) \$98 per ounce. These are facts.

Assuming the correctness of the decrease by forty per cent of the use of platinum in bulky articles, this continued high price is indicative of either diminishing imports (we have no figures at hand), absorption by the expanding chemical industries, increased manufacture of platinum jewelry (not included in the list of the Jeweler's Committee), or perhaps hoarding of platinum.

Whatever the explanation, it would seem that we are rapidly approaching the point where our Government may be compelled to follow the example of England in taking over all domestic supplies of platinum and apportioning them to the various industries in conformity with the interests of the national welfare.

THE CHEMIST, THE DRAFT, AND PATRIOTISM

In the June issue of *THIS JOURNAL* we wrote under the title "In the Light of Experience," urging upon all in authority to conserve for the best interests of the country the chemically trained men, using them in, or not calling them from, work for which their chemical training fitted them. May we now address a word to those chemically trained young Americans within the age limits subjecting them to the operations of the selective draft?

We have no desire to criticize and we sympathize fully with the fine spirit which prompts every young man to wish to get to the front and offer his life for the cause of his country. Nevertheless we know, personally, chemically trained men who have avowedly hurriedly sought commissions in whatever line of the service offered a chance for such, rather than risk serving as a private through the selective draft law.

If this country had a surplus supply of chemists, and if chemistry played no especial rôle in this war, such action would be purely personal and not rightly subject to comment. In view, however, of the present great dearth of chemists, of the practical exodus of all advanced students of chemistry from our universities, of the recognized vital importance of the work of the chemist both in the government service and in the industries, we do not hesitate to say that such abandonment of opportunity for chemical service for the sake of insuring a commission is not patriotism but selfishness. This may sound harsh, but it is a time for plain speaking.

The events of the last few weeks have convinced all that we must prepare for a long war and throw into the scales the full resources of this great country. The selective draft is the officially adopted method for raising our army. We have believed in its principles from the first. The Nation is indebted to President Wilson for his foresight and broad grasp of the part America is to play in the war when he so consistently and persistently urged the adoption by Congress of the selective draft rather than the volunteer principle. Only through this means can this country contribute its maximum share.

To those chemists, therefore, who have asked our advice, we repeat, and to those who will soon be subjected to the second call under the draft law we urge: "Wait for the operation of the draft law! Do not sacrifice the right of our country to your chemical training for the sake of a commission in the field service. Be prepared to serve wherever and in whatever capacity your country may most need you!"

AN APPEAL TO THE NATIONAL ASSOCIATION OF RETAIL DRUGGISTS

The spirit of cooperation is so keenly alive at the present that the time seems appropriate to make an appeal which we have long had in mind. Will not the National Association of Retail Druggists cooperate with the chemists by discouraging the use of the word "chemist" on the signboards of retail drug stores?

The request may seem trivial but there is a deeper significance than appears on the surface, and the request carries with it no suggestion of the relative values of the two classes of men. It is made simply for the sake of clarity of thought by the public at large of what the functions of the chemist really are in our national existence.

During the past two years much sincere effort has been made to acquaint the nation with the work of its chemists, and to bring about a more cordial and sympathetic relationship between chemists as a class and our American people. The lack of an adequate understanding of the work of the chemist was partly responsible for some of the shortages the country suffered from at the outbreak of the war. Much progress has been made in this campaign of understanding. It should be complete through all classes of our citizens.

The sign "Chemist" above a drug store, however, still leads to confusion or misunderstanding. Many in all walks of life still think of the druggist whenever the chemist is mentioned. An artist recently called in to design, for a Liberty Loan Bond parade, a float illustrative of the contribution of chemists to the winning of the war, at once began the delineation of a mortar and pestle as the central theme.

True it is that in the iatro period chemistry had chiefly to do with drugs and equally true it is difficult, even to-day, if contentiously inclined, to define precisely the term chemist; nevertheless the work of the chemist and that of the retail druggist are now so clearly differentiated that there can be no real justification for the retention by our modern druggists of the term chemist, a heritage of English practice.

Moreover, the druggists have such an abundance of choice in the terms druggist, apothecary and pharmacist that they can well afford to dispense with any further designations. May we not hope, therefore, that this appeal may meet with a sympathetic response on the part of the members of the National Association of Retail Druggists?

WONDERS WILL NEVER CEASE

The spirit of the times is not conducive to frivolous thoughts, yet from the quarter least expected, the Congress of the United States, frivolity is thrust upon us. Doubtless it was unwittingly the rebound from intense war debate and prolonged consideration of appropriation bills mounting into the billions which led both Senate and House to pass with all due dignity the joint resolution of acceptance for test of the proposed gift to the United States on the part of citizen Garabed T. K. Giragossian of Boston, Mass., of the "Garabed," an appliance which, in the printed words of House Joint Resolution 101 of the 65th Congress, 1st Session, embodies a principle through which or by means of which (we don't know which which), "unlimited energy can be generated without expense"—all of this in exchange for the slight courtesy of the "Government protecting the said discoverer, his heirs and assigns,

in the use and disposition of the said discovery or invention."

To administer this remarkable transaction the Secretary of the Interior was specifically designated as the trusted agent of the Government. If this was an attempted joke upon the proverbially genial Secretary of the Interior, it was shameful. Mr. Lane has always proved himself ready, willing and abundantly able to throw himself into any old breach for the public good, but this is carrying matters too far, especially as Section 2 is to the effect that Mr. Lane is not to begin the job until he shall have approved "a commission of five eminent scientists to be appointed by the said Garabed T. K. Giragossian" which high commission should certify to "the entire practicability of his (Garabed T. K. Giragossian's) discovery," pursuant to a demonstration.

We remember the interesting remarks by Dr. A. D. Little at the smoker during the recent Boston Meeting of the American Chemical Society in which he assembled in brief narrative some of the more striking scientific fakes for which Boston inventors had readily fallen: the extraction of gold from sea water, the manufacture of artificial rubber by a real new process, etc., etc. Perhaps the Bostonians have at length gotten wise and in a spirit of revenge decided to pass the buck to Congress. At any rate President Wilson saved the day by declining to sign the bill.

We realize fully the dangers run by scoffing at anything new—and yet there is a difference, which leads us unhesitatingly to congratulate the President for saving the dignity of the nation and allowing the Secretary of the Interior to go on about his regular business.

AN A. C. S. PIN FOR EVERY MEMBER

It was a happy thought that led to the adoption of an official emblem for the American Chemical Society. As a decorative feature of programs, stationery, dinner menus and for official decoration in general, this now well-known emblem has contributed largely to that increased esprit de corps which characterizes the present organization.

Particularly noticeable is the steadily increasing number of members of the Society who constantly wear the official pin, generally on the lapel of the coat. Thus worn it serves as an introduction and produces at once a feeling of community of effort and ideals.

The pins at present available, however, are expensive—needlessly so for these days of necessary economy of personal expenditures. Correspondence has been shown us recently which assures the ability to produce, at a cost of one dollar each, rolled-gold pins conforming fully to the design and beauty of the official pin. We hope the Directors at their December meeting will authorize the manufacture and sale of such inexpensive pins, under order of course from the Secretary, as is now required. Their availability would undoubtedly result in a largely increased use of the emblem by the members of the Society.

THE SCHOOL OF CHEMICAL ENGINEERING PRACTICE A YEAR'S EXPERIENCE

By WILLIAM H. WALKER, Professor of Chemical Engineering, Massachusetts Institute of Technology

The School of Chemical Engineering Practice of the Massachusetts Institute of Technology announced in *THIS JOURNAL* last summer has, by the results achieved in the year just closed, proved that the basic principles upon which it was founded are sound, and that the practical operation of these principles is entirely feasible when applied to selected men who have already had at least three years of preparatory scientific instruction. The year just closed has been most successful.

The aims of the course as enumerated in our original outline have been in great measure realized, and other advantages not anticipated have appeared. Extracts from some letters written by the students to their fellows at the Institute are appended, which reflect, more clearly than could be dictated, the advantages they have enjoyed. The thirty students who made up the School are enthusiastic regarding the manifold benefits received, while the manufacturing companies which are coöperating in carrying out the plan are well satisfied, not only with the results obtained from the research work of the organized staff, as part of the coöperative idea, but with the advantages which have accrued from large scale test work carried on by the students.

It will be recalled that the School was made up of five stations located at the plants of The Eastern Manufacturing Co., Bangor, Maine; The New England Gas & Coke Co., Everett, Mass.; The Carborundum Co., Niagara Falls, N. Y.; The American Synthetic Color Co., Stamford, Conn.; and The Atlas Portland Cement Co., Northampton, Pa. At each station there was provided a conference and library room for the students, and a research laboratory for the factory. A complete line of books, measuring instruments and other equipment selected with reference to the work to be done at each station was supplied. As Director of each station a man of enthusiasm and enviable record of achievement was obtained, who in turn was supplied with an assistant of energy and ability. This staff became a part of the Institute faculty, and it is largely to the ability and enthusiasm of each and all of the members of this staff that the great success of the plan is due.

The underlying principles of the Course may be made clear by the following considerations. A great advance in educational methods was made when laboratory work was introduced into the curriculum of science courses. By this means the principles of science were emphasized, clarified and made an integral part of the student's knowledge and experience. But such applications of scientific facts and principles are of necessity limited to the facilities of the laboratory, or, as we say, experimentation on a laboratory scale. There are many fundamental principles of science which possess a different interest and value when

studied under factory conditions, and there are also many problems susceptible of a scientific solution, which assume unfamiliar shape when viewed through the hazy atmosphere of large scale production.

Again there is a great gulf fixed in the minds of most students between the applications of science in the laboratory, where the thermodynamic environment is such as to make relationships quantitative and hence calculation comparatively easy, and the factory, where conditions are such as to make necessary at best a scientific guess or a rational assumption. And yet, if we involve our scientific knowledge in the solution of our problems only when a rigorously quantitative treatment is possible, we must in the majority of cases revert to a "rule of thumb" method of solution.

Therefore, the first general object of the School of Chemical Engineering Practice was to introduce the laboratory method of instruction into a study of factory operations and processes, to make the factory a chemical engineering laboratory. This was based upon the tenet that it is entirely possible to study the performance of a piece of apparatus or the progress of a reaction or process, without interfering with production in either quantity or quality.

The advantages gained by this method of study are twofold. First, the men get a personal first-hand knowledge of the unit operations involved in chemical industry, and the part played by such unit operations in the success of a chemical-manufacturing process; and second, they acquire a knowledge of men and the organization of men necessary to carry on a coördinated and interdependent plant. The students mix with the laboring men, coöperate with the foremen and observe the method of control from those high in authority to those with none.

It is interesting to note that the rock on which nearly every one predicted our educational ship would most probably be wrecked was this one of relations between the students and the factory organization. I am glad to be able to state that not the slightest difficulty of any description has been experienced. On the contrary, the superintendents have been interested and uniformly anxious to make our stay at the plant both pleasant and profitable, while the laboring men have been most helpful in every way.

The second general object of the School was to allow the student to realize the opportunities which exist in industry for the application of science. Provided first, the student can detect the presence of the problem and diagnose it promptly, and second that he has the training necessary to carry that knowledge of science which he possesses. In other words, to show him that two things are necessary for success, first, a knowledge of science, and second, a training in its applications.

In organizing the work at the several stations it

was classified roughly under heads providing for the following objects:

I—To study the chemical control of industrial processes through the laboratory, and to acquire ability in the interpretation of laboratory data in terms of factory practice.

Instruction in analytical chemistry to prospective engineers is handicapped, in that it is difficult to combine in the student's work the necessary accuracy with that speed on which depends his effectiveness as part of a laboratory organization. The average student is generally either accurate and painfully slow or rapid and unreliable. When placed in a cement mill, however, he learns that the composition of the rock from the quarry must not only be accurately determined, but it must be known by the time the rock has passed through the rough crushers and driers. The importance of the analytical work now strikes him with its full significance. To reap the benefit of life in an active industrial laboratory where both wonderful speed and accuracy are obtained, each student spent five days in the laboratory of Station *E*, where raw material and finished product were analyzed according to the methods of the Atlas Portland Cement Co., and his work checked, both as to result and time consumed, against the standard practice of the laboratory.

Special methods of analysis employing a wide variety of instruments are involved in controlling the factory experimental work at the different stations. Two types of optical pyrometers, and a variety of thermal junctions are used in the heat balance run on the cement kilns. Gas analysis in all forms is in use at Station *B* and elsewhere; polarizing and petrographic microscopical work at Station *C*, and so on. Analytical chemistry takes on an unexpected attractiveness when it becomes the most important source of knowledge by which the progress of a reaction or a process must be determined.

II—To acquire a first-hand knowledge of the processes of the plant and the machines with which it is equipped.

A process or a machine may be studied in two ways: first, by making a quantitative run or test upon it, in which input of energy and material is balanced against output; and second, by operating the unit machine and determining how well it does the work for which it was designed, how resistant it is to both mechanical and chemical wear and tear, how easily cleaned and repaired, and how nearly perfect the product is when viewed from its various commercial standpoints.

Both of these methods were used at the different stations. For example, the squad of six men were placed in the electrolytic bleach plant of Station *A* and directed to decide what mechanical measurements must be made, what data secured, what and where samples for analysis must be drawn, and in short, to outline in detail a test run of 36 hours, which would furnish answers to the following type of questions:

What per cent of the energy supplied to the bus bars is converted into calcium hypochlorite as delivered to the storage tanks?

What per cent of the salt drawn from the storage bins appears as caustic soda in the concentrated liquor tank?

Same question as to lime consumption, and so on.

From two to three days were consumed in deciding all the details and making necessary arrangements for withdrawing samples, recording measurements and doing the necessary analytical work. A 36-hour run was then made and calculated very completely. The daily practice of the plant relative to temperature, current density, concentration of feed liquor, rate of flow, composition of cell effluent, resistance of diaphragm and other working conditions were then studied and interpreted in the light of the laws of electrochemistry already learned in earlier years of the Course. Each squad then tested the accuracy of the predictions in reference to one variable. For example, the influence of the rate of flow of the brine through the diaphragm on the efficiency, for cells of different ages, was determined. Incidentally many data of service to the company were obtained.

This method of applying the principles of science to industrial problems under factory conditions was found to adapt itself to almost every important operation, and when applied to the widely differing conditions of the five stations, a most comprehensive experience was obtained.

The second method of studying a process and machine is so obvious as to need no example. It was found that much valuable experience was obtained by putting the students, one at a time, on the regular factory repair gang for a period of 3 to 6 days. In some cases, for example in the routine repair of the Huntington Mills of the Cement Plant, the work was so heavy that but few students could take an active part in it: but in the majority of cases a student can do the work of a helper and learn how most quickly to do the thing which is needed to be done.

III—To obtain the wider view-point which comes from contact with those who are employed to superintend or carry on the factory operations, and to acquire the degree of confidence in handling industrial processes and large sized apparatus which comes from actual participation in the active work of the plant.

No part of the plan has received more hearty endorsement on the part of the students than the opportunity to mix with the operations of the factory and to share in the work of the plant. For example, at Station *A* each student was for a time assistant to the assistant cook in the digester house; at *B* he helped run the ammonia stills and the sulfate recovery; at *C* he operated both the magnetic and electrostatic separators, and made runs on large scale electric furnaces; at *D* he worked on the phenol plant, from the sulfonation to the final distillation; at *E* he fired the cement kilns, and so on. Although at few times was the entire responsibility for operation placed on the student, yet he was at most times sufficiently in charge to gain a fair measure of self-confidence in handling industrial processes. He realized the importance of the human element in industry, and observed the efforts being made at the different companies toward welfare work, task and bonus systems, and other methods by which

ORIGINAL PAPERS

COMPARATIVE TESTS OF CHEMICAL GLASSWARE¹

By PERCY H. WALKER AND F. W. SMITHER

Received October 23, 1917

The cutting off of imports from Germany and Austria has forced us to rely upon American manufacturers for practically our entire supply of glass beakers and flasks. In order to give chemists some information as to the quality of this ware, the Bureau of Standards has examined five brands of American-made ware in comparison with the two best known wares of European make.

The tests included chemical analysis, determination of coefficient of expansion, refractive index, condition of strain, resistance to repeated evaporation, to heat, and to mechanical shock, and resistance to chemical reagents.

In all cases beakers and flasks approximating in size the 400-cc. Jena beaker and flask were used. All

ers, consisted in repeated evaporation to dryness of sodium chloride solution with examination for cracks after each evaporation. None of the wares developed cracks after twelve evaporations.

One of the heat shock tests consisted in filling the beakers with cold water, which was then rapidly heated to boiling. Other tests included the plunging into ice water of vessels containing boiling water, paraffin at 150° C., and paraffin at 200° C., and the dropping of beakers bottom down upon a thick board from heights increased by intervals of 5 in.

The solubility tests were made by determining the loss in weight of pieces of the wares upon treatment with water and various solutions commonly used in the laboratory. With water on beakers the action was continued about 72 hrs., the water being heated about 24 hrs.; on flasks, the action was continued about 17 hrs., keeping the water boiling during 5

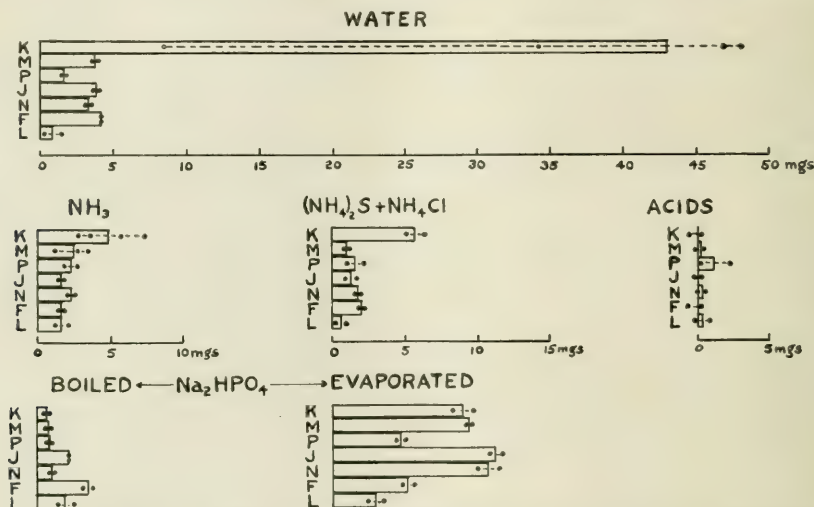


FIG. 1.—LOSS IN WEIGHT OF BEAKERS WITH WATER, AMMONIA, AMMONIUM SULFIDE AND CHLORIDE, ACIDS AND SODIUM PHOSPHATE SOLUTIONS

the ware tested bore permanent trade marks. From 45 to 50 beakers and flasks of each ware were secured for this series of tests.

Table I gives the composition of the different wares tested.

Details regarding the methods of analyses, weight and size of pieces tested, coefficient of expansion, refractive indices, and condition of strain will appear in a publication of the Bureau of Standards and are not given here, since little information bearing on the suitability of the various glasses for laboratory use can be obtained from these results. The Pyrex ware has low coefficient of expansion and refractive index.

The evaporation test, which was made only on glass-

ware, with mineral acids, solutions containing sodium chloride and sodium nitrate were mixed with a large

TABLE I—ANALYSES

WARE	Kava- iller	M. E. G. Co.	Pyrex Beaker	Jena Beaker	Jena Flask	Nonsol Beaker	Fry Beaker	Libbey Beaker
Al ₂ O ₃	0.14	1.0	2.0	4.2	4.2	2.5	2.7	2.1
Fe ₂ O ₃	0.08	0.35	0.25	0.25	0.27	0.23	0.22	0.44
PbO.....	...	5.6	...	10.9	10.9	7.8	3.6	...
MnO.....	0.02	0.02	0.01	0.01	0.01	0.01	0.03	0.03
CaO.....	8.7	0.66	0.29	0.63	0.56	0.79	2.6	0.42
MgO.....	0.17	4.3	0.06	0.21	0.25	3.4	2.6	0.08
Na ₂ O.....	7.1	10.8	4.4	7.5	7.8	10.9	9.8	8.2
K ₂ O.....	7.9	0.30	0.20	0.37	0.31	0.30	1.5	0.67
SiO ₂	75.9	73.0	80.5	64.7	64.7	67.3	68.6	75.9
B ₂ O ₃	3.6	11.8	10.9	10.6	6.2	8.1	10.8
PrO.....	0.08
SO ₃	0.20	0.02
As ₂ O ₃	Trace	0.02	0.70	0.14	0.19	Trace	0.18	0.36
Sb ₂ O ₃	0.60	0.62
TOTAL.....	100.29	100.27	100.21	99.81	99.79	100.05	99.93	100.00

Selenium and fluorine were not found, but lithium was detected spectroscopically by Mr. Paul W. Merrill in all the samples.

¹ Published by permission of the Director of the Bureau of Standards. An abridgement of a longer and more complete publication to be issued by the Bureau of Standards.

TABLE II—HEAT AND MECHANICAL SHOCK TESTS
No. refers to Number Tested. U, Unaffected. F, Failed. B, Broken. C, Cracked

WARE	Water at 4° C. Heated to Boiling over Direct Flame				Boiled Water and Plunged into Ice Water				Paraffin Heated in Vessel to Indicated Temperature and Vessel Plunged into Ice Water Heated to 150° C.				Vessel to 200° C.				DROP TEST—BEAKERS ONLY (6 of Each Ware Tested)					
	BEAKERS		FLASKS		BEAKERS		FLASKS		BEAKERS		FLASKS		BEAKERS		FLASKS		No. that Broke on Drop of:					
	Result		Result		Result		Result		Result		Result		Result		Result		5	10	15	25	30	
	No. U. F.	No. U. F.	No. U. F.	No. U. F.	No. U. F.	No. U. F.	No. U. F.	No. U. F.	No. U. F.	No. U. F.	No. U. F.	No. U. F.	No. U. F.	No. U. F.	No. U. F.	No. U. F.	in.	in.	in.	in.	in.	Note
Kavalier.....	4	1	3c	0	2	2	0	0	4	0	4b	0	
M. E. G. Co.....	2	2	0	4	2	2c	2	2	0	2	2	0	4	0	4b	2	0	2b	3	3	1	
Pyrex.....	2	2	0	2	2	0	2	2	0	2	2	0	4	4	0	5	3	2c	1	(m)
Jena.....	2	2	0	2	2	0	2	2	0	2	2	0	4	1	3b	4	1	3b	
Nonsol.....	2	2	0	2	2	0	2	2	0	2	2	0	4	4	0	4	0	4b	3	1	2	
Fry.....	2	2	0	2	2	0	2	2	0	4	3	1c	4	..	4b	4	0	4b	1	2	..	1
Libbey.....	2	2	0	2	2	0	2	2	0	4	4	0	4	4	0	4	0	4b	2	1	..	2 (n)

(m) One broke on bound at 25 in. and 2 did not break at 45 in. (n) One broke on bound at 20 in.

excess of sulfuric acid, boiled and heated for an hour after fumes of SO_3 appeared. With sodium and potassium carbonates and hydroxides and sodium phosphate half-normal solutions were boiled for 20 mins. in the vessels and in the case of beakers fresh half-normal solutions were subsequently evaporated in the same beakers. With ammonia, strong ammonia was allowed to stand 24 hrs. in the vessel, then diluted and boiled for 30 mins. With ammonium sulfide and chloride, mixtures of twice normal salts were allowed to stand in the vessels 24 hrs., then boiled for 30 minutes.

Table II shows the results of heat and mechanical shock tests. Figs. I to IV show the effects of the various reagents on the wares tested. In these figures

individual accepted determinations are shown by dots, determinations which are believed to be in error and therefore omitted from the averages by circles. The lengths of the rectangles indicate the averages of accepted values. The letters K, M, P, J, N, F, and L indicate Kavalier, M. E. G. Co., Pyrex, Jena, Nonsol, Fry, and Libbey, respectively.

Table III gives a general summary of the resistance to the various solutions and to mechanical and heat shock of the wares tested. In this table the numerical exponents indicate the minor differences in resistance, the lowest number being the most resistant. The absence of an exponent indicates that the differences in resistances are too small to justify any differentiation between the wares graded in the same group.

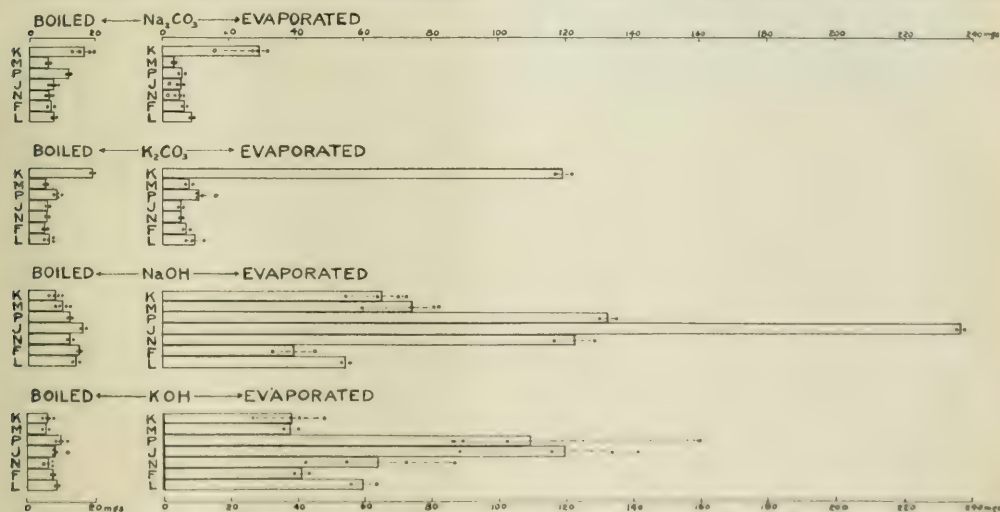


FIG. II.—LOSS IN WEIGHT OF BEAKERS WITH SODIUM CARBONATE, POTASSIUM CARBONATE, SODIUM HYDROXIDE, AND POTASSIUM HYDROXIDE SOLUTIONS

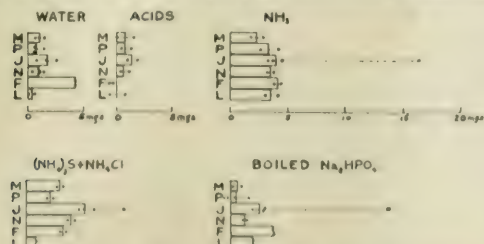


FIG. III.—LOSS IN WEIGHT OF FLASKS WITH WATER, ACIDS, AMMONIA, AMMONIUM SULFIDE AND CHLORIDE, AND SODIUM PHOSPHATE SOLUTIONS

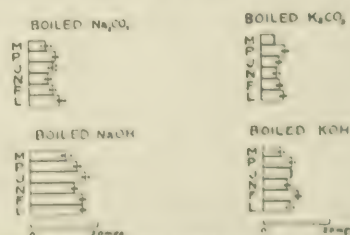


FIG. IV.—LOSS IN WEIGHT OF FLASKS WITH SODIUM CARBONATE, POTASSIUM CARBONATE, SODIUM HYDROXIDE, AND POTASSIUM HYDROXIDE SOLUTIONS

TABLE III.—GENERAL SUMMARY OF TESTS

RESISTANCE TO:	Water	Mineral Acids	Car-bonated Alkalies	Caustic Alkalies	Am-mo-nia and Salts	Heat Shock	Me-chanical Shock
Kavalier.....	Poor	Good	Poor	Good ¹	Good ²	Poor	Poor
M. E. G. Co.....	Good ³	Good	Good ¹	Good ¹	Good	Poor	Poor
Pyrex.....	Good ³	Good	Good ¹	Fair	Good	Good ¹	Good ⁴
Jens.....	Good ³	Good	Good ¹	Fair	Good	Good ¹	Fair
Nonsol.....	Good ³	Good	Good ¹	Fair	Good	Good ¹	Fair
Fry.....	Good ⁴	Good	Good ¹	Fair	Good	Poor	Good
Libbey.....	Good ⁴	Good	Good ¹	Fair	Good	Good ¹	Good

* Far superior to any of the other wares.

In the rating of resistance to caustic alkalies the boiling tests only have been considered. These results indicate that all the American-made wares tested are superior to Kavalier and equal or superior to Jena ware for general chemical laboratory use.

BUREAU OF STANDARDS
WASHINGTON, D. C.

EFFECT OF COPPER ON CRUDE RUBBER¹

By CHAS. P. FOX

Manufacturers of rubber goods, following the teachings of Pearson,² have carefully avoided the use of copper salts in their compounds. Coppered iron was used to a limited extent in vulcanizing rubber to iron. Copper in this operation has recently been superseded by a plating of other metals.

The accidental observation of Dewar concerning the marked change of a rubber gasket used in contact with a copper pipe led him to compare its action with other metals. His tests were made by covering sheet rubber with disks of metals and exposing them to a heat of 150° F. for several days. His findings were that copper gave the greatest effect, and that the action was due to oxidation, copper being an oxygen carrier.

Thompson and Lewis³ took up the matter and made an exhaustive study of the action of metals and their salts on vulcanized rubber. Their work was with sheet rubber vulcanized by the Parkes process (cold-cured). The metals, in form of powder, were sprinkled over the surface of the sheet and the salts, if soluble in water, were made into a paste and applied as a paint. The treated sheets were then exposed for 10 days at a temperature of 60° C. The action was determined by stretching the test piece. Their results sustained those of Dewar: "Of the metals used copper was by far the worst. Copper salts completely destroyed the rubber."

Foden, English textile expert, found that wherever cloth containing copper (used in dyeing) was used in *water-proofing*, the rubber became hardened and was soon destroyed.

Weber⁴ gives an explanation of the action of copper on rubber, experimental data and a method of estimating copper in cloth. This method is simple and reliable, and should replace the methods now used in determining copper in foods. Weber places the maximum limit of copper in cloth for *water-proofing* at 0.005 per cent. Weber also noted that the presence of grease or oils in the cloth facilitated the action of the copper.

¹ Presented at the 55th Meeting of the American Chemical Society, Boston, September 10 to 13, 1917.

² "Crude Rubber and Compounding Ingredients."

³ *Abstract Journal, Soc. Chem. Ind.*, **10** (1891), 717-718.

⁴ "Chemistry of Rubber."

Esch¹ attributes the action of copper to the formation of copper chloride which acts as an accelerator.

Morgan² states that the presence of copper compounds may cause "*tackiness*" in crude rubber, and strongly advises against the use of copper vessels in the preparation of crude rubber, and even against the use of copper insecticides or fungicides on trees during the tapping operation.

By experiments made by adding copper salts to rubber latex, Morgan concludes that the rate at which tackiness is induced is dependent upon the amount of copper salts used.

The formation of resins is the main factor in the *copper-induced* tackiness. Schidrowitz³ says that tackiness is due to a physical degradation of the rubber molecule and not to a change in its chemical composition.

There seems to be a distinct difference between "*perished*" or "*decayed*" rubber (Thompson and Lewis), and the "*tackiness*" observed by Morgan. Tackiness as understood by the practical rubber-worker is a soft sticky condition affecting crude rubber.

Several years ago I became interested in the action of copper on dry crude rubber. Some of these experiments have recently been repeated. In this particular case the work shows the action of copper in the form of acetate on Pale Plantation sheet crude rubber.

Small pieces of this grade of crude rubber were treated with a 1 per cent water solution of neutral copper acetate; copper acetate solution with 10 per cent acetic acid; copper acetate solution with 10 per cent ammonia; and oil carrying 1 per cent of dry copper acetate. Action was checked against blanks of untreated specimens, and with straight oil-treated samples. To observe the action of light two series were run, one (A) being exposed to bright light in a warm room, and the other (B) placed in a cool and dark closet. Extremes in *application* of the chemical are represented by a *single spot*, and by *immersion* for 24 hours. Duration of experiment was approximately 3 months. Each set consisted of six pieces.

The original test pieces were mounted on cardboard. These cards were unavoidably lost in transit, preventing their reproduction, and a written description is substituted herewith.

Each series was subdivided into two subdivisions:

No. I. DROP TEST—One drop of reagent was allowed to dry on the surface of the specimen.

No. II. IMMERSION TEST—The entire specimen was immersed in the reagent for 24 hrs., then dried. The "spot test" gave *tackiness* at point of contact between reagent and the rubber. The "immersion test" gave *tackiness* over the entire surface of the specimen. With the oil experiments even a single drop was too much, while those immersed were ruined (the specimens softened and "run").

All the treated samples showed *tackiness* due to the reagent. The ammonia copper acetate combination shows a much greater action than copper acetate alone or in combination with acetic acid. The oil-

¹ "Manufacture of Rubber Goods."

² "Preparation of Plantation Rubber."

³ "Rubber."

REPORT ON TESTS

No. 1 was the control or check, untreated. The checks showed no change in color or texture (a good index of the character of this grade of crude rubber).

No. 2 was treated with a 1 per cent water solution of copper acetate (neutral). The reagent produced *lackiness*.

No. 3 was treated with copper acetate solution made acid with 10 per cent glacial acetic acid. The reagent produced *lackiness*, but not materially greater than in No. 2.

No. 4 was treated with copper acetate solution made alkaline with 10 per cent of strong ammonia. It reacted strongly with the rubber, giving a hard surface which easily cracked. The product resembled "perished rubber" (Spiller's resin).

No. 5 was treated with lubricating oil (containing 25 per cent of rancid vegetable oil) carrying 1 per cent of dry powdered copper acetate.

No. 6 was treated with the same lubricating oil as No. 5 but without copper acetate.

In Nos. 5 and 6 the "immersion" test pieces were spoiled. The test was too severe, the specimens being destroyed (dissolved in oil). The "drop" tests in both Nos. 5 and 6 showed much action, the oil spread over the entire surface. Those of No. 5 (with copper) showed stronger action than those of No. 6 (without copper).

OBSERVATIONS

1—Copper acetate will produce *lackiness* in crude rubber.

2—The action is proportional to amount of reagent and time of contact.

3—Influence of light and heat is not as great (compared with darkness and a lower temperature) as expected.

4—The ability of the check samples to "stand up" under the light conditions indicates the value of Pale Plantation Crêpe variety of crude rubber.

5—The presence of acetic acid did not materially aid in the production of *lackiness*.

6—The presence of ammonia exerted a pronounced influence. The specimens, however, exhibited a much different appearance, the surface hard and cracked.

7—Lubricating oil (containing rancid vegetable oil) with 1 per cent of dry copper acetate gave a greater action than the same oil when used alone.

treated samples should be considered in a separate group as they show results that may arise from washing-mills in bad order. While oils alone exert a powerful action on crude rubber, the presence of copper magnifies this action. Results with oil and copper on crude rubber coincide with the observation of Weber concerning the presence of oil in cloth aiding the action of copper on rubber.

The action of the reagent is proportional to the time of application. The influence of light and heat is not as great as expected. This feature of the experiment emphasizes the fact that copper salts induce *tackiness* in crude rubber independently of the usual causes of this trouble.

Considered as a whole the work sustains the views of Dr. Morgan.

CLEVELAND, OHIO.

COPPER IN SEWAGE AT THE NEW HAVEN SEWAGE EXPERIMENT STATION

By F. W. MOOREHEAD

Received September 21, 1917

REASONS FOR INVESTIGATION

In the summer of 1916 representatives of the United States Public Health Service, under the direction of Dr. H. S. Cummings, made an investigation of the sanitary condition of New Haven Harbor. They found that it was seriously polluted by the sewage and industrial wastes of New Haven. They recommended that the taking of shellfish from the harbor be prohibited, that bathing be prohibited, and that the city take steps to insure the proper disposal of the sewage.

Following these recommendations, the City Council appropriated a sum of money for the establishment of a sewage experiment station, and a citizens' committee was appointed to take charge of the work. Prof. C. E. A. Winslow, of Yale University, is the chairman of this committee and the director of the experiments. During his absence in Russia with the Red Cross Commission, Mr. Henry B. Sargent is chairman of the committee. The plant was designed by Prof. S. E. Barney, of Yale University, assisted by Mr. R. H. Skelton. The writer is chemist and engineer-in-charge of the station, with Mr. W. S. Sturges

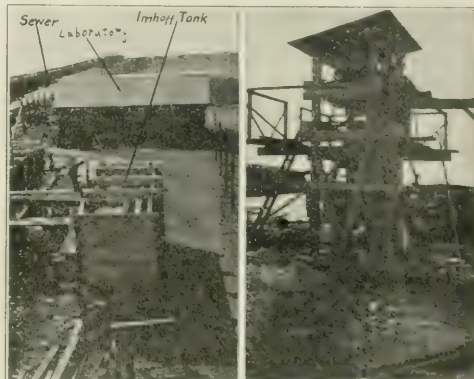


FIG. 1—EXPERIMENT STATION

FIG. 2—BUCKET ELEVATOR

as bacteriologist. Continuous operation started in June of this year.

New Haven is an important manufacturing city of 150,000 inhabitants. The sewerage is on the combined system. Wastes from most of the larger factories are discharged into the East Street sewer, which has an average dry-weather flow of 13,000,000 gallons per day. Since it was thought that trade-wastes might interfere with the treatment of this sewage it was decided to locate the Experiment Station at the outfall of this sewer (Fig. 1). The sewer discharges into tide-water and at high tide the sewage is backed up in the sewer for a distance of several blocks.

DESCRIPTION OF THE PLANT

The sewage for the testing station is pumped by a bucket-elevator, which was erected in a concrete fore-bay on one side of the sewer (Fig. 11). The sewage is collected into the fore-bay by a gutter from the deflecter head set nearly at the corner and in the lower end there lead into the sewer at the lower end of the fore-bay. It was believed that a fair sample of the sewage could be obtained in this way, including the floating solids and grease, and that the suspended matter would not be broken up to so great an extent as if a centrifugal pump were used. Operation of the elevator has shown that it fulfills these expectations. It delivers approximately 2,000 gallons of sewage per day into a large cylindrical receptacle from which it flows over to the station through a smaller pipe.

supported by wooden bents. Before flowing into the weir-box, where it is measured, the sewage passes through a grit chamber 15 ft. long, 12 in. deep at the inlet end, 4 in. deep at the outlet end, and 4 in. wide, with a detention period of 0.24 minute. The velocity of the sewage is checked to 0.7 ft. per sec. at the inlet end, increasing to 2.1 ft. per sec. at the outlet end. This velocity is so high and the detention period so short that very little grit has been removed from the sewage.

Following the grit chamber there is a butterfly valve in the flume which is automatically controlled by a float in the weir-box. This butterfly valve keeps the sewage at a constant level in the weir-box, the excess sewage being deflected over weirs 4 ft. long cut in the sides of the flume. The apparatus for maintaining a constant level was constructed by Wallace and Tiernan, of New York City.

From the weir-box the sewage flows to the various tanks over adjustable weirs, small amounts of 10,000 gallons per day being measured by 60° V-notch weirs, a larger amount, 100,000 gallons per day, by a rectangular weir 7 1/2 in. long.

PROCESSES UNDER INVESTIGATION

The processes being studied are:

- (1) Activated Sludge, (2) Imhoff, (3) Miles Acid, (4) Screening, (5) Disinfection by Liquid Chlorine.

(1) THE ACTIVATED-SLUDGE EXPERIMENTS are on the continuous-flow basis. The aerating tank is 16 ft. long, 4 ft. wide and 8 ft. deep. At the bottom of the tank the sides slope at 45° to a trough 1 ft. wide, which runs the full length of the tank. An iron frame in which are cemented 15 filtros plates is cemented into this trough. The air is admitted at the inlet end of the trough, and the water which filters through the plates can be drawn off at the outlet end. The air is compressed to 3.5 lbs. pressure by a Nash Hydro-turbine having a capacity of 20 cu. ft. of free air per minute. It is measured by means of a Venturi tube.

The settling tank is 4 ft. × 4 ft. in plan, and 12 ft. deep to the bottom of the hopper. This hopper slopes at 60° to a sump in which is cemented a 3-in. ell connected to the suction of an air-lift pump. Sludge is pumped back to the aerating tank, where it is measured in an orifice box. A baffle 7 1/2 ft. deep extends across the center of the settling tank. This baffle was first placed 3 ft. from the inlet weir and 1 ft. from the outlet weir, but the upward velocity of the effluent carried particles of sludge over the outlet weir. Since placing it in the center of the tank no sludge has been lost in this way. The theoretical upward velocity is now 2.4 in. per min. and was formerly 4.8 in. per min. The capacity of the aerating tank is 3100 gallons, the settling tank 1150 gallons. At present, while treating 17,000 gallons of sewage per day with 50 per cent as much sludge returned, the aeration period is 3 hrs., the settling period 66 min.

(2) THE IMHOFF TANK is 16 ft. long × 4 ft. 6 in. wide × 11 ft. 6 in. deep. The flowing-through chamber extends the full length of the tank, with gas vents 8 in. wide on each side. Its capacity is 840 gallons,

giving a detention period of 2 hrs., when treating 10,000 gallons of sewage per day.

(3) THE MILES TANK is 16 ft. long × 3 ft. 6 in. wide × 4 ft. deep, having a capacity of 1680 gallons. When treating 10,000 gallons per day the theoretical detention period is 4 hrs. Liquid sulfur dioxide in cylinders is used for acidifying the sewage, supplemented at times by gas produced by a sulfur burner.

(4) SCREENING EXPERIMENTS were planned with the expectation that an experimental Riensch-Wurl screen could be obtained, which was to be operated at the rate of 100,000 gallons per day. In view of the impossibility of obtaining this screen, experiments with a mechanically operated screen had to be abandoned. Fixed screens of 30-mesh Monel metal wire cloth are used in a screen chamber through which raw sewage flows at the rate of 100,000 gallons per day. The screens are removed when the loss of head reaches 2 ft., and are cleaned by hand. The operation of the screens is discontinuous, approximately 3,000 gallons of sewage being screened for one experiment.

(5) The effluents from the Imhoff tank, activated-sludge tank, and screening chamber run through baffled tanks where they are treated with LIQUID CHLORINE. The periods of detention are from 2 to 5 mins.

ANALYSES OF SAMPLES COLLECTED HOURLY

Four-ounce samples of raw sewage and effluents are collected every hour and combined into composites for chemical analysis. Samples are collected for bacterial analysis as often as time permits. On May 7-8, 24 samples were collected, one each hour, and a complete analysis made of each sample (Table I).

TABLE I—ANALYSES OF SAMPLES OF RAW SEWAGE COLLECTED HOURLY, MAY 7-8, 1917

Time	PARTS PER MILLION						O Consumed	SOLIDS		Bacteria per cc. 20° C.	Gas Formers per cc. 37° C.
	Chlorine	Alkalinity	As NH ₃	(NITROGEN)		Total		Suspended	Total		
				Organic	NO ₂ + NO ₃						
8 A.M.	2075	76	10.4	17.6	3.8	50	165	4430	4,200	100	100
9	2750	94	7.6	14.0	2.6	49	445	6178			
10	2725	70	6.0	11.0	2.4	50	230	5880	4,500	100	100
11	2875	90	4.0	13.6	2.4	50	122	5057			
12	2775	104	4.2	12.6	2.5	51	133	5872	70,000	1,000	1,000
1 P.M.	2675	98	4.0	13.6	2.2	50	189	8440			
2	2675	66	3.4	11.0	2.5	45	155	4513	97,000	1,000	1,000
3	2100	72	3.2	10.4	3.2	51	107	5583			
4	1600	80	3.6	10.8	3.8	42	87	3325	33,000	1,000	1,000
5	1350	48	3.4	5.6	1.1	37	97	2840			
6	100	56	4.8	12.8	2.4	48	126	540	25,000	1,000	1,000
7	47	108	4.2	13.4	1.4	52	90	433			
8	38	72	4.6	15.4	1.5	50	97	342			
9	36	80	5.8	10.2	1.2	49	80	312			
10	37	72	5.4	9.0	1.6	35	65	262	10,000		
11	32	70	5.6	9.4	1.1	33	47	230			
12	29	64	4.8	7.2	1.0	22	42	170	10,000		
1 A.M.	23	56	3.2	5.6	1.1	15	21	108			
2	21	48	2.0	5.2	1.0	14	18	115	1,000		
3	17	46	1.8	3.0	1.3	15	9	93			
4	14	42	1.6	2.4	1.2	9	14	93	150,000	10,000	10,000
5	17	42	2.0	3.6	1.4	15	17	122			
6	20	56	3.6	10.0	1.3	24	42	182	51,000	100,000	100,000
7	1350	68	5.4	17.0	1.2	34	87	2655	362,000	10,000	10,000
AVERAGE	1058	70	4.4	10.4	2.0	37	104	2275	88,500	12,100	12,100

These results indicate that some trade-waste containing large amounts of chlorides is discharged into the sewer from 7 A.M. to 6 P.M. The nitrogen determinations show that the sewage is very fresh, the ratio, *Ammonia-Nitrogen* : *Total-Organic-Nitrogen*, being unusually low. The presence of large amounts of nitrite and nitrate nitrogen also testifies to the fresh-

ness of the sewage. The alkalinity, oxygen consumed, and suspended solids are unusually low. The dilute character of the sewage is due largely to the high consumption of water in New Haven, amounting approximately to 180 gallons per capita per day.

The most unusual features of the analyses are the large amounts of chlorides and total solids, and the low bacterial content during the daytime. During the week of July 9-16, samples collected at the plant during the daytime had the bacterial content indicated in Table II. These results clearly show the

TABLE II—BACTERIAL CONTENT OF SEWAGE, WEEK JULY 9-16

DAY	TOTAL COUNT, AGAR, 20° C.				GAS FORMERS, 37° C.			
	8 A. M.	10 A. M.	1 P. M.	4 P. M.	8 A. M.	10 A. M.	1 P. M.	4 P. M.
Mon.....	1,500,000	225,000	59,000	16,000	100,000	1,000	1,000	100
Tues.....	1,080,000	128,000	5,000	7,500	100,000	100	1,000	100
Wed.....	1,670,000	81,000	7,000	100,000	100,000	100	100	1,000
Thurs.....	1,100,000	148,000	1,500	12,000	100,000	10,000	100	10
Fri.....	1,125,000	42,000	9,000	9,000	100,000	100	100	100
Sat.....	68,500		7,100	800,000*		100	10	100,000*
Average.....	1,295,000	115,400	14,700	159,000	100,000	1,900	385	17,000
Sun.....		3,355,000	2,275,000	2,535,000		100,000	100,000	100,000

* Factories shut down at noon Saturday.

presence of some disinfecting substance in the week-day sewage. Although the sewage is found to be acid at times, the composite samples are never acid, and it is believed that none of the above samples for bacterial analysis was acid.

SOURCE OF COPPER IN SEWAGE

The ignited residue from the mat of suspended solids deposited in a Gooch crucible was usually of a brilliant red color, quite similar to the residue of cuprous oxide obtained in the determination of reducing sugars with Fehling's solution. Qualitative tests of the mat for copper were positive. This led to the conclusion that the disinfection of the sewage is due to copper salts.

The bactericidal action of the copperion is well known. Copper sulfate was first proposed as a disinfectant for water and sewage by B. Kröhnke¹ in 1892. It was first used in America by Moore² and Kellerman in 1903. Extensive studies were made by Johnson³ and Copeland in 1904 at the Columbus Testing Station on the use of copper sulfate as a disinfectant for sewage. By treating Columbus sewage with copper sulfate they obtained the results given in Table III. These data indicate that 5.0 p. p. m. of copper in solution in sewage are sufficient to exert a marked disinfecting action. Quantities as low as 2.5 p. p. m. were almost as effective as 5.0 p. p. m. when treating the effluents from a contact bed.

In order to find the source of the copper and the high chlorides in New Haven sewage, samples were collected from manholes at various places in the sewer from the source to the outfall (Table IV). Copper was determined by evaporating the sample to dryness with 2 cc. of concentrated nitric acid taking up the residue in distilled water, filtering, and adding 2 cc. of concentrated sulfuric acid. This solution was electrolyzed between platinum electrodes for 3 hrs. at 70° C., using 3 dry cells as a source of current. Experiment showed that all the copper was deposited in this time. The cathode was removed, the copper

dissolved in nitric acid, the acid driven off on the steam bath, and the residue dissolved in distilled water. An aliquot portion of this solution was diluted to 50 cc. in a Nessler tube, and 10 cc. of alkaline sodium sulfide added. The color developed was compared with that produced by known quantities of a copper-sulfate solution containing 0.2 mg. of copper per cc., when treated with 10 cc. of the alkaline sodium sulfide. This method is similar to that in "Standard Methods of Water Analysis" with a few modifications.

The entrance of the high chlorides is clearly shown

TABLE III—EFFECT OF COPPER SULFATE ON BACTERIA IN COLUMBUS SEWAGE

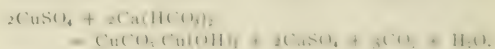
Johnson and Copeland, 1904			
COMPOSITION OF SEWAGE			
Organic Nitrogen	Alkalinity	Bacteria	
6.3 P. p. m.	374 P. p. m.	1,200,000 per cc.	
P. p. m.	TOTAL COUNT ON GELATIN AT 20° C.	24 hrs.	
Cu CONTACT: 0	1	6	
0	1,200,000	1,200,000	14,000,000
5	1,200,000	14,000	700
25	1,200,000	9,500	250
250	1,200,000	3,000	190

to be between Samples 6 and 7. Inquiry showed that a large rubber factory in this vicinity was pumping 2,000 gallons of sea-water per minute for condenser purposes, all of which was discharged into the sewer.

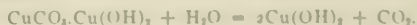
TABLE IV—SOURCE OF COPPER AND CHLORIDES IN NEW HAVEN SEWAGE

DESCRIPTION OF SAMPLE	PARTS PER MILLION				Bacteria per cc. 20° C.	Gas Formers per cc. 37° C.
	No.	Alkalinity	Chlorine	Copper		
Near source of sewer.....	1	54	67	0.0	990,000	100,000
Below munitions factory.....	2	90	144	8.8	3,000	100
	3	165	74	5.6	3,000	1,000
Small branch sewer.....	4	134	72	0.0	559,000	10,000
Main sewer.....	5				70,000	100
	6	156	71	1.9	380,000	10,000
Below rubber factory.....	7	90	2700	3.5	65,000	1,000
Experiment Station.....	8	130	2500		53,000	1,000

Between the places where Samples 1 and 2 were collected there is a large munitions factory which employs 15,000 people. This factory manufactures brass cartridges and cannon shells. In stamping out these shells the brass must be annealed several times, and after each annealing the scale must be removed. The shells are washed with hot water and dilute sulfuric acid after each annealing, 1600 lbs. of acid and 120,000 gallons of water being used per day for this purpose. The waste goes into catch basins, in which some of the solid particles are removed, but the residual acid wastes, containing copper and zinc sulfates, go into the sewer. Here the acid is neutralized by the bicarbonates in the sewage, and the copper sulfate is changed to the basic carbonate:



This basic carbonate is gradually changed to the hydroxide:



Ellm⁴ has shown that the presence of carbon dioxide and organic matter greatly retards the precipitation. He found that quantities as great as 5 p. p. m. of copper may be retained in solution by organic matter for long periods of time. Since the sewage from the munitions factory reaches the Experiment Station approximately 1 hour it is probable that most of the copper is still in solution. Its germicidal power is in-

¹ J. Gasbel and Wasserman, 20 (1893), 513.

² U. S. Bur. of Plant Industry, Bull. 64 (1904).

³ J. Infect. Dis. Sup. 1 (1905), 327.

⁴ U. S. Eng. Water Works Assoc. 19 (1905), 499.

creased by the high temperature of the sewage, averaging 84° F. during August.

There is a noticeable correlation between the number of bacteria and the amount of copper, as shown in Table III. In order to determine whether the disinfecting action is greatest at the time when the copper content is greatest, samples were collected at the Experiment Station from 6 A.M. to 9 P.M., on August 10. Four-ounce samples were incubated at 20° C. with

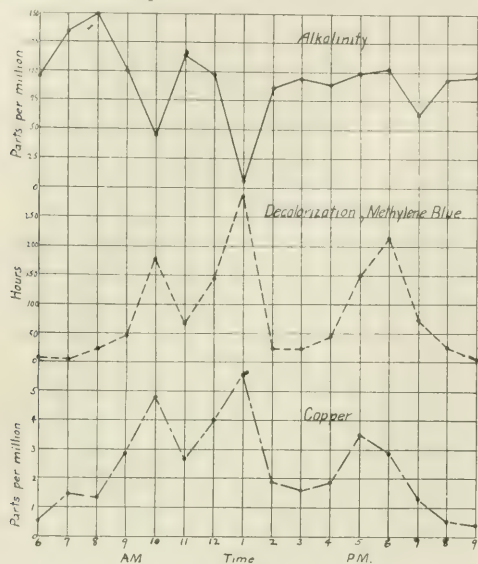


FIG. III

methylene blue, the time required for decolorization being a rough measure of the strength of the disinfecting action. Diluted samples were also incubated, and bacterial counts made (Table V and Fig. III).

TABLE V—DISINFECTION OF SEWAGE BY COPPER, AUG. 10, 1917

Time	PARTS PER MILLION				HOURS METHYLENE BLUE Undiluted sewage luted 2 water	Bacteria per cc. 20° C.	Gas Formers per cc. 37° C.
	Chlorine	Alkalinity	Iron	Copper			
6 A.M.	30	94	0.1	0.56	6	120	3,700,000
7	3750	136	0.2	1.52	6	24	
8	3100	160	5.0	1.36	24	72	2,500,000
9	2900	101	1.8	2.88	48	120	1,000,000
10	2800	43	0.3	4.80	168	192	19,000
11	2750	114	0.4	2.72	60	144	
12	2800	98	0.2	4.00	144	168	559,000
1 P.M.	3075	6	5.5	5.60	240	240	1,000
2	3200	86	0.9	1.92	24	72	187,000
3	3325	91	0.7	1.60	24	120	10,000
4	3375	88	0.2	1.92	48	96	39,000
5	3450	98	0.1	3.52	150	144	45,000
6	130	103	0.4	2.88	216	100	1,000
7	95	63	1.4	1.28	72	80	
8	52	92	0.2	0.64	24	96	33,000
9	50	96	0.0	0.44	6	24	

The time of decolorization varies directly and the alkalinity and bacterial content vary inversely, with the amount of copper. The physical appearance and tests showed markedly the effect of the copper. The samples collected at 6 A.M., 8 P.M., and 9 P.M. became septic within a few days, developed a strong odor and lost their colloidal appearance. The remaining samples, with the exception of the one collected at 1 P.M., retained their original odor, that of fresh sewage,

and remained colloidal and opalescent. The relatively high iron content of the one o'clock sample produced a floc of iron hydroxide which coagulated the suspended matter and clarified the sewage. The results obtained by incubating diluted samples show that in some cases, notably at 5 P.M. and 6 P.M., the diluted samples were decolorized before the undiluted ones. This shows how impossible it is to apply the "dilution method" for the determination of the oxygen demand of this sewage. By incubating the composite sample of raw sewage with methylene blue, however, it is possible to obtain a rough measure of the amount of germicide present. The Sunday sewage will reduce the methylene blue to the leuco-base within 6 hrs.; some week-day composites have not produced the colorless compound for more than 20 days.

The effect of the copper on the various processes being studied remains to be seen, since operation has not been continued sufficiently long to allow any conclusions to be drawn. The company producing the copper-bearing wastes has investigated the recovery of the copper and acid, and claims that such recovery would not be profitable because of the great concentration necessary. If the wastes interfere seriously with the solution of the sewage disposal problem, their removal will probably be considered again.

The writer wishes to express his thanks to Mr. Sturges for the bacterial data contained herein, and to Prof. Winslow for suggestions and advice.

SEWAGE EXPERIMENT STATION
NEW HAVEN, CONNECTICUT

TANNIN CONTENT OF PACIFIC COAST TREES

By H. K. BENSON AND FRANK M. JONES

Received August 28, 1917

In a previous article it was shown¹ that the tannin content of Douglas fir slabwood when properly selected contained sufficient tannin to be considered a suitable raw material for the extract industry. In order to ascertain what other species common to the Pacific Northwest might be available for extract manufacture this study was undertaken.

METHODS OF EXTRACTION AND ANALYSIS—The samples in each case were taken from four or five trees of the same species, were first chipped in a Mitts & Merrill "hog", carefully quartered and the final sample finely ground in a Koerner drug mill. The extractor was of the same type as used in the previous study, extraction carried on for 16 hours and analyzed according to the method of the American Leather Chemists' Association (1914). All calculations are made on a moisture-free basis.

EFFECT OF SEASONING ON DOUGLAS FIR

The sample of sawmill slab reported in the previous study (*l. c.*) was still available, having been kept in a loosely stoppered jar. It was thought of interest to ascertain its tannin content after a year's storage. The average of seven analyses is given in Table I for comparison with previous results.

From these results, it would seem that the effect of seasoning is to bring about hydrolysis and possibly

¹ THIS JOURNAL, 7 (1915), 915.

TABLE I—EFFECT OF SEASONING ON TANNIN CONTENT OF DOUGLAS FIR

PERCENTAGES	FIR SLABWOOD Analyzed by Thompson in 1914	Same sample analyzed by Jones one year later
Total Solids.....	14.92	15.8
Soluble Solids.....	13.02	13.7
Reds.....	1.90	2.1
Non-Tannins.....	7.10	6.2
Tannins.....	5.92	7.5
Moisture.....	6.91	10.0

oxidation, thereby increasing the tannin content by 1.6 per cent (27 per cent of the former). The total solids are increased and the non-tannin decreased, each 0.9 per cent.

PART I—CONIFERS

WESTERN LARCH (*Larix occidentalis*)—The sample was taken from four trees, averaging 28 in. in thickness, growing in the Whitman National Forest in Oregon. The trees were felled in December, 1910, and transported by skidding and log train to the station. The cross-sections were cut 18 in. from the ground and showed a very wet and pitchy surface. The wood is dull red in color and the bark averaged 2 1/4 in. in thickness. The sample was dried for one week at 40° C. before extraction. The analyses were made in March, 1916.

The tannin content of this, as well as of the other species tested, is given in Table II.

The wood extract was bright red in color and unimportant from the standpoint of either tannin content or dye. The extract from the bark was a dull red and gave a pleasing light red color to the tanned hide.

Inasmuch as this species ranks ninth in the order of most prevalent trees in the states of Oregon and Washington, often occurring in pure forests in North-eastern Washington, Northern Idaho, and North-western Montana, is a prolific seeder and well adapted to reforest burned-over areas, its importance as a source of tannin must not be overlooked. Investigations carried on in the U. S. Forest Products Laboratory also show¹ that this species produces a high yield of alcohol by hydrolysis.

Considering the high tannin content of its bark and the exceptional yield of alcohol, it would seem that this species might be especially adapted to chemical utilization, rather than for lumber and timber purposes.

TABLE II—TANNIN CONTENT OF PACIFIC COAST SPECIES

PERCENTAGES:	Total Solids	Soluble Solids	Reds	Non-Tannins	Tannins	Moisture
Western Larch (Wood)(a).....	28.9*	27.6*	None*	23.9*	6.7*	7.8*
Western Larch (Bark)(b).....	20.5	17.0	3.5	6.4	10.6	11.0
Western Yellow Pine (Wood)(c).....	19.6	16.9	2.7	8.0	8.9	...
Western Yellow Pine (Bark)(c).....	22.3	19.3	3.1	8.3	10.9	4.0
Western Hemlock (Wood)(c).....	4.2	4.1	0.1	3.1	1.0	9.5
Western Hemlock (Bark)(c).....	20.8	19.5	1.3	8.57	10.93	9.8
Dogwood (Wood).....	8.3	7.1	1.2	5.8	1.3	5.0
Dogwood (Bark).....	8.3	7.9	0.4	6.2	1.7	5.0
Cottonwood (Wood).....	10.8	9.1	1.7	7.3	1.8	6.5
Cottonwood (Bark).....	25.3	24.3	1.0	19.6	4.7	2.0
Alder (Wood).....	3.5	3.3	0.2	2.6	0.7	6.8
Alder (Bark).....	10.2	9.6	0.6	6.2	3.3	9.8

(a) Results are averages of 2 extractions.

(b) Results are averages of 3 extractions.

(c) Results are averages of 4 extractions.

* Analysis by W. E. Gailey.

YELLOW PINE (*Pinus ponderosa*) This sample was obtained from the Whitman National Forest, the cross-sections being cut 18 in. in diameter. The bark averages 2 in. in thickness. The trees were felled 4 months before extraction.

¹ THIS JOURNAL, 7 (1915), 922.

This species ranks second in quantity of the standing timber of Oregon and Washington. The bark on old trees is often 3 to 4 in. thick. The yellow pine is chiefly used in making boxes, but both the quantity of the bark and of the tannin in the bark and wood make the use of the sawmill waste of this species feasible for tannin extract manufacture.

WESTERN HEMLOCK (*Tsuga heterophylla*)—Various published analyses of the western hemlock bark show that the tannin content of the western species is equal to or exceeds that of the eastern species. The bark of the western hemlock has been regularly used by tanneries on the Pacific Coast. Inasmuch as considerable second growth hemlock occurs on the logged off lands of the Northwest, a composite sample of four trees taken from the University campus was prepared. One tree was 18 in. in diameter and the other three averaged 9 in. The bark was 1 1/2 in. thick. The trees were felled 9 months before extraction. The tannin content is less than that found by other investigators, due probably to the difference in the ages of the trees.

PART II—DECIDUOUS SPECIES

DOGWOOD (*Cornus nuttallii*)—The western dogwood is essentially the same as that of the East. The wood is a dull pink and the bark a reddish black. Its dye possibilities have been utilized by the Pacific Coast Indians for coloring clothing and moccasins deep red. It ranges from the southern coast of British Columbia through Washington, Oregon and California, usually thriving in low altitudes and damp soils and mixed singly or in groups under all the trees of the Pacific slope except the yellow and sugar pines.

For the sample, cross-sections of five trees on the University campus were cut 3 ft. from the ground. They ranged from 8 to 24 in. in diameter, and were air dried for 6 months. The bark averaged less than 1 1/2 in. in thickness and was not easily peeled. The extract is reddish brown in color and imparts a light reddish brown color to the tanned hide in the case of the wood extract and a deeper red from the bark. It is believed that dogwood extract might be used with other tanning extracts to furnish the dye property.

COTTONWOOD (*Populus trichocarpa*)—The cottonwood tree is found growing in damp, sandy land from Alaska to Mexico. It is a very rapid grower, a tree growing to 15 in. in as many years. The sample was obtained from a tree 2 ft. in diameter, felled 3 months before extraction. The bark ranged from 1 1/4 to 3/4 in. in thickness.

ALDER (*Alnus Oregona*)—This species occurs to a considerable extent as a second growth on the logged off lands of Oregon and Washington. Four trees were cut on the University campus 9 months before extraction. Cross-sections were taken about 2 ft. from the ground. The average diameter of the tree was 10 in., the bark averaging 1 1/4 in. in thickness. The quality of the tannin is of distilled value.

CONCLUSIONS

1. Douglas fir slabwood, selected for tanning extraction, can advantageously be seasoned for one year.

II—In addition to the western hemlock bark, that of the western larch and western pine seems to yield extract satisfactory both in quantity and quality.

III—Of the deciduous species examined, the dogwood alone appears suitable for use in extract manufacture but only as a dye.

LABORATORY OF INDUSTRIAL CHEMISTRY
UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON

SATURATED HYDROCARBONS IN BASKING-SHARK LIVER OIL

By MITSUMARU TSUJIMOTO

Received July 25, 1917

Basking-shark (Japanese: "Uba-zamé"), *Cetorhinus maximus* (Gunner), (*Cetorhinidae*), is the largest of all living sharks and indeed of all fishes. It reaches a length of 14 meters and has an enormous weight. This shark is a dull and sluggish animal of the arctic seas, being occasionally found off the coast of Japan. The liver of basking-shark is very heavy, often weighing as much as 1 ton and yielding some 5 cwt. of oil.¹

Three authentic samples of basking-shark liver oil examined by the writer were pale yellow to orange-yellow liquids of low specific gravity and contained 41.92–55.51 per cent of unsaponifiable matter. They contained squalene, $C_{30}H_{50}$, a highly unsaturated hydrocarbon found by the writer in certain Japanese shark liver oils.² This is important as an instance showing that the occurrence of squalene is not limited to the liver oils from the sharks belonging to the family *Squalidae*. The experimental details concerning squalene will, as the writer hopes, be published shortly in another paper, together with the results of the experiments performed on the liver oils obtained from some twenty-three species of Japanese sharks. In the present paper, the writer describes the remarkable occurrence of saturated hydrocarbons in a sample of basking-shark liver oil.

Of the three samples of the oil above referred to, the one from the Province Hidachi had the following properties:

Specific gravity at 15°/4° C.	0.8839
Acid value.	1.09
Saponification value.	102.45
Iodine value (Wijs).	178.30
Refractive index at 20° C.	1.4773
Butyro-refractometer at 20° C.	78.2
Unsaponifiable matter.	41.92 per cent

The unsaponifiable matter was, for the most part, a liquid. One hundred grams of the oil were distilled under 5 mm. pressure. At the temperature of 170–190° C. (the temperature of the oil bath, 250–270° C.), 10 g. (or 10 per cent) of a pale yellow liquid distilled over. It had the refractive index 1.4775 at 20° C. This substance was, therefore, different from squalene. On changing the receiver and raising the temperature

of the oil bath to 290–315° C., a further distillate was obtained at the boiling temperature of 244–260° C., amounting to 25 g., or 25 per cent of the original oil. This latter distillate was found to consist mainly of squalene.

The first distillate was washed with aqueous NaOH solution to remove free fatty acids, and then 8 g. of this purified substance were distilled under 13 mm. pressure. It distilled over at 160–166° C., mainly at 164° C. (the temperature of the oil bath, 200–205° C.), leaving a small residue. The distillate was a colorless, mobile liquid which did not solidify even when cooled to below 0° C. It had the specific gravity 0.7868 at 15° C., 0.7815 at 20° C., 0.7789 at 28° C. (water at 4° C. = 1), and the refractive index 1.4398 at 20° C. Its iodine value was determined to be only 4.40, so that it was nearly saturated. It dissolved in alcohol; when mixed with concentrated sulfuric acid, the acid layer turned brown, and on raising the temperature to about 100° C., the coloration became darker, but the distillate on the upper layer was not readily attacked. No insoluble hydrochloride was formed by passing dry HCl into the well-cooled ethereal solution of the substance.

When heated under 766 mm. pressure, the substance began to boil at about 294° C., and mainly distilled over at 296° C. The distillate thus obtained had the refractive index 1.4395 at 20° C., which was nearly identical with that of the original substance.

0.2011 g. original substance (distilled under 13 mm. pressure) gave 0.6223 CO₂ and 0.2700 H₂O:

C = 84.39 per cent; H = 15.02 per cent.

Molecular weight determined by the depression of the freezing point of benzene solution, (1) 265, (2) 252, mean 259.

	C	H	Mol. wt.
$C_{17}H_{34}$ requires.....	84.89 per cent	15.11 per cent	240.3
$C_{18}H_{36}$ requires.....	84.96	15.04	254.3
$C_{19}H_{38}$ requires.....	84.98	15.02	268.3

The substance was, therefore, a hydrocarbon or a mixture of hydrocarbons, the percentage of carbon and hydrogen amounting to 99.4 per cent. Its elementary composition corresponded to any of the above-mentioned three paraffins. It is not safe to say that the substance was a single chemical compound, but judging from its boiling point and molecular weight, it appears to be very probable that it consisted mainly of $C_{18}H_{36}$ or an octadecane. But as the normal octadecane is a solid at the ordinary temperatures, the substance must be at least an iso-octadecane. Its comparatively low boiling point may be attributed to this cause. A quite similar relation has already been observed between solid triacontane and the hydrogenation product of squalene, $C_{30}H_{62}$, a liquid not solidifying even at –20° C.¹

COMPOUND	Melting Point ° C.	Boiling Point ° C. (mm.)	Specific Gravity –4° C.
Normal Heptadecane, $C_{17}H_{34}$..	22.5	303 (760)	0.7768 (22.5° C.)
Normal Octadecane, $C_{18}H_{36}$..	28	317 (760)	0.7768 (28° C.)
Normal Nonadecane, $C_{19}H_{38}$..	32	330 (760)	0.7774 (32° C.)

¹ Loc. cit.

¹ L. E. Andes, "Animal Fats and Oils," 1898, p. 194.

² THIS JOURNAL, 8 (1916), 889. Spinaene, a hydrocarbon found by C. Chapman [J. Chem. Soc., 66 (1917), 111], in a Portuguese shark liver oil appears to be identical with squalene. The writer has already prepared squalene hexahalogen hydrates of the general formula $C_{30}H_{50}HX_6$, which crystallize well and serve for the convenient identification of squalene.

Employing the n_D^{20} formula, the specific refraction of the saturated hydrocarbon of the basking-shark liver oil is 0.3283, and the molecular refraction (adopting the formula $C_{18}H_{38}$) 83.4. The calculated molecular refraction for $C_{18}H_{38}$ (adopting Eisenlohr's numbers) is 85.3.

The saturated hydrocarbons in the sample of the basking-shark liver oil were not due to some adulteration, inasmuch as their properties differed considerably from petroleum or other hydrocarbons, more especially from Japanese petroleum which consists chiefly of naphthenes. Then, the occurrence of about 10 per cent of saturated hydrocarbons in a shark liver oil is a fact hitherto unknown. However, the hydrocarbons appear not to be the essential constituents of basking-shark liver oil, since they were not found in the other two samples of the oil examined by the writer.

IMPERIAL INDUSTRIAL LABORATORY
YETCHU-SHIMA, TOKYO, JAPAN

SOME DATA ON SPERM OILS USED FOR BURNING PURPOSES

By ABRAHAM G. BLAKELEY and EDMUND A. REILLY

Received September 10, 1917

A considerable quantity of sperm oil is used as a burning oil in Miners' Safety Lamps of the Davy type. Some trouble experienced with a shipment of supposedly pure sperm oil led the writers to conduct an investigation, results of which are given in Table I.

DESCRIPTION OF SAMPLE	Abbreviations: N W, Natural Winter; B W, Bleached Winter; E W, Extra Winter; B L, Bleached											
	R-1	R-2	R-3	F-1	F-2	F-3	N-1	N-2	N-3	N-4	S-1	T-1
Kind of Oil	N W	B W	B W	N W	F-2	F-3	N W	B W	B W	B W	E W	F-4
"Cold Test," °C.	45	45	38	45	45	38	Below 38	42	42	42	42	42
Specific Gravity at 15.6° C.	0.882	0.876	0.877	0.881	0.879	0.879	0.883	0.881	0.882	0.879	0.883	0.879
Refractive Index at 15.6° C.	1.4649	1.4649	1.4649	1.4665	1.4661	1.4665	1.4649	1.4650	1.4650	1.4644	1.4669	1.4665
Flash Point, °C.	245	260	260	245	255	250	260	255	265	255	265	250
Fire Point, °C.	285	295	300	285	295	290	295	295	295	295	295	285
Saponification Value	142.1	128.9	130.2	136.1	130.1	130.6	142.2	135.0	139.6	127.7	133.8	140.8
Iodine Value (Hanus)	86.6	86.4	89.6	83.1	86.3	85.7	89.3	87.9	87.1	88.1	85.3	85.6
Per cent Free Acid (calculated as oleic)	3.60	0.21	0.20	2.28	0.46	0.14	1.34	0.03	0.58	0.04	0.19	0.23
Flake Test, °F.	52	51	43	50	43	39	39	38	38	38	38	38
Cloud Test, °F.	46	46	35	45	39	34	36	34	34	34	34	34
Pour Test, °F.	35	30	25	36	31	25	31	29	30	34	38	30
Viscosity (Tagliabue): at 70° F.	110	107	105	112	108	105	109	106	112	116	114	111
at 210° F.	91	93	94	93	90	88	90	90	90	90	90	90
Viscosity (Saybolt): at 100° P.	117	110	111	117	110	111	127	118	120	119	118	118
at 130° P.	82	82	83	79	76	76	80	74	80	74	88	88
at 210° P.	52	48	48	49	50	48	47	47	49	47	46	46
PERCENTAGES: Fatty Anhydrides	63.1	59.8	59.6	55.5	61.3	56.3	63.0	57.4	64.1	58.0	63.7	60.1
Alcohols	35.2	39.1	39.9	43.3	37.1	43.2	35.4	46.2	33.6	41.4	33.6	36.3
FATTY ACIDS:												
Specific Gravity at 15.6° C.	0.899	0.896	0.897	0.897	0.895	0.894	0.896	0.899	0.896	0.894	0.895	0.893
Refractive Index at 15.6° C.	1.4623	1.4609	1.4600	1.4595	1.4595	1.4595	1.4587	1.4600	1.4585	1.4580	1.4609	1.4595
Neutralization Value	216.2	208.9	206.2	201.6	201.1	194.3	226.3	198.8	210.7	197.7	196.8	224.8
Iodine Value (Hanus)	88.8	82.2	86.5	86.6	87.7	88.1	86.0	85.6	84.8	85.9	91.8	86.7
Titler Test, °C.	13.6	11.5	10.5	12.9	10.6	10.1	7.9	7.7	9.6	6.2	13.2	11.0
ALCOHOLS:												
Refractive Index at 60° C.	1.4475	1.4450	1.4455	1.4495	1.4490	1.4490	1.4461	1.4484	1.4465	1.4464	1.4383	1.4465
Iodine Value (Hanus)	67.4	65.9	70.2	68.9	72.3	73.2	71.4	74.1	74.1	72.5	71.6	63.9
Melting Point, °C.	27.0	25.5	25.0	24.5	24.0	23.8	24.0	20.0	24.1	25.9	21.1	24.0
Saponification Value of Acids	193.2	216.0	204.3	202.9	193.4	200.1	204.6	199.9	200.1	197.1	198.5	208.3

¹ Low acidity.

(a) Sample representing shipment. (b) Oil which gave trouble.

The Flake Test indicates the temperature at which occurs a separation of solid matter. This test corresponds to the "cold test" of the sperm oil manufacturer. The cloud test indicates the temperature at which the lower half of the sample becomes opaque. The pour test indicates the temperature at which a sample of oil in cylindrical form of specified diameter and length will just flow under specified conditions. The iodine values were determined by the Hanus method. The melting points were determined by the ordinary capillary tube method.

¹ Proceedings of the American Chemical Society, 1917, p. 281, 282.

No glycerol was found in any sperm oil tested.

Samples R-1, R-2, and R-3 (received Dec. 1, 1916) were supplied by the same manufacturer. The manufacturer stated that the oil was probably taken from one or two different lots of Atlantic Ocean Sperm Oil. The oil was all from the Sperm or Cachalot Whale. The head and body oils were thoroughly mixed. The "boats catch this oil in moderately warm waters, say from about as far north as the Azores to as far south as the coast of Brazil." Samples R-2 and R-3 were entirely satisfactory as burning oils. Sample R-1, the Natural Winter Oil, was not satisfactory for burning.

Samples F-1, F-2, and F-3 (received December 11, 1916) were all supplied by a second manufacturer. The oils were from the Sperm or Cachalot Whale, and were mixtures of head and body oils. No further information was available. Samples F-2 and F-3 were entirely satisfactory as burning oils. Even Sample F-1, the Natural Winter Oil (containing 2.28 per cent free oleic acid), gave fairly good results, although showing a slight tendency to incrust the wick.

Samples N-1, N-2, N-3, and N-4 (received January 4, 1917) were supplied by a third manufacturer. The manufacturer stated that the oils were all from the same cargo. The oil is bought from the whalers in original casks. The oil in these casks, in refining, is put into a press, and in one pressing there may be three or four different casks of oil. These casks may contain head and body oil from two or three different

whales. The cargo from which the four samples were prepared consisted of some 16,000 gallons of oil of "very fine quality." The oil is all strictly pure sperm oil from the Sperm or Cachalot Whale. Sample N-1 represents the Natural Winter Oil. Sample N-2 represents the same oil after "bleaching" to remove free acid. Sample N-3 represents Sample N-1 bleached by passing through fuller's earth to make it of white color. Sample N-4 represents Sample N-3 "auto"-bleached; that is, this sample had been treated both to remove color and to remove acidity. Sample N-3

and N-4 gave entirely satisfactory results in burning. Sample N-2 was satisfactory but inferior to samples N-3 and N-4. Sample N-1, the Natural Winter Oil, was fairly good as a burning oil.

Sample S-1 represents an oil sample submitted by a fourth company. No information was furnished with this oil. The oil gave satisfactory results as a burning oil.

Sample F-4 represents an oil shipment which was entirely satisfactory. Samples T-1 and T-2 are from two different barrels of the shipment which caused considerable trouble. These oils encrusted the wicks very badly and were altogether unsatisfactory.

The nature of the adulteration in the unsatisfactory oils has not been determined. The table shows abnormal figures for refractive index (saponification value) and iodine value of the oil as well as for iodine values of fatty acids and alcohols, and for melting point of alcohols.

Results for the constants of the genuine sperm oils agree, in the main, with results given in the literature. For some constants, the writers have found a somewhat wider variation than is generally noted in the technical literature (see Table II).

TABLE II

	Data given in Literature	Data from Authors' Tests
SPERM OILS:		
Refractive Index (15.6° C.)	1.4664 to 1.4673	1.4649 to 1.4669
FATTY ACIDS:		
Specific Gravity (15.6° C.)	0.899	0.893 to 0.899
Neutralization Value.....	183	186.8 to 216.2
Titer Test, ° C.....	11.1 to 11.9	6.2 to 13.6
ALCOHOLS:		
Iodine Value.....	64.6 to 65.8	63.9 to 74.1
Melting Point, ° C.....	25.5 to 27.5	20.0 to 27.0
Saponification Value of Acetate.....	161 to 190	189.5 to 216.0

In connection with the writing of Specifications for Sperm Oil it has been the general custom to include requirements as to the maximum percentage of free acid allowed. In order to determine the effects of free acid upon the burning properties of sperm oil, experiments were made with sperm oil to which had been added varying amounts of pure oleic acid. The oil was in each test burned in a Davy Miners' Safety Lamp. It was found that sperm oil containing 1, 2, 3 and up to 4 per cent added oleic acid caused a slight crust to form on the wick, but that oil with even 4 per cent oleic acid gave fairly satisfactory results. The addition of 5 per cent oleic acid caused heavier crust, while the addition of 6 per cent made the sperm oil entirely unsatisfactory for burning in a Davy Safety Lamp. It must be admitted that free acid has a harmful effect upon a burning oil, but it seems also that this effect has been somewhat overestimated in the case of sperm oil.

In judging the suitability of a sperm oil for burning purposes, one would do well to consider the iodine value and refractive index as well as the other constants and the free acid.

Some of the work above tabulated was done by Mr. Donald Thorn, to whom the authors would acknowledge indebtedness.

PHILADELPHIA & READING COAL & IRON COMPANY
POTTSVILLE, PENNSYLVANIA

SOME EFFECTS OF CERTAIN SOLVENTS ON TARS IN THE "FREE CARBON" DETERMINATION

By G. S. MONROE AND H. J. BRODERSON

Received July 2, 1917

The work to be described was carried out in order to obtain some additional data which might throw some light on the probable condition of free carbon in tars, and the extent to which it or other substances in the tar might react with solvents used in the free carbon determination. There is much uncertainty as to the physical and chemical nature of free carbon as it exists in the original untreated tar. The fact that only part of the free carbon existing in tars, as shown by analysis, can be removed by filtration suggests the probability that it is present in a finely divided state. According to Abderhalden¹ this free carbon exists in the tar as an emulsion, the emulsifying agent being the pitch oils present in the tar.

The first series of determinations was made to show the effect on the free carbon content of tars when the latter are allowed to stand in contact with the solvent at room temperature for different periods of time. The results showed a gradual increase in free carbon when benzene, bromobenzene, and chloroform were used. The numerical data are not given for this series of determinations as the results were of the same general nature as those recorded by Weiss.²

The next series of experiments was made to show the effect on the free carbon content of tars by digesting the tars with the solvent for different periods of time. In each determination 10 g. of tar were added to 100 cc. of solvent in an Erlenmeyer flask and digested on the water bath for a certain period of time, after which the tar solution was filtered through a weighed extraction thimble. This thimble was then placed in a Soxhlet extractor, extracted with the same solvent as that used in digestion, then dried and the insoluble residue weighed as free carbon. When chloroform was used as solvent, analyses were made for halogen in the free carbon residues by the peroxide method.³ These analyses were not made, however, in case of water-gas tar because the free carbon residues obtained were too small to work with conveniently. The results obtained by hot extraction are given in Table I.

TABLE I—FREE CARBON BY HOT EXTRACTION

MATERIAL TREATED	SOLVENT USED	Period of Digestion	Per cent Free Carbon	Per cent Cl in Free Carbon Residue
Water-Gas Tar	Benzene	1 hr.	1.06	..
		4 hrs.	1.33	..
		7 hrs.	1.13	..
		43 hrs.	1.17	..
Gas-House Tar	Benzene	1 hr.	4.28	..
		4 hrs.	4.47	..
		40 hrs.	5.16	..
		96 hrs.	4.68	..
Coke-Oven Tar	Benzene	1 hr.	6.13	..
		4 hrs.	6.73	..
		50 hrs.	9.33	..
		98 hrs.	9.46	..
Water-Gas Tar	Chloroform	8 days	11.83	..
		1 hr.	0.77	..
		4 hrs.	0.68	..
		45 hrs.	0.97	..
Gas-House Tar	Chloroform	1 hr.	3.77	0.55
		42 hrs.	4.63	1.34
		3 days	5.76	2.64

¹ *J. Gas Light.*, 123 (1913), 46-47.

² *This Journal*, 6 (1914), 279-83.

³ J. F. Lemp, "A Method for the Determination of Halogens in Organic Compounds," Senior Thesis, University of Illinois, 1917.

The results given above show that in case of water-gas tar and gas-house tar the free carbon percentages gradually approached a maximum value and then decreased when benzene was used as solvent. The same general behavior was observed in determination of free carbon in gas-house tar when toluene was used as solvent. In case of coke-oven tar, however, no maximum point was reached. This is due perhaps to the possibility that digestion was not continued long enough to reach the maximum point. It hardly seems wise to theorize as to the explanation of this maximum point until more data of this kind are available.

In the determination of free carbon made with chloroform as solvent no maximum value was observed, but the amount of free carbon gradually increased. This variation in free carbon which takes place when benzene, toluene, chloroform, etc., are used as solvents has been thought to be due to chemical reactions¹ between the solvent and some of the tar constituents producing insoluble compounds which are continuously precipitated. That chemical reaction does take place in case of chloroform is shown conclusively by the fact, as observed by Weiss, that small crystals of amber

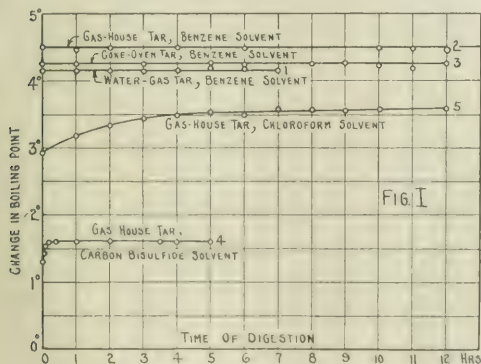


FIG. 1

color were found throughout the free carbon residue when gas-house tar was digested with this solvent for three days. The amount, however, of this substance was too small to account for the observed increase in weight. The probability of chemical reaction in the tar solution in case of chloroform is also indicated by the presence of chlorine in the free carbon residues from gas-house tar, although the same might be explained in part on the basis of adsorption of some of the solvent by the free carbon present in the tar. This is especially true when it is considered that there is no definite relation between the amount of chlorine found and the total amount of so-called free carbon.

If the theory of chemical reaction is to explain partly, if not completely, the variations observed in the free carbon content of tars by continued digestion, there should be a fluctuation in the boiling temperatures of such solutions on digestion due to the change in the chemical nature of the constituents in the tar solution. The following experiments were not designed to predict

the nature of the chemical reactions, if such take place, but to show whether such chemical changes do occur. The experiments were performed in the following manner: In each case 5 g. of tar diluted with 50 cc. of solvent were placed in a standard type of apparatus used in determining the molecular weights of compounds by the boiling point method. To prevent the escape of solvent the condenser attached to the inner tube was closed with a mercury seal. The boiling points of solutions of tars with different solvents were observed at different intervals with a Beckmann thermometer. The barometric pressure was observed at the different intervals but was not found to be great enough to make any appreciable difference in the boiling temperature. The actual boiling temperatures were not observed but simply the changes in such temperatures. The results are shown by the curves in Fig. 1. The Curves 1, 2, 3, representing the digestions of water-gas tar, gas-house tar, and coke-oven tar, respectively, are horizontal and show no fluctuations, hence no appreciable chemical reaction takes place between the tars and benzene. The experiment using carbon bisulfide as solvent shows the same probability as mentioned in case of benzene (Curve 4). The rapid rise observed in the first portion of the curve is perhaps due to the possibility that temperature equilibrium was not reached between the tar solution and the surroundings.

In the case where chloroform was used as solvent the boiling point showed a continuous rise, thus showing that chemical reaction took place appreciably in the tar solution (Curve 5). Unfortunately, only one tar (gas-house tar) was investigated using chloroform as solvent, but it is reasonable to suppose that other tars would give similar results.

CONCLUSIONS

The results thus far obtained are not sufficient to warrant any general conclusion as to what happens between the tars or parts of the tar and the solvent but the following are some of the indications:

I—Variations in percentages of free carbon for different periods of digestion should not be entirely attributed to chemical reactions between tar and solvent, thereby producing insoluble material which is gradually precipitated. It may be that due to dilution some of the free carbon which may have been in the colloidal condition has been precipitated.

II—While it is very probable that chemical reactions take place between tar and chloroform when the latter is used in determining free carbon in tars, such reactions cannot account completely for the gradual increase in free carbon on continued digestion.

III—If the solution of a mixture which when added to tar will not give rise to chemical reactions is the proper criterion in devising a method for the determination of free carbon, benzene, toluene, and carbon bisulfide should be selected in preference to chloroform.

¹ Weiss, THIS JOURNAL, 6 (1914), 279-83.

THE ESTIMATION OF PHENOL IN CRUDE CARBOLIC ACID AND IN COAL-TAR OILS

By E. W. SKIRROW

Received September 5, 1917

Until quite recently no satisfactory method was to be found in the literature for the estimation of phenol in tar oils or in crude carboic acid. In a recent paper, Masse and Leroux¹ give a method based on preliminary fractionation of the crude carboic acid and subsequent estimation of the phenol from determinations of the solidifying point. This method suffers from the disadvantage that the cresols and other higher boiling bodies may vary in the fraction containing the phenol, while they assume a constant and arbitrary ratio of the cresols to be present.

More recently Weiss and Downs² have published a method in which the crude carboic acid is fractionated in such a way as to obtain the whole of the phenol in a fraction supposed to contain only phenol and the cresols, and in this fraction the phenol is then estimated by simultaneous determination of the specific gravity and the solidifying point, whence by reference to graphs the amount of phenol present is deduced. These graphs also are drawn up with fixed ratios of meta- and para-cresol.

In 1909 the author worked out a method for the estimation of phenol in coal tar which depended on quite other properties of the constituents for their estimation, and which gave a fair indication of the amount of the cresols also present. The method gave satisfactory results and was used in the author's laboratory for some years, but was not at that time published. It is thought that the method of attack may not be without interest at the present time, and the author desires to thank the Directors of Messrs. Hardman and Holden, Ltd., of Manchester, England, for permission to publish the results.

In a paper on the determination of phenols in gas liquor,³ the author determined the "Oxygen Absorption" due to the various constituents of the effluent from a sulfate of ammonia works and incidentally of the phenol and cresols, respectively, in that effluent. This suggested the possibility that the oxygen absorption might furnish a means to estimate the amount of phenol in a mixture of phenolic bodies.

OXYGEN ABSORPTION OF PHENOL, o-, m- AND p-CRESOL, SOLUTIONS REQUIRED

Standard Potassium Permanganate..	0.79 g. in 2 liters
Standard Sodium Thiosulfate.....	7.00 g. crystals in 1 liter
Dilute Sulfuric Acid (1 : 3) faintly tinged with Permanganate	
Potassium Iodide Solution.....	10 per cent
Starch Solution.....	4 g. in 1 liter

The phenol, etc., was diluted so that 50 cc. of the solution contained 0.002 g. of the particular phenol or cresol.

METHOD

Portions (50 cc.) of the permanganate were measured into stoppered bottles and 15 cc. of the dilute sulfuric acid added to each. These bottles were placed in a rack

in a thermostat which was maintained at 23° C. The solutions of the tar acids were also brought to the temperature of the thermostat: 50 cc. of the tar acid solution were then run into the permanganate solution from a pipette also warmed to 23° C., and the time noted when the first drop entered the permanganate. When the whole had been added, the bottle was quickly shaken to insure uniformity. At the end of 3 min. the action was stopped by quickly adding 1 cc. of the potassium iodide solution. The liberated iodine was then titrated with the thiosulfate solution. Sufficient excess of permanganate was used so that 30 to 40 per cent of the permanganate remained at the end. The results were then calculated to grams of oxygen absorbed by 1 g. of the respective tar acid. The concordance of the results is shown in the case of the phenol, the others being equally good.

TABLE I—GRAMS OXYGEN ABSORBED

Phenol.....	1.435 / Mean	o-Cresol.....	1.170 / Mean
	1.434 / 14.34	m-Cresol.....	1.156 / Mean
		p-Cresol.....	1.062 / Values

OXYGEN ABSORPTION OF MIXTURES

In order to see if any considerable difference would be found in the rate of oxidation of phenol if cresols were simultaneously undergoing oxidation, known mixtures were made up containing varying proportions of phenol to cresols, the cresol taken being a mixture of equal proportions of *ortho*, *meta* and *para*.

TABLE II—OXYGEN ABSORBED

Per cent Phenol.....	11.1	25.0	50.0	75.0	88.9
Oxygen { Calculated..	1.163	1.205	1.281	1.358	1.400
{ Found.....	1.167	1.212	1.281	1.364	1.405
Difference.....	+0.004	+0.007	0.000	+0.006	+0.005

There appears to be slightly increased oxidation in most of the cases, but this is not sufficient to cause serious error in the use of the oxygen absorptions.

The rate is naturally dependent on the temperature and it is necessary to work in a thermostat. Attempts were made to work with solutions ten times as concentrated as the solutions quoted, but the results were much less steady owing no doubt partly to the considerable temperature disturbance due to the increased heat of reaction.

The phenol can thus be estimated with reasonable accuracy provided that the ratio of the cresols to one another be known. The difference in the rate of oxidation of the three cresols from one another, while much less than the difference between the rate of oxidation of any one cresol and the rate of oxidation of phenol, is still much too great to allow of estimation in this way unless the ratio of the cresols present is known. It is thus necessary to get some idea as to the ratio of cresols present in order to proceed.

FRACTIONATION EXPERIMENTS

It is obvious that in dealing with a mixture of phenol, cresols and higher boiling phenolic bodies, which are present in a crude carboic acid, preliminary fractionation would have to precede any attempt at titration, and experiments were carried out in this direction on crude carboic acid, which was the average from a very large amount of tar from widely differing sources. This crude carboic acid was fractionated

¹ *Compt. rend.*, 165 (1916), 361.² *This Journal*, 9 (1917), 309.³ *J. Soc. Chem. Ind.*, January, 1908.

through still heads of various types and the progress of the fractionation observed by taking the oxygen absorption of the fractions.

OXYGEN ABSORPTION OF HIGHER BOILING BODIES

A large sample of higher boiling bodies was obtained which had had most of the phenol and cresols removed in a works column still. This was freed from H_2S and was fractionated several times in the laboratory to remove any phenol and cresols which might still remain. Fractions were then collected and their oxygen absorption measured with the results given in Table III.

TABLE III

FRACTION.....	205 to 210° C.	210 to 215° C.	215 to 220° C.
Oxygen Absorption....	0.942	0.879	0.831

The oxygen absorption decreases steadily with increasing boiling point and will thus throw light on the progress of the fractionation.

COMPARISON OF THE EFFICIENCY OF STILL HEADS

The two still heads giving the best results with crude carbofic acid were found to be the "LeBel" bulbs and the "Pear" bulbs. The Hempel column was not so efficient and had the disadvantage that a large amount of liquid is held up in the glass beads. The Young dephlegmator, although excellent for lower boiling liquids, did not give as good results in the author's hands as did the Pear bulbs.

COMPARISON OF A 4-BULB LEBEL WITH A 12-BULB PEAR STILL HEAD—The total length of the two columns to the side tube was practically the same. In both cases 1000 cc. of the crude carbofic acid was taken in a copper flask and distilled through the respective head. An air condenser was used leading into receivers closed with a calcium chloride tube. Any moisture was first distilled off and the temperature carried to 180° C. The phenol was recovered from this, dehydrated, and returned to the distilling flask and the fractionation then proceeded with. The rate of distillation was regulated carefully to one drop per second, a seconds pendulum being placed behind the receiver. The flask was protected by a shield of asbestos paper and the column enclosed in one thickness of glazed paper to prevent draughts and to diminish somewhat the radiation from the column. Under these conditions extremely steady conditions were easily maintained. A small Anschütz thermometer graduated in tenths was used and this was compared with a standard "N. P. L." thermometer.

The oxygen absorption of each fraction was measured and the fractions then submitted to a second and to a third systematic fractionation. The oxygen absorption of the fractions of the second and of the third fractionations were also measured. Table IV contains the results so obtained. The two first temperature intervals in the first fractionation are different from those in the second and third fractionations, but in all subsequent work the latter intervals were used.

If we examine these fractionations we see that the oxygen absorption of the fractions is much the same whether the "Pear" or the "LeBel" column is

used, being a little to the advantage of the "Pear" form but that with the Pear a greater volume accumulates in the first fraction which contains the largest proportion of phenol. The use of the Pear head is further to be preferred on account of the smaller amount of liquid remaining after a distillation. In all subsequent work the Pear form was used. This superiority of the Pear still head was also established by Weiss and Downs.¹

It will further be seen by comparing the second and the third fractionations, confining our attentions now to the values for the Pear head only, that the "quality" of the fractions does not alter very materially after the second fractionation, but that the chief difference is in the volume of the first fraction. From this it was inferred that more than two fractions would not bring any commensurate advantage, and that with two fractionations a steady state of affairs had been reached which would be easily reproducible. The examination of these fractions was then proceeded with, to ascertain the amount of phenol in each.

The oxygen absorption of the fractions obviously gives us no quantitative measure of the amount of phenol which they contain as we have no information as to the ratio in which the cresols exist in each.

MATCHING EXPERIMENTS

In order to establish definitely the percentage of phenol, ortho-, meta- and para-cresol in these fractions, use was made of a fact previously observed by the author in the course of work on the phenols in gas liquor¹ but not at that time alluded to, *vis.*, that if the Messinger and Vortman method for the estimation of phenol be applied to solutions of *o*-, *m*- and *p*-cresol, respectively, the end-product obtained (triiodophenol etc.) has widely different colors in each case. The colors of these end-products are extremely characteristic and may be described as follows:

PHENOL	<i>o</i> CRESOL	<i>m</i> CRESOL	<i>p</i> CRESOL
Bright Rose Pink	Brown	Slate-Blue	Dirty Yellow

Preliminary experiments showed that if a known mixture of phenol and the cresols be taken, the percentage of each constituent could be determined with good accuracy by first measuring the oxygen absorption of the mixture and then making up mixtures with the same oxygen absorption, forming the iodo-compounds, and by the method of trial and failure gradually approaching the exact shade of the so-called tri-iodo-compound of the mixture to be analyzed. (The end product in the case of the results to be given is exactly the tri-iodo compounds.)

The iodo-compound was prepared in each case as follows: 1 gm. of water and 1 gm. of NaOH were mixed, 1 g. of the fat acid was dissolved in 10 cc. of water and 10 cc. of the mixture was added to the dilute sodium hydroxide solution. This was heated to 12° C. in a stoppered flask and 10 cc. of 4% *N* (phenol solution) added and well shaken. After standing for 1 hour the flask was sealed under the tap the solution slightly acidified with sulfuric acid and the excess of sodium removed with a weak mineral solution.

¹ *loc. cit.*

TABLE IV—COMPARISON OF 4-BULB LEBEL WITH A 12-BULB PEAR STILL HEAD

(1)—FIRST FRACTIONATION						(2)—SECOND FRACTIONATION						(3)—THIRD FRACTIONATION					
No.	Temperature	12-BULB PEAR		4-BULB LEBEL		No.	Temperature	12-BULB PEAR		4-BULB LEBEL		No.	Temperature	12-BULB PEAR		4-BULB LEBEL	
		Vol.	O	Vol.	O			Vol.	O	Vol.	O			Vol.	O	Vol.	O
1	To 185.5	76	1.293	27	1.292	1	180 to 184	143	1.342	124	1.337	1	180 to 184	202	1.351	165	1.340
2	185.5 to 187	155	1.305	112	1.300	2	184 to 187	179	1.293	174	1.299	2	184 to 187	100	1.297	100	1.297
3	187 to 190	234	1.257	243	1.266	3	187 to 190	75	1.233	114	1.236	3	187 to 190	87	1.240	90	1.236
4	190 to 193	103	1.204	130	1.214	4	190 to 193	78	1.188	79	1.189	4	190 to 193	90	1.236	90	1.236
5	193 to 196	69	1.159	81	1.166	5	193 to 196	65	1.133	66.5	1.139	5	193 to 196	53	1.140	53	1.140
6	196 to 199	61	1.117	62	1.125	6	196 to 199	66	1.098	69	1.099	6	196 to 199	85	1.104	66	1.137
7	199 to 202	67	1.074	69	1.079	7	199 to 202	61	1.068	54	1.060	7	199 to 202	71	1.060	67	1.094
8	202 to 205	57	1.037	51	1.036	8	202 to 205	62	1.028	44	1.022	8	202 to 205	62	1.028	44	1.022
9	205 to 208	35	1.003	31	0.999	9	205 to 208	23	0.972	23	0.978	9	205 to 208	23	0.972	23	0.978

thiosulfate solution. The precipitated iodo compound was allowed to settle, washed once by decantation and placed in a small clear glass weighing bottle for comparison. It is essential that the compound be freshly prepared as it becomes lighter in color after standing one or two hours. The method is clearly cumbersome but it was used only to establish the percentages present in the fractions once and for all, *i. e.*, as a method of standardization.

In this way the percentages of phenol, *o*-, *m*-, and *p*-cresol were determined in the fractions through the Pear still head for the second and third fractionations quoted in Table IV, (2) and (3).

TABLE V—RESULTS OF MATCHING EXPERIMENTS

1—SECOND FRACTIONATION PERCENTAGES—Cresol					2—THIRD FRACTIONATION PERCENTAGES—Cresol				
No.	Vol. Cc.	Phc. mol	<i>o</i>	<i>p</i>	No.	Vol. Cc.	Phc. mol	<i>o</i>	<i>p</i>
1	143	71.0	14.8	14.2	0	1.117	202	73.5	14.5
2	179	56.0	20.8	23.2	0	1.114	100	57.1	21.4
3	75	40.5	18.7	40.8	0	1.096	87	40.5	25.5
4	78	30.0	22.2	47.8	0	1.083	56	25.0	50.0
5	65	15.9	18.7	65.4	0	1.076	53	15.4	21.1
6	66	6.9	18.6	65.7	8.8	1.073	85	3.2	19.8
7	61	0	11.3	72.8	15.9	1.068	70	0	11.3

The mixtures were made up to have the same oxygen absorptions as the respective fractions with the exception of the higher fractions—where it was found that better matches could be obtained by making mixtures with slightly higher oxygen absorptions than the fractions. This was probably due to the small amounts of higher boiling bodies in the higher fractions. (The color of the "iodo-compounds" of the higher boiling bodies is not pronounced, while their oxygen absorptions are progressively less than the cresols.) Table V gives the results of these matching experiments. The last column gives the mean oxygen absorption of everything except phenol in the fractions, calculated from the oxygen absorption of the fraction, the oxygen absorption of pure phenol and the found percentage of phenol in the fraction. Here we see more definitely that the percentage of phenol

in the third fractionation has not changed very materially from that in the second fractionation.

RESULTS OBTAINED WITH OTHER MATERIALS

The preceding results were obtained with a large stock sample of crude carboic acid representing the total extract from a very large amount of tar. Similar experiments were then carried out with other materials as follows:

- A—For comparison: Material already quoted
- B—Sample of Refined Cresylic Acid
- C—Sample of "60's" Carboic Acid
- D—Another sample of Refined Cresylic Acid of different origin
- E—Another sample of Crude Carboic Acid of different origin to that quoted in "A"

These were submitted to preliminary purification to free them from H_2S , etc., and were then fractionated twice in the manner described. In A the volume of the fractions was measured; in all subsequent operations the fractions were weighed to the nearest decigram. Results are given in Table VI.

In Table VII is given the mean oxygen absorption of everything except the phenol in the fractions, calculated as before indicated from the oxygen absorption of the fraction, the oxygen absorption of pure phenol and the found percentage of phenol in the fraction. From these data we see that the mean oxygen absorption of the cresols, etc., in the fractions is very constant for one and the same fraction and varies very little with the nature of the material distilled. Thus it seems evident that the larger variation of the oxygen absorption of the fractions themselves is caused principally by variation in the percentage of phenol present.

METHOD OF ANALYSIS ADOPTED

Thus the method adopted for the analysis of any unknown sample of crude carboic acid was to fractionate about a liter of the sample in the manner outlined and then determine the oxygen absorptions of the fractions of the second fractionation. The per-

TABLE VI—RESULTS WITH VARIOUS MATERIALS

1. AMOUNT OF FRACTIONS									
No.	Temp. °C.	A Cc.	B Cc.	C Cc.	D Cc.	E Cc.			
1	180 to 184	143	64	377.3	7.4	44.9			
2	184 to 187	179	173.8	152.1	58.3	183.0			
3	187 to 190	75	200.6	68.7	171.2	104.3			
4	190 to 193	78	115.5	45.1	151.1	76.0			
5	193 to 196	65	109.6	37.7	128.3	70.1			
6	196 to 199	66	104.2	23.5	125.5	56.9			
7	199 to 202	61	106.1	22.6	147.4	63.7			

3. MATCHING EXPERIMENTS									
FRACTIONS FROM B PERCENTAGES IN: Phc. o p m					FRACTIONS FROM C PERCENTAGES IN: Phc. o p m				
1	67.5	17.5	15.0	0	75.0	13.0	12.0	0	50.0(a)
2	55.6	23.1	21.3	0	57.3	20.1	22.6	0	54.2
3	40.5	18.7	40.8	0	40.9	17.5	41.6	0	44.0
4	26.7	18.2	55.1	0	26.7	18.2	55.1	0	31.0
5	15.2	17.6	61.4	5.8	15.0	26.7	33.37	25.9	18.1
6	5.8	17.1	60.5	16.6	4.7	19.2	57.3	18.8	9.4
7	0	9	62	29

FRACTIONS FROM D									
No.	Phc.	o	p	m	No.	Phc.	o	p	m
1	22.2	27.8	0	0	50.0(a)	22.2	27.8	0	0
2	21.5	24.3	0	0	54.2	21.5	24.3	0	0
3	23.3	32.7	0	0	44.0	23.3	32.7	0	0
4	18.1	40.9	0	0	31.0	18.1	40.9	0	0
5	18.1	51.9	6.9	20.6	18.1	23.1	51.9	6.9	20.6
6	17.5	61.8	11.3	10.6	17.5	17.5	61.8	11.3	10.6

FRACTIONS FROM E									
No.	Phc.	o	p	m	No.	Phc.	o	p	m
1	66.5	16.1	17.4	0	50.0(a)	66.5	16.1	17.4	0
2	58.6	20.3	21.1	0	54.2	58.6	20.3	21.1	0
3	45.4	18.7	35.9	0	44.0	45.4	18.7	35.9	0
4	35.5	23.3	41.2	0	31.0	35.5	23.3	41.2	0
5	20.6	14.1	61.9	3.4	18.1	20.6	14.1	61.9	3.4
6	10.6	21.2	59.9	8.3	9.4	10.6	21.2	59.9	8.3

(a) On the first fractionation the volume of the first fraction was so small that it could be distilled only through a 3-bulb Pear-head.

TABLE VII—MEAN OXYGEN ABSORPTION OF THE CREOLS, ETC.

No.	A	B	C	D	E	Mean
1.....	1.117	1.120	1.118	(1.110)	1.114	1.117
2.....	1.114	1.119	1.113	1.113	1.113	1.115
3.....	1.096	1.099	1.102	1.097	1.099	1.099
4.....	1.083	1.081	1.077	1.088	1.082	1.082
5.....	1.076	1.078	1.076	1.084	1.076	1.078
6.....	1.073	1.078	1.070	1.069	1.062	1.070

centage of phenol in each fraction was then calculated from the oxygen absorption of pure phenol and the oxygen absorption of the cresol, etc., in that fraction as given in Table VII. In Table VIII comparison is made of the percentages of phenol found in the materials A, B, C, D and E.

- (1) By direct matching of the fractions.
- (2) By calculation, as described, from the mean oxygen absorptions of the cresols, etc., in the respective fraction.

These results are not, of course, independent, as the results in the second case also depend on the matching experiments, but the result indicates how far the mean oxygen absorption of the cresols, etc., in the fractions may be regarded as fixed points, thus avoiding the necessity for the tedious matching experiments in each case dealt with.

TABLE VIII—PERCENTAGES PHENOL

Material	By Direct Matching	By Calculation
A.....	30.0	30.0
B.....	27.7	28.0
C.....	44.0	43.9
D.....	20.5	20.7
E.....	24.6	24.5

SOURCES OF ERROR IN THE PRECEDING WORK

1—It has been noted that in the case of the higher boiling fractions better matches were obtained when mixtures were made up having slightly higher oxygen absorption than the fractions to be matched, and it was pointed out that this was probably due to increasing amounts of higher boiling bodies in these fractions. It would undoubtedly have been better to have taken some of this higher boiling material as well as phenol and the cresols in the matching experiments.

2—It was found after the method had been in use for some time that in practically all experiments with crudes a disturbing factor was present in the form of small amounts of pyridine.

3—It was further observed that crude carboic acid tenaciously retains small amounts of dissolved sodium phenate when water is also present. Thus water is much more soluble in crude-tar acids in presence of sodium phenate, and, on the other hand, sodium phenate is considerably soluble in tar acids in presence of water. This sodium phenate remains in the distilling flask when the mixture is distilled. It was found necessary to treat the crude carboic acid with successive washes of dilute sulfuric acid, followed by washes of water to remove pyridine and decompose the dissolved sodium phenate. The tar acids in the acid and water washes were recovered and returned to the bulk.

When these disturbing factors were discovered, time was not available to repeat the work herein recorded, but the effects were partially eliminated by using the constants already determined on a series of synthetic mixtures with known amounts of phenol

and varying and known amounts of the cresols and higher boiling bodies. In that way a correction was found to be applied to all results as so obtained.

The resulting corrections when plotted against the percentage of phenol found gave a smooth curve. Typical points from this curve are given in Table IX.

TABLE IX

Per cent Phenol Taken.....	10.00	25.00	50.00	75.00
Found.....	9.62	23.98	47.50	70.54
Correction (per cent).....	0.38	1.02	2.50	4.46

Duplicate determinations when carried out with the precautions mentioned on the same sample of material gave results with a maximum variation of not more than about 0.2 to 0.3 per cent and with the above corrections applied were not very much farther than that from the truth.

OXYGEN ABSORPTION OF THE FRACTIONS OF TAR ACIDS FROM VARIOUS KINDS OF TAR

The method was also used to estimate the phenol in the tar acids from inclined retorts, vertical retorts, blast furnace creosote and producer gas tar. In Table X are quoted the oxygen absorption of the fractions of the second fractionation of these materials. The first column contains results already given which were largely for the material from horizontal retorts. With the exception of the first column the tar acids received the preliminary treatment with dilute sulfuric acid, and were further carefully freed from any neutral oils by conversion to phenate and extraction with benzene, with all necessary precautions to recover any phenol which was so washed out.

It will be seen that these oxygen absorptions all lie in much the same range.

TABLE X—OXYGEN ABSORPTION OF FRACTIONS

No.	Horizontal	Inclined	Vertical	Blast	Producer
1.....	1.342	(1.288)
2.....	1.293	1.293	(1.256)
3.....	1.333	1.344	1.243	(1.198)	(1.187)
4.....	1.188	1.202	1.201	1.175	1.195
5.....	1.133	1.155	1.152	1.123	1.128
6.....	1.098	1.102	1.108	1.095	1.101

The figures given in parentheses were for very small fractions which could not be handled through the 12 bulbs.

REMARKS

It will be noted from the matching experiments that the fraction from 199 to 202° always contains definite and easily detectable percentages of phenol, but that in the fraction above 202° no phenol was ever detected. Weiss and Downs also distilled twice, but collected only two fractions, viz., "to 190°" and "190 to 202°" on the first fractionation, while on the second they collected everything up to 191°. It seems certain that under these conditions some phenol must have been left in the distilling flask, while some of the higher boiling bodies must have inevitably appeared in the distillate.

Another point which is of interest in connection with the work of Weiss and Downs as to be found in the amount of *m*-cresol present. In the materials investigated by the author the amount of *m*-cresol in the fractions up to 202° was generally far less than the amount of *p*-cresol or of *o*-cresol. Thus from the figures in Tables IV, V and VII the following

ratios may be calculated for the materials designated "A," "B," and "C."

$$A - a : p : m = 0.5 : 12.8 : 1$$

$$B - a : p : m = 0.0 : 13.0 : 1$$

$$C - a : p : m = 8.3 : 11.5 : 1$$

As meta-cresol boils only 3° higher than *p*-cresol, it seems certain that in the original materials dealt with the amount of *p*-cresol must much exceed the amount of *m*-cresol. Weiss and Downs in the preparation of their graphs made up synthetic mixtures in which the ratio of para to meta was fixed at about 1:1 and they state that that is the approximate ratio in which they exist in their oils.

The question arises whether their method would give reliable results when applied to the tar acids dealt with by the author. In the present method such variation in the ratios of the cresols present would be eliminated, at any rate to a considerable extent, although the ratio of cresols worked with in the preparations of the synthetic mixtures was not varied as far as to include a ratio, $m : p = 1 : 1$, so that definite figures cannot be given.

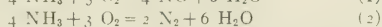
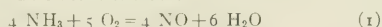
It would be interesting to follow up this and the other points raised at greater length but the author has not now access to the necessary crude materials.

CHEMICAL DEPARTMENT, MCGILL UNIVERSITY
MONTREAL, CANADA

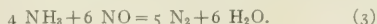
ANALYTICAL CONTROL OF THE AMMONIA OXIDATION PROCESS¹

By GUY B. TAYLOR AND JOS. D. DAVIS
Received October 17, 1917

In the manufacture of nitric acid from ammonia, a mixture of air and ammonia gas is passed over a suitable catalytic material heated to temperatures above red heat. Two reactions occur:



It has been suggested that reaction (2) may come about by means of the intermediate reaction,²



In testing out a particular type of commercial oxidizer, the authors believe they have found evidence that under certain conditions this reaction does occur. The oxidizer in question was so constructed that the burned gases remained hot for some time. Further, there was irregular local cooling of the catalyst due to eddy currents in the burned gases. Consequently, there must have been considerable ammonia passing such points unburned. In fact, analysis of samples taken from points near the cold spots showed ammonia while in samples taken outside the catalyst chamber the ammonia content was very low. The authors believe that most of the NH_3 passing through the cold spots was subsequently "burned" by the hot NO . Results with this apparatus were uniformly about 10 per cent lower than those obtained with the same lot of catalytic material in a differently constructed oxidizer.

The nitric oxide is converted into nitric acid by passing the gases through suitable absorption towers,

much the same as in the arc process of direct fixation of atmospheric nitrogen.

The efficiency of an ammonia converter depends upon establishing conditions favorable to reaction (1) and suppressing as far as possible reaction (2). If the ultimate product desired is nitric acid, little or no free ammonia should be allowed to pass the converter unchanged.

In order to test the efficiency of conversion, analyses of the entering ammonia-air mixture and the exit nitrose gases must be made. The former offers no special difficulties but the nature of the acid gas creates a special problem. As soon as the gas sample cools, the nitric oxide begins to react with the excess oxygen present to form NO_2 , which partially dissolves in the condensed water, so that the gas taken into any sampling device consists of a mixture of nitrogen, oxygen, and nitrogen oxides of indeterminate molecular species.

The principle upon which the efficiency calculation is based is as follows: the ratio of the nitrogen combined as ammonia to total nitrogen in the intake gas is equal to the ratio of the nitrogen derived from the ammonia to total nitrogen in the exit gas.

Let a = nitrogen combined as NH_3 in the air-ammonia sample
 b = free nitrogen
 c = nitrogen combined as nitrogen oxides in the exit gas sample
 d = free nitrogen
 f = nitrogen combined as ammonia escaping oxidation

The nitrogen in each sample must of course be expressed in terms of the same unit. Then

$$\frac{a}{a+b} = \frac{c+f+x}{c+d+f} \quad (3)$$

where x is the free nitrogen derived from the reaction expressed by Equation (2). The efficiency is then expressed by the relation

$$\frac{c}{c+f+x} = \text{Yield} \quad (4)$$

or, substituting the value of x from (3),

$$\frac{c(a+b)}{a(c+d+f)} \times 100 = \text{Per cent Yield.} \quad (5)$$

EXPERIMENTAL METHODS

In the course of some experiments on ammonia oxidation, several methods of procedure were developed:

METHOD 1—The apparatus is sketched in Fig. I. Air was passed through the meter A , the water seal and pressure gauge B , and the bottles C containing ammonia liquor (7 to 8 per cent NH_3). The ammonia-air mixture passed over the catalyzer in D and the acid gases out through E .

The tubes H H' , capacity about 1200 cc., were filled with water. K contained 20 cc. $N/5$ H_2SO_4 and K'' 15 cc. $N/2$ NaOH plus 3 cc. of 3 per cent hydrogen peroxide.

The ammonia-air sample was drawn through K by allowing a measured volume of water to flow from H . Before drawing the acid sample the air in K'' was displaced by pure oxygen passing in at G and out at F . The two samples were then drawn simultaneously so

¹ Published by permission of Director of U. S. Bureau of Mines.

² Reinders and Cats. *Chem. Weekblad*, 9 (1912), 47-58.

that about one liter of gas was taken into each sample in about one hour. The excess acid in *K* was titrated with $N/5$ alkali for the determination of the value of *a*. The gas in *K'* was displaced with oxygen into *H'*, noting the total volume of water drawn therefrom. The two tubes *H H'* were then detached and immersed in a large tank of water, a manometer attached and the temperature and pressure noted. The gas in *H'* was analyzed for nitrogen by absorbing the oxygen in alkaline pyrogallol. The composition of the air in *H* was taken as 79 per cent nitrogen. This furnished the data necessary for the calculation of the values *b* and *d*.

For determination of the value *c* the contents of *K'* were washed into a small Erlenmeyer flask and boiled for about 5 minutes, then thoroughly cooled and the excess alkali titrated with $N/5$ NaOH, methyl orange indicator and a companion flask. The nitrite present tended to destroy the indicator in acid solution, turning the color a permanent yellow, unaffected by either acids or alkalis. By taking care not to run over the end-point, noting the first change in shade from the color of the companion flask, this titration was accurate and satisfactory. The boiling and cooling was found to be absolutely necessary in order to recognize the end-point at all. Carpenter¹ condemned the alkali H_2O_2 reagent for absorbing nitrous gases on account of the difficulty

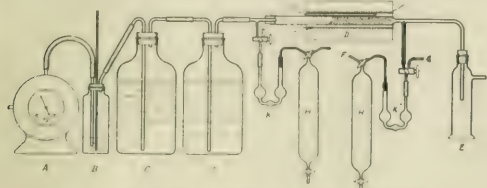


FIG. 1—ANALYTICAL CONTROL OF AMMONIA OXIDATION

of the end-point and proposed the use of a solution of hydrogen peroxide alone, but we have not found it as efficient as the alkali, when the gas is bubbled through it.

When methyl red or sodium alizarine sulfonate is used as an indicator, the boiling is not necessary, both indicators working fairly well in the presence of nitrites. Sodium alizarine sulfonate is rather the better indicator to use, being more sensitive. Methyl red is destroyed to some extent by the nitrite but the end-point is sufficiently sharp even when $N/10$ solutions are used.

Since no appreciable ammonia escaped oxidation in tests where this method was used, the value of *f* is zero. The absorption of the acid in *K'* was practically complete. The water drawn from *H'* was never acid and that remaining in the tube was titrated after shaking when especial accuracy was required. This rarely increased the value of *a* more than one per cent.

METHOD II.—This method was essentially the same as Method I, except that the nitrogen oxygen mixture, after absorption of the acid, was drawn over hot copper to remove the oxygen, thus eliminating the analysis of the gas collected in *H'*. A small Meyer sulfur bulb was used as an absorber and a 4 liter aspirator bottle substituted for *H'*, Fig. 1.

The above methods were especially useful in small scale experiments where sampling into evacuated bottles as described below would have seriously interfered with the constancy of the gas flow through the catalyzer tube.

METHOD III.—For larger scale experiments samples taken into evacuated bottles have been found convenient. This is the only method permitting determination of the ammonia escaping oxidation, *f*. Bottles of known volume, 1 to 2.5 liters capacity, were provided with single capillary stopcocks and evacuated to less than 2 mm. pressure. Ground glass stoppers were more satisfactory but soft rubber stoppers served well enough when the samples were drawn immediately after evacuating.

Sufficient $N/5$ H_2SO_4 was admitted to the ammonia sample and a measured volume of water, after absorbing the ammonia, until the residual air was at atmospheric pressure.

Enough condensation occurred in the acid sample to permit sucking in a measured volume of water containing hydrogen peroxide to absorb the acid fumes. The volume of the bottle minus that of solution introduced gave the volume of the oxygen-nitrogen gas which, together with its analysis, furnished the necessary data for calculating the free nitrogen. The acid solution was titrated with $N/5$ NaOH for free acid and then distilled with caustic into $N/5$ H_2SO_4 for determination of ammonia *f*. Since this ammonia was present as nitrate, its equivalent was added to the free acid already found for the calculation of *c*. While this method requires rather more manipulative skill than the average works chemist possesses, the authors consider it the best available and have used it quite extensively for control work with very satisfactory results. Duplicate determinations on samples taken at the same instant should agree within 1 per cent, but in practice agreement so close will hardly be consistently obtained unless the gas flow is very uniform. It is desirable to check the analysis method and the standard solution used by the analysis of gas samples containing a known amount of nitric oxide. The NO required may be conveniently prepared by means of a nitrometer.

It is often desirable to know whether or not there has been a leak between the point where the NH_3 sample was taken and the point where the nitrous gases were sampled. To determine this it is only necessary to measure the amount of oxygen liberated to the sample of nitrous gases and use water to which a known amount of standard H_2O_2 has been added for absorption. All the combined nitrogen in the sample will now be present as nitric acid. After the excess oxygen gas has been determined the liquid is divided into two parts. In one part the acid is determined by titration with standard alkali and in the other part the excess H_2O_2 is determined by titration with potassiumate. The oxygen used is now known and the amount required for the oxidation of the ammonia converted may be calculated, any excess being due to leakage. Obviously, the yield may be calculated from a knowledge of the relation of combined nitrogen to oxygen in both the NH_3 air sample and the sample of nitrous gas. A few such calculations

¹ "Note on Some Conditions Affecting the Oxidation of Nitrous Acid to Nitric Acid," *J. Soc. Chem. Ind.*, 6 (1906), 287.

were made with results agreeing fairly well with those by the regular method of calculation.

The vacuum method offers a convenient means of following the reactions in an absorption system; for example, it is a simple matter to determine the efficiency of a given tower by sampling and analyzing the gas on both sides of it. Ordinarily the leakage will not be great enough to interfere.

OTHER METHODS—Analysis of the ammonia-air intake gas may be made by ordinary gas analysis methods by taking proper precautions. In common gas analysis practice it is customary to make all volume readings with the gas saturated with water vapor. When mercury is used as a confining liquid, the walls of the burette are always kept wet. This precaution is essential because of the very different vapor pressures of the solutions used as selective absorbers.

In dealing with ammonia gas it is obviously necessary to have the walls of the burette dry and to absorb the ammonia in a reagent whose vapor tension is equal to the partial pressure of the water vapor in the sample. Now this result is accomplished if the gas is thoroughly dried and the absorption made in a reagent whose vapor tension is practically zero.

The apparatus employed consisted of a special bulb form of compensated burette with graduations extending from 140 to 165 cc., easily readable to ± 0.02 cc. Clean, dry mercury was used as a confining liquid and the ammonia was absorbed in concentrated sulfuric acid. The sample was introduced into the burette through a U-tube filled with pieces of solid potassium hydroxide, which thoroughly dried it.

This method proved very satisfactory in practice, and checked the vacuum bottle method. Its advantages are ease of manipulation and simplifying of the calculation, since no temperature or barometer observations are required and no titrations are made. The calculation follows:

a = contraction in volume of the sample

b = volume after contraction $\times 0.79 \times 2$.

An equally simple method suggested itself for analysis of the nitrous gases. It was thought that a sample of the nitrous gases drawn into a nitrometer containing mercury and sulfuric acid, and then shaken, would convert all the nitrogen oxides to NO and cause the excess oxygen to disappear. Analysis of the remaining mixture of nitrogen and nitric oxide would give the values for c and d in volumes as in the burette method for the NH_3 -air mixture.

In experiments with this method it was found that a concentrated solution of chromic acid¹ rapidly absorbed NO and effected quantitative separation of this gas from artificially prepared mixtures of nitrogen and nitric oxide. When the method was applied to the nitrous gases the results were always low. A series of experiments was then made by introducing a measured volume of air into the decomposition bulb of a duPont nitrometer and adding a known quantity of nitric acid dissolved in concentrated sulfuric acid. After shaking several minutes the residual gas was measured, transferred to a gas analysis burette and the NO absorbed

by passing into a pipette containing the chromic acid reagent. Mercury was used as a confining liquid and the walls of the burette were kept wet. The results in every case showed that the residual gas measured corresponded to that calculated, assuming disappearance of the oxygen in the volume of air used and evolution of nitric oxide from the nitric acid introduced. However, analysis of this gas always showed a considerably less percentage of NO than that calculated as well as a small amount of oxygen as determined by absorption in alkaline pyrogallol. Evolution of the NO in the nitrometer bulb in the presence of nitrogen instead of air gave more nearly the correct percentage of NO in the residual gas. In view of these results the nitrometer method appeared unavailable.

A second method for eliminating titrations was devised. Fig. II shows the essential details of the apparatus. The ammonia air sample is drawn into the gas burette (2) through the drying tube (1) containing pieces of solid potassium hydroxide. Burette (2) is provided with a right angle two-way stopcock at the top and a leveling tube below not shown in figure. It is filled with

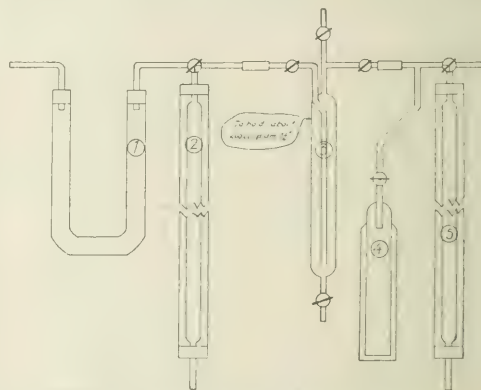


FIG. II—ANALYTICAL CONTROL OF AMMONIA OXIDATION

dry mercury. Bulb (3) is detached from the apparatus and completely filled with water containing hydrogen peroxide and indicator.¹ A small leveling bottle is attached by means of a flexible rubber tube at the bottom. About 10 cc. of pure oxygen, which need not be measured, are introduced into the bulb through one branch of the T tube. The nitrous gases are then drawn from the oxidizer into the bulb through the same tube by allowing 70 to 80 cc. of water to run out into the leveling bottle. This can be done without loss of acid since the indicator shows plainly the diffusion of any acid through the water while the sample is being taken. The bulb is then shaken until all the nitrogen oxides are absorbed. It is then restored to its position (Fig. II) and the residual gas transferred to the mercury-filled burette (5). The walls of this burette are kept wet. The gas is now passed into alkaline pyrogallol in the Williams pipette (4), the residual nitrogen brought back into the burette and measured. This volume is called d , and is discarded. The ammonia sample in (2) is

¹ Bohmer, *Z. anal. Chem.*, **21** (1882), 212.

¹ Methyl red or sodium alizarine sulfonate.

now bubbled slowly into the acid liquid in (3) until neutral, noting the volume required. The air from (3) is measured in burette (5) and this volume multiplied by 0.79 corresponds to the nitrogen volume b .

In calculating the yield by the general formula

$$\frac{c(a+b)}{a(c+d+f)}$$

neglecting f , since by the above procedure a and c are equal, we have

$$\frac{a+b}{a+d}$$

The volume of dry gas introduced from (2) into (3) corrected to moisture saturation, minus the volume of air measured, gives the volume of ammonia. This volume must be divided by two to obtain the corresponding volume of nitrogen, a , to be applied in the formula. When the yield is known to be in the neighborhood of 90 per cent approximate results may be obtained by simple division of the measured nitrogen volumes, *i. e.*, b/d .

While the method has not been thoroughly tested experimentally, it is presented here because the principle involved offers possibilities for development of a rapid method of works control.

DISCUSSION

It was realized at the beginning of this investigation that no method of determining the efficiency of an industrial process appeals to a manufacturer more than pounds put in to pounds taken out. In order to put our analytical results upon an unquestionable foundation, the method was checked by experiments in which the ammonia input was determined by weight and the total acid produced absorbed.

These experiments were carried out as follows: two tared flasks containing a known weight of carefully analyzed ammonia solution were connected in series so that air could be blown through them, the air-ammonia mixture passing over a catalyzer in a glass tube. The acid gases were absorbed in a series of wash bottles containing water and finally in the last ones 10 per cent NaOH solution. The ammonia was determined by weighing the flasks and re-analyzing; the acid, by titrating the HNO₃ absorbed in the water and analyzing the alkaline solutions for nitrate and nitrite. Although the absorption system was quite elaborate some acid passed through unabsorbed. This was estimated by frequent samples of the issuing gas. Method II was used for checking the above outlined procedure because the time in drawing the samples could be made to coincide more nearly with the length of the run. The results follow:

Time Min.	Liters Air	Room Grams H ₂ O	GRAMS		GRAMS		PURE CONC.		
			HNO ₃ Recovered		HNO ₃ lost		% Vol. conc.		
			Alkali	Bottles	Loss	Grams	By	By	
			Water	Nitrate	from	Total	Weights	Analysis	
144	300	10.87	34.40	1.40	4.50	0.90	31.60	19.0	8.5
180	270	13.43	33.00	1.40	6.80	1.05	47.75	88.1	87.0
172	187	8.74	22.20	0.60	3.15	0.60	27.05	83.8	85.5

There is no doubt in our minds that the analysis method gives the true efficiency of conversion. The complete absorption of the acid gases was exceedingly difficult and losses undoubtedly occurred through leaks at rubber connections. These facts account for the

slightly lower results of the total absorption method. Had we cared to elaborate the train, no doubt all the acid could have been absorbed and the agreement would have been better.

In a recently published article Fox¹ has raised the question of possible oxidation of ammonia to ammonium nitrite by hydrogen peroxide. This point was carefully tested in a number of experiments and no evidence secured of any such oxidation in significant quantity under the conditions obtaining in the above outlined procedures. The following experiment seems to be conclusive.

A sample of the nitroso gases was drawn into a 2-liter evacuated bottle from an experimental converter running at low velocity so that no unchanged ammonia passed the catalyzer. A solution containing 40 cc. *N*/5 NaOH, 15 cc. 3 per cent hydrogen peroxide and 3.5 cc. *N*/5 NH₄OH was introduced into the bottle immediately, followed by 100 cc. distilled water. The NaOH was in excess of that needed to neutralize the acid present. After vigorous shaking the bottle was allowed to stand several minutes. Then an excess of *N*/1 H₂SO₄ was added to fix the ammonia. The contents of the bottle were transferred to a Kjeldahl distillation apparatus, made alkaline with NaOH, and the ammonia distilled into *N*/5 acid. Exactly that amount of ammonia taken was recovered. No ammonia was oxidized.

We have further evidence pointing to the fact that under the conditions of analysis the use of H₂O₂ in alkaline solution does not affect the accuracy of the results by oxidation of NH₃ to nitrite.

Two chemists using the vacuum method described above made a number of analyses of parallel samples, one using alkali with H₂O₂ and the other using water with H₂O₂ for absorbing the nitrous gases. The results agreed very well, showing that there could not have been appreciable oxidation of NH₃ by H₂O₂ in alkaline solutions.

Moreover, Hoppe-Seyler² found no evidence of oxidation of ammonia in solutions of ammonia, or ammonium carbonate, or when a fixed alkali was present, by dilute hydrogen peroxide on 24 hrs. standing. It was necessary to concentrate such solutions by evaporation to small volume before nitrite could be detected by colorimetric methods. The statements of Schönbein, Weith, and Weber³ are not to be taken to mean that ammonia is oxidized by hydrogen peroxide "abundantly" under all conditions.

Fox's⁴ analytical method is based on the assumption that NO in the presence of an excess of oxygen reacts immediately to NO₂ (or N₂O₄). It has been shown by a series of experiments that the reaction $2\text{NO} + \text{O}_2 \rightleftharpoons 2\text{NO}_2$ occurs in an appreciable time and that a mixture of NO and NO₂ behaves in a way identical with a mixture of NO₂ and N₂O₄ in the above method. In Fox's method all the NO₂ would be absorbed but it is

¹ Trans. Am. Chem. Soc., 39, 1005 (1917).
² Ber. 16, 1000 (1873).
³ Ber. 7, 111 (1874).
⁴ J. Ind. Eng. Chem., 21, 1005 (1929).
⁵ J. Ind. Eng. Chem., 21, 1005 (1929).
⁶ J. Ind. Eng. Chem., 21, 1005 (1929).
⁷ J. Ind. Eng. Chem., 21, 1005 (1929).

extremely doubtful that the NO could go completely to NO₂ in his apparatus, in which case results calculated by the formula given would be too low.

ACKNOWLEDGMENTS

The authors have had valuable assistance, in the work on which this paper is based, from Lieut. G. A. Perley, Mr. J. H. Capps, and Mr. L. R. Lenhart; Mr. A. S. Coolidge performed many of the experiments in trying out the nitrometer method.

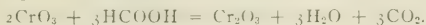
BUREAU OF MINES
WASHINGTON, D. C.

A VOLUMETRIC METHOD FOR THE DETERMINATION OF FORMIC ACID OR FORMATES IN THE PRESENCE OF HYDROXIDES, CARBONATES, OXALATES AND ACETATES

By F. TSHIROGINAS

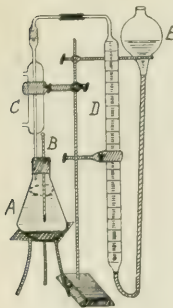
Received August 16, 1917

This method is based upon the well-known fact that formic acid is quantitatively oxidized to carbon dioxide by chromic acid in boiling solution, and that therefore every 44 parts by weight of carbon dioxide correspond to 46 parts of formic acid according to the equation,



APPARATUS—The accompanying sketch shows the arrangement of the apparatus used: *A* is an Erlenmeyer flask of resistant glass with a capacity of about 500 cc.; *B* is a thermometer for the control of the temperature of the contents of the flask; *C* is a 15-in.

Liebig reflux condenser, for the condensation of the vapors produced during the boiling of the liquid and is connected by means of a glass tube and heavy rubber tubing to *D*, the gas collector. The latter consists of a glass tube, about 1.5 in. in diameter, having a capacity of approximately 600 cc. and is graduated in cc.'s; connected to this gas collector by means of a rubber tube is the reservoir *E*, by means of which the air in the collector may be discharged and the water level



obtained, when the CO₂ gas has been collected in the graduated tube. To prevent the absorption of gas by the water used for leveling purposes, a 1-in. layer of paraffin oil is floated upon the surface.

REAGENT—50 g. of C. P. sodium bichromate are dissolved in 500 cc. of distilled water, 80 cc. of C. P. concentrated sulfuric acid added and the liquid boiled for 5 minutes to expel all dissolved gases; then it is allowed to cool to room temperature.

PROCEDURE (1)—In the absence of other substances which give CO₂ when boiled with chromic acid, the procedure is as follows: A solution is prepared, so that 50 cc. of the same will contain from 0.5 to 1.0 g. of formic acid; 50 cc. of this solution are emptied by means of a pipette into the clean Erlenmeyer flask and if alkaline, 2 to 3 drops of methyl orange are added, and the solution made acid with dilute sulfuric acid (1 : 1); 400 cc. of the chromate solution are now

added and the flask attached to the condenser; the stopper at the top of the condenser is removed and the reservoir raised until the graduated tube is filled to the zero mark. The stopper is now firmly replaced and a reading is made upon the graduated tube for correction of the air displaced by the stopper. The reservoir is then lowered and observation is made to assure that the apparatus is air-tight. If no leakage is observed, the reservoir is again raised to a level slightly below that of the liquid in the collector, the cooling water turned on, and the contents of the flask are heated to boiling. As the gas collects, the reservoir is lowered from time to time so that atmospheric pressure is maintained. The boiling is continued until the volume of the gas is practically constant, which requires from 15 to 20 minutes. The flame is now removed and the flask placed in a water bath and cooled until the temperature is reduced to that at which the operation was started; the reservoir is brought to the same level as the liquid in the collector and the volume of the gas noted. A correction is made for the air displaced by the stopper at the beginning of the operation and atmospheric pressure and room temperature are recorded. The volume of the gas must now be reduced to normal barometric pressure and a temperature of 0° C. according to the following well-known formula,

$$V_1 = \frac{V(C - h)}{760(1 + at)}$$

where *V*₁ = reduced volume, *V* = volume actually found, *C* = barometric pressure, *h* = tension of water vapor at temperature *t*, *a* = 0.00366, and *t* = room temperature.

Taking the results of Guye, the weight of 1 cc. of CO₂ gas at 760 mm. and at 0° C. is 0.0019768 g. Therefore, the number of cc. multiplied by 0.0019768 gives the weight of carbonic acid gas generated. This result calculated to 100 g. of material and multiplied by 46/44, or 1.04545, will give the percentage of formic acid.

Trial experiments with known quantities of C. P. sodium formate (recrystallized from alcohol) gave the following results:

(0.5 Gram Sodium Formate Used in Each Case)

Temp. ° C.	Pressure Mm.	Cc. of CO ₂		Difference Gm.
		Generated	Found	
25° C.	747	187	163.1	0.4988
21° C.	743	185	165.7	0.5001
26° C.	743	188	162.2	0.4955
27° C.	743	190	163.0	0.4979

PROCEDURE (2)—In the presence of carbonates, bicarbonates, oxalates and acetates, the following procedure is to be followed: take sufficient material that the formic acid content will range between 2.5 and 5.0 g. Dissolve in 50 cc. of water, boil a few minutes, make alkaline with NaOH if bicarbonates are present and add a 10 per cent solution of calcium chloride in sufficient quantity to precipitate all of the carbonates and oxalates. Allow the precipitate to settle, filter into a 250 cc. graduated flask, wash thoroughly with boiling water, cool to room temperature and fill to the mark. Take 50 cc. of the filtrate and proceed as directed under Procedure (1). Trial experiments with known quantities of C. P. sodium formate mixed with

different quantities of sodium carbonate, oxalate and acetate (which is not oxidized by the chromate solution) gave the following results:

(0.5 Gram Sodium Formate Used in Each Case)					
Temp. ° C.	Pressure Cm. Hg.	CC. OF CO ₂ GENERATED		Difference Gram	
		Actual	Corrected		
22° C.	739	186	162.9	0.4976	—0.0024
25° C.	739	188	162.2	0.4955	—0.0045
18° C.	737	184	163.9	0.5005	+0.0005
18° C.	737	183	163.0	0.4979	—0.0021
28° C.	748	190	163.2	0.4985	—0.0015
27° C.	748	189	163.3	0.4989	—0.0011
16° C.	746	180	163.8	0.5004	+0.0004
20° C.	746	183	163.4	0.4974	—0.0026
Average.....				0.4982	

SUMMARY

I—From the above results it can be seen that this method is an accurate and reliable one for the technical determination of formic acid or formates in the presence of carbonates, oxalates and acetates.

II—An added advantage is that the time required for an analysis does not exceed one hour and, furthermore, it requires but little attention; and preparations for subsequent determinations can be made during the intervening time.

NOTE—Thorpe in his "Dictionary of Applied Chemistry" calls attention to a method devised by Rupp and published in the *Archiv. der Pharmazie*, **243**, 69 for the determination of formates. Rupp uses sodium hypobromite as the oxidizing agent and not potassium bichromate, as stated by Thorpe.

INDUSTRIAL CHEMICAL INSTITUTE OF MILWAUKEE
MILWAUKEE, WISCONSIN

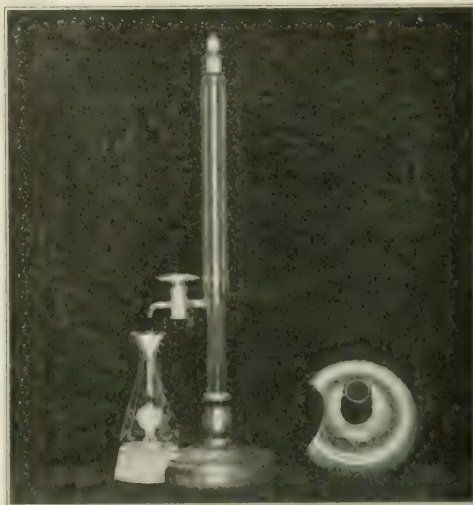
A STUDY OF THE ESTIMATION OF FAT IN CONDENSED MILK AND MILK POWDERS¹

By C. H. BIESTERFELD AND O. L. EVENSON

It was found by Röse² that, if whole milk was treated with ammonia and alcohol, the casein was dissolved to such an extent that the fat could be removed quantitatively by a mixture of equal volumes of ethyl and petroleum ethers. Subsequently, E. Gottlieb³ failed to corroborate the results of Röse, but found that if he extracted, after the treatment with ammonia and alcohol, first with ethyl ether and then with petroleum ether, he was able to obtain more accurate results than he could by the procedure outlined by Röse. Harding and Parkin⁴ claim that results from the application of the Röse-Gottlieb procedure to evaporated milk or milk powders show that the fat is not completely extracted. For the fat determination in evaporated milk they proposed to dissolve the protein in acetic acid and the fat in a mixture of alcohol and carbon tetrachloride before extracting the fat with petroleum ether. During shaking and centrifuging, rubber stoppers were used in contact with the solvents. The action of the solvents on the rubber stoppers would seem to be the cause of the higher results obtained by Harding and Parkin when the fat was extracted by the procedure

they outline rather than when it was extracted by the Röse-Gottlieb method. O. Laxa's¹ work on separator slime indicates that a small amount of fat adheres tenaciously to the protein. It would probably adhere none the less tenaciously in evaporated milk or milk powder. The presence of free fatty acids would not be expected in any appreciable quantity in condensed milk, but milk powder, on account of its tendency to develop rancidity, might have appreciable quantities, as shown by Eccher.² Hence, the Röse-Gottlieb method, which extracts only neutral fats, might fail to show the original fat content of the powder. Hunziker³ used dilute acetic acid to dissolve casein in condensed milk before extracting the fat with ether. It has been shown⁴ that acetic acid does not react chemically with butter fat.

In the work recorded here, the errors in the Röse-



Mounting Röse's Tube (Biesterfeld)

Height of tube over all (not including stopper), 37 cm., about
Narrow part below spigot, 19 mm. outside diameter
Capacity of narrow part, to middle line of spigot, 28 cc.
Upper part (above spigot), 27 mm. outside diameter.
Tube must have a tight-fitting glass stopper
No vent hole in neck. No graduations.

Gottlieb's method have been studied and the method compared directly with a modified method in which a small amount of ammonia is used as an aid in separating the fat from the casein, mixtures of petroleum ether, ethyl ether and ethyl alcohol, which are recoverable for repeated use, and a modified Röse tube have been used.

The two mixtures, which must be kept separate, are used as follows: The proportions for Mixture 1 are 100 cc. of petroleum ether, 100 cc. of ethyl ether and 100 cc. of 95% (v/v) ethyl alcohol. For Mixture 2 the proportions are 100 cc. of petroleum ether, 100 cc. of ethyl ether and 100 cc. of 95% (v/v) ethyl alcohol.

¹ *Anal. Chem.*, **6**, 191 (1913).

² *Anal. Chem.*, **6**, 191 (1913).

³ *Anal. Chem.*, **6**, 191 (1913).

⁴ *Anal. Chem.*, **6**, 191 (1913).

⁵ *Anal. Chem.*, **6**, 191 (1913).

¹ Published by permission of the Secretary of Agriculture. Presented at the 44th Meeting of the American Chemical Society in Kansas City, Mo., April 10 to 14, 1917.

² *Z. anorg. Chem.*, **1889**, 190.

³ *Landw. Vers. St.*, **40** (1897), 1.

⁴ *Trans. Roy. Soc.*, **1913**, 141.

proportions are 350 cc. of petroleum ether, 280 cc. of ethyl ether and 63 cc. of 95 per cent ethyl alcohol. The ethyl ether of commerce was washed with water, and the petroleum ether redistilled slowly and the portion boiling below 65° C. was reserved for this work.

A larger tube than Röhrig's¹ is necessary because the amount of alcohol used is so much greater than has been used previously. A modification devised by Mr. Biesterfeld is shown in the accompanying photograph. Its large capacity permits vigorous and rapid mixing and affords sufficient volume for the ethers to boil quietly during the heating with little danger of mechanical loss. It may also be adapted to the Röse-Gottlieb method by increasing proportionately the quantities in that method.

To recover the ethers and use them again separately would require laborious fractionation. Mixed ethers cannot very well be used with the Röse-Gottlieb proportions, as extraction is incomplete, due to the lack of sufficient alcohol. The problem here is to obtain a

proportion in which the two are mixed. Practically, however, the mixtures prepared in the quantities stated have been used, as described below, until a volume of 50 cc. remained and such a disturbance in proportions, if it has occurred, has not produced any observed differences in the final results.

In a Biesterfeld tube, 4 to 4.5 g. of evaporated milk, or 7 to 7.5 g. of a 40 per cent emulsion of sweetened condensed milk, were diluted to a volume of 9 cc. with water and, after mixing with 1.5 cc. of concentrated ammonium hydroxide, 15 cc. of 95 per cent alcohol were added and the whole mixed again. It was then shaken vigorously for two minutes with 50 cc. of Mixture 1. After standing for 10 min. the ethers were filtered through a 4 cm. Dreverhoff No. 86 fat-free filter paper into a 100 cc. Erlenmeyer flask, previously dried and weighed with a similar flask as counterpoise. The tip of the spigot and the paper were washed with a few cc. of Mixture 1 and the funnel with the paper set aside for future use. The ethers were distilled on a hot plate, using cork stoppers

TABLE I—FAT EXTRACTION
SWEETENED CONDENSED MILK

"SOLVENTS RECOVERED" METHOD		RÖSE- GOTTLIEB METHOD		Dif- fer- ence
Weight Taken Grams	Per cent Fat	Weight Taken Grams	Per cent Fat	
7.2550	10.05	10.7731	3 10.01	+0.04
7.4945	10.45	10.6182	3 10.40	+0.05
7.5570	7.94	10.9948	3 7.88	+0.06
7.6284	9.47	10.5559	3 9.45	+0.02
7.9267	7.95	10.7370	3 7.90	+0.05
6.7503	10.20	10.6095	3 10.18	+0.02
7.1397	10.32	10.6489	3 10.26	+0.06
7.2141	10.04	10.6880	.. 9.97	+0.07
7.0509	10.68	10.9410	6 10.68	=0.00
6.9584	10.03	10.6125	3 9.97	+0.06
7.0508	10.22	10.7829	6 10.25	-0.03
7.3238	8.21	10.8739	3 8.15	+0.06
7.5140	9.94	10.8006	.. 9.91	+0.03
7.3009	9.13	10.7248	3 9.12	+0.01
7.3343	9.00	10.6195	3 8.96	+0.04
7.2240	9.64	10.2433	3 9.53	+0.11
7.9940	8.00	10.8825	3 7.93	+0.07

Average, +0.04

TABLE II—FAT EXTRACTION
UNSWEETENED CONDENSED MILK

"SOLVENTS RECOVERED" METHOD		RÖSE-GOTTLIEB METHOD (EXTRACTED)		Dif- fer- ence
Weight Taken Grams	Per cent Fat	Weight Taken Grams	Per cent Fat	
4.2443	8.01	4.4234	7.99	+0.02
4.4698	7.98	4.2453	7.98	+0.00
4.5526	8.07	4.4469	8.02	+0.05
4.2029	9.05	4.2110	9.02	+0.03
4.0204	7.97	4.1455	7.92	+0.05
4.4006	7.56	4.5140	7.51	+0.05
4.5701	6.77	4.5376	6.77	+0.01
4.2514	8.05	4.3135	7.97	+0.08
4.6008	7.92	4.5975	7.88	+0.04
4.6910	7.89	4.7650	7.87	+0.02
4.6818	8.06	4.4123	8.01	+0.05
4.4807	8.30	4.5186	8.27	+0.03
4.1328	8.29	4.6730	8.23	+0.06
4.1293	8.26	4.3654	8.23	+0.03
4.6571	7.50	4.7469	7.44	+0.06
4.1668	7.89	4.1738	7.83	+0.06
4.6525	8.09	4.5167	8.06	+0.03
4.0960	8.40	4.6118	8.34	+0.06
4.0236	8.12	4.3327	8.08	+0.04
4.1875	8.45	4.2732	8.42	+0.03

Average, +0.04

TABLE III—FAT EXTRACTION
OLD CONDENSED MILK
Residual Fat Obtained from Old Condensed
Milk by Acetic Acid Treatment
3 or more Röse-Gottlieb Extractions

RÖSE- GOTTLIEB METHOD		FAT EXTRACTED BY ACETIC ACID TREATMENT	
Weight Taken Grams	Per cent Fat	Weight Taken Grams	Per cent Fat
4.6815	3	0.0053	+0.11
3.2980	3	0.0030	+0.06
5.3470	3	0.0018	+0.03
5.0120	3	0.0025	+0.05
4.7290	3	0.0021	+0.04
5.4065	3	0.0032	+0.06
5.8110	3	0.0021	+0.03
5.4350	3	0.0038	+0.07
4.7598	6	0.0012	+0.02
4.0000	4	0.0017	+0.04
5.0000	4	0.0026	+0.05
4.3000	3	0.0021	+0.05
4.4627	3	0.0027	+0.06
5.4285	3	0.0021	+0.04
10.3950	3	0.0018	+0.04
10.1945(a)	3	0.0007	+0.02
9.8425(a)	3	0.0019	+0.05
9.5320(a)	3	0.0021	+0.05
9.6965(a)	3	0.0021	+0.05
9.8945(a)	3	0.0022	+0.05

(a) Sweetened.

Average, +0.048

mixture of the two ethers and alcohol which will readily give a large percentage of pure fat in the first extraction. C. H. Biesterfeld found that by diluting the quantity of milk taken to 10.5 cc. with water and adding 1.5 cc. of ammonium hydroxide, as in the Röse-Gottlieb method, and increasing the alcohol to 15 cc., a mixture of equal parts of ethyl and petroleum ethers extracted fat very easily. A method was developed accordingly.

As the method was studied further it was found that in the sweetened condensed milk the extra alcohol tends to extract a small amount of impurity with the fat. Although a mixture of equal parts of the two ethers is to be preferred for the unsweetened condensed milk, the proportion of petroleum ether was increased in order to obtain a method applicable to the sweetened condensed milk as well.

Theoretically, it would appear that a mixture of ethyl and petroleum ethers should have a definite rate of solubility for the separate ethers, and hence, repeated use of a mixture of this kind should disturb the

covered with tin foil for connecting with the condensers, until approximately 4 cc. remained. The recovered ethers were returned to Bottle 1. The liquid in the tube was mixed with 3 cc. of glacial acetic acid. The tube, immersed in water at 60 to 65° by a wire so that the tip of the spigot was just above the water, was heated to 80° in about 10 min. The tube was removed and cooled in running water. It was then shaken vigorously for about 2 min. with 50 cc. of Mixture 2. After standing a few minutes the ethers were filtered through the reserved filter paper into an unweighed 100 cc. Erlenmeyer flask, distilled and returned to Bottle 2. This extraction was repeated with 50 cc. of Mixture 2 and the ethers filtered into the same unweighed flask. The tip of the spigot and filter paper were washed with Mixture 2 and the ethers distilled as before. This flask was freed from the residual liquid and acetic acid vapors and dried completely by heating on a steam bath while applying suction. The fat was then dissolved with 25 cc. of petroleum ether, using small quantities at a time, and filtered through the same filter as before

¹ Z. Nahr. Genussm., 9 (1905), 531.

into the weighed flask containing the first extract. This petroleum ether was recovered and used again. The fat was dried at 100° to constant weight, weighing with the same counterpoise flask.

As the solvents were used repeatedly, the proportion of alcohol changed to such an extent that after a time the line of separation between the aqueous and ethereal liquids reached the spigot. When this occurred the solvent mixture in Bottle 1 or Bottle 2, as the case might be, was shaken with water in a separatory funnel. For each 50 cc. of mixed solvent, 2 cc. of water were used. A portion of the alcohol was removed in this manner.

A comparison of the results obtained by the method here described in which the solvents are recovered and the Röse-Gottlieb method is shown in Tables I and II. As may be seen from these tables the former method averages 0.4 per cent higher on both the sweetened and the unsweetened milk.

Some observations were then made on the Röse-Gottlieb method to ascertain if any residual fat remains after the third extraction, and the results obtained on different brands of milk are shown in Table III.

The residual fat was obtained by adding 3 cc. of concentrated acetic acid to the liquid remaining in the tube, heating for 10 min. near 80° and re-extracting with 15 cc. each of ethyl and petroleum ethers, as usual. The ethers were filtered through a fat-free filter paper into an unweighed flask, distilled and the flask freed from acetic acid vapors and dried completely. The fat was then dissolved out with petroleum ether and filtered into a weighed flask. This avoided the introduction of any impurity resulting from the acid treatment. The average residual fat obtained is nearly 0.05 per cent. These milks were old and some were not in good condition. In Table IV, however,

"SOLVENTS RECOVERED" METHOD					RÖSE-GOTTLIEB METHOD				
PER CENT					RATIO				
FAT EXTRACTED					FAT EXTRACTION				
Weight of Sample Grams	1st Ammon. Acid	2nd Acid	Per cent	Total	Weight of Sample Grams	Per cent	Per cent	Per cent	Total
4.1446	8.08	0.06	8.14	4.0607	8.16	0.0017	0.04	8.20	8.20
4.2962	8.13	0.02	8.15	4.1573	8.08	0.0028	0.06	8.14	8.14
4.2220	7.73	0.02	7.75	4.2198	7.71	0.0021	0.05	7.76	7.76
4.2308	7.74	0.03	7.77	4.1394	7.72	0.0018	0.04	7.76	7.76
4.2017	7.72	0.04	7.76	4.1977	7.71	0.0021	0.05	7.76	7.76
4.2760	8.19	0.03	8.22	4.2676	8.17	0.0010	0.02	8.19	8.19
4.1897	8.33	—	—	4.0954	8.30	0.0019	0.05	8.35	8.35
4.1030	7.73	0.03	7.76	4.3536	7.73	0.0011	0.03	7.76	7.76
4.1594	8.19	0.03	8.22	4.4458	8.18	0.0012	0.03	8.21	8.21
4.2054	8.44	—	—	4.2687	8.35	0.0010	0.02	8.37	8.37
7.9670(a)	7.93	0.02	7.95	10.7420(a)	7.90	0.0015	0.04	7.94	7.94
2.5510(a)	7.93	0.01	7.94	10.9948(a)	7.88	0.0007	0.05	7.93	7.93
7.9940(a)	7.97	0.02	7.99	10.8858(a)	7.93	0.0010	0.02	7.95	7.95
—	—	—	—	4.8694	8.10	0.0017	0.04	—	—
—	—	—	—	4.2903	8.19	0.0013	0.08	—	—
—	—	—	—	4.3810	6.71	0.0030	0.07	—	—

(a) Sweetened.

Average, 0.04

is shown the residual fat obtained in like manner from milks in good condition. Here the average is 0.04 per cent. The results obtained by the method in which the solvents are recovered are also shown.

The per cent of fat recovered by the second extraction in presence of acid is here given separately to show that two extractions remove all but the last traces of fat.

The error of the Röse-Gottlieb method then, when applied to condensed milk, is small, the usual range being from 0.02 to 0.06 per cent. This residual fat may be recovered by an acid extraction in the same manner as described before.

In Table V are shown the results obtained with the two methods on different products. The powders used had been kept in the laboratory for several years. In the method in which the solvents are recovered, the weight of the powder taken was stirred with 1.5 cc.

TABLE V—RESULTS ON DIFFERENT PRODUCTS
"SOLVENTS RECOVERED" METHOD
(3 Extractions)

No.	SUBSTANCE	RÖSE-GOTTLIEB METHOD (3 Extractions)		PER CENT FAT		Charge Grams	Reg. Meth.	Acid Total	FAT
		Charge Grams	Per Fat	Grams	Extr.				

1	Lard.....	0.1217	99.89	0.1329	96.26	3.68	99.94		
2	Condensed Milk + 2.5% Oleic Acid.....	4.2041	10.65	4.1803	9.30	1.18	10.48		
3	Milk Powder.....	1.0000	11.72	1.0000*	10.82	0.70	11.52		
4	Cereal Milk Powder.....	1.0000	4.80	1.0000	4.50	0.26	4.76		
5	Milk Powder.....	1.0000	2.56	1.0000	2.19	0.27	2.46		
6	Milk Powder.....	1.0000	1.68	1.0000	1.53	0.24	1.77		
7	Cream.....	2.1380	20.15	1.8807	20.08	0.13	20.21		
8	Cream.....	2.2870	19.89	2.5005	19.76	0.12	19.88		
9	Cream.....	1.8592	19.50	1.8488	19.31	0.14	19.45		
10	Cream.....	2.9554	19.44	2.8740	19.30	0.10	19.40		
11	Cream.....	1.4209	35.49	1.6219	35.20	0.28	35.48		
12	Cream.....	1.4050	36.04	1.5011	36.00	0.23	36.23		

* Four extractions.

of ammonium hydroxide and 8 cc. of water and digested on a steam bath until the casein was well softened before adding 15 cc. of alcohol and proceeding with the extraction. In the Röse-Gottlieb method the same procedure was followed, using 1.5 cc. of ammonium hydroxide, 9 cc. of water and 10 cc. of alcohol. The effect of free fatty acids is most plainly seen in Expt. 2 where oleic acid was added to condensed milk. Numbers 7 to 10, inclusive, are samples of manufactured cream made from condensed skimmed milk and butter. The results obtained on the powders as well as on the cream show that the Röse-Gottlieb method may fail to remove the fat quantitatively. The method in which the solvents are recovered appears to give higher results but a sufficiently large number of determinations have not yet been made to show that it may universally be applied to milk powder.

As a result of his work on the Harding-Parkin¹ method, Biesterfeld came to the conclusion that the higher results obtained with this method were due to the use of rubber stoppers in contact with the solvents. In Table VI data are given showing the effect of using rubber stoppers.

TABLE VI. SHOWING THE EFFECT OF USING RUBBER STOPPERS IN THE HARDING-PARKIN METHOD

Method	HARDING-PARKIN		RÖSE-GOTTLIEB	
	Sample	Per cent	Sample	Per cent

No.	1	2	3	4
1	1.0000	8.11	1.0000	7.88
2	1.0000	8.11	1.0000	7.88
3	1.0000	8.11	1.0000	7.88
4	1.0000	8.11	1.0000	7.88

(a) Without rubber stoppers.

(b) With rubber stoppers.

With the last upgrade the Harding-Parkin procedure was compared with and without rubber stoppers. It is believed that the great difference in results obtained by the two methods as reported by Harding and Parkin is to be explained by the error arising from the use of rubber stoppers.

¹ Loc. cit.

SUMMARY

I—The error of the Röse-Gottlieb method as applied to condensed milk is small, the average being about 0.4 per cent; the method may also give low results when applied to milk powder or cream. This error may be corrected by an extraction in the presence of acetic acid.

II—The method in which the solvents are recovered, by its acid treatment extracts free fatty acids and more completely separates fat from protein, in this manner recovering a trace of fat not obtained by alkaline extraction. Moreover, it is economical in the use of solvents.

BUREAU OF CHEMISTRY
DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

A RAPID METHOD FOR THE DETERMINATION OF LIME AS CALCIUM SULFATE

By L. C. WILLIS AND W. H. MACINTYRE

Received August 6, 1917

The determination of lime by weighing as sulfate possesses distinct advantages, and its accuracy is vouched for by several authentic texts. The use of a factor and the constancy of the sulfate commend the method to analysts.

Treadwell-Hall¹ state that the technic is well adapted to the determination of lime occurring as organic salts in the absence of other bases. Fresenius-Cohn² outline a method, by which lime salts are converted to the sulfate by the addition of a slight excess of sulfuric acid and then precipitated by increasing the volume fourfold with ethyl alcohol. The precipitate is then filtered and washed free of the salts of other bases, and gently ignited. Glasse-Harriman³ dissolve the salts of calcium and other bases in an ether-alcohol solution and then effect the sulfate precipitation by adding sulfuric acid. The filtered and washed precipitate is then gently ignited. Olsen⁴ prescribes a similar procedure, stipulating a strength of 35 to 40 per cent for the alcohol washing solution. All of the foregoing schemes of manipulation effect the precipitation of lime as sulfate. It is quite feasible, however, to make the usual oxalate precipitation and then convert this to the sulfate. Gooch⁵ utilizes the sulfate conversion method, using H₂SO₄ in a procedure involving the separation of strontium salts from those of calcium. Crookes⁶ recommends the use of a conversion solution made by neutralizing 1 : 1 sulfuric acid with ammonium hydrate and adding ammonium chloride. The necessity for more definite provision for a positive excess of SO₃ will be shown by the data given in this article. The necessity for evaporation of the conversion solution is also an undesirable feature of this procedure. Fresenius-Cohn⁷ state: "The calcium oxalate may also be converted into sulfate. Schrötter ignites in a covered platinum crucible with pure

ammonium sulfate. Or one may ignite in a covered platinum dish till the precipitate is for the most part converted into oxide, add a little water, then hydrochloric acid to effect solution, then pure sulfuric acid in excess, evaporate and ignite moderately. This process is also quite accurate." Lincoln and Walton¹ give essentially the same directions as in the preceding scheme. They direct, however, that the addition of acid and the gentle ignition be repeated. An unpublished modification of the procedures given by Lincoln and Walton, as advanced by Dr. Paul Potter, has been used by the writer for a number of years. In this modification ethyl alcohol is added to the oxide-carbonate residue before the addition of hydrochloric acid, in order to eliminate spattering when the determination is carried out in a small platinum crucible. The alcohol and hydrochloric acid are then driven off. The CaCl₂ is next dissolved in water, and a few drops of sulfuric acid are then added. The excess of acid is dispelled and the containing crucible gently ignited. This method is extremely accurate if carefully carried out with absolutely pure chemicals. Both the Lincoln and Walton and the Potter procedures require an evaporation in order to remove either water or alcohol. This evaporation consumes considerable time and necessitates great care to prevent mechanical loss. In order to obviate this feature we substituted powdered ammonium chloride for hydrochloric acid, and effected the preliminary conversion to chloride by means of a dry melt.

However, in using the ordinary "C. P." sulfuric acid this modification is often uncertain, as regards the attaining of constant weight of ignited calcium sulfate. In making determinations of large amounts of lime it was found that even with careful and moderate heating, during the initial conversion to sulfate, it was generally necessary again to add sulfuric acid and repeat the ignition. The reason or reasons for the irregularities in weights were then considered.

CONCERNING LOSS OF SULFUR UPON IGNITION OF CaSO₄

It has been pointed out that heating CaSO₄ to a bright red will cause a considerable loss in weight. Treadwell-Hall² attribute this to the dissociation of the CaSO₄ and loss of SO₃. Mitscherlich³ states that no loss of SO₃ occurs at a dull red heat but fusion with loss of SO₃ ensues with ignition to bright red heat. Boussingault⁴ asserts that continued heating at white heat for a long period results in the loss of all the combined SO₃. While it is undoubtedly true that loss of SO₃ does take place, it appears that the loss of weight incurred in carrying out the sulfate ignition may also be attributed to other causes. In carrying out the conversion of the ignited lime residue by the use of concentrated H₂SO₄ it was noted that wherever a result was apparently low and where an increased weight would occur with a second addition of acid an unmistakable odor of hydrogen sulfide followed the

¹ "Analytical Chemistry," 1st Ed., 2 (1904), 66.

² "Quantitative Chemical Analysis," 1 (1906), 269.

³ "Quantitative Analysis," 5th Ed., 1903, p. 102.

⁴ "Quantitative Chemical Analysis," 2nd Ed., 1905, p. 173.

⁵ "Methods in Chemical Analysis," 1st Ed., 1913, p. 166.

⁶ "Select Methods in Chemical Analysis," 1st Ed., 1886, p. 47.

⁷ "Quantitative Chemical Analysis," 1 (1903), 272.

¹ "Elementary Quantitative Agricultural Chemical Analysis," 1907, p. 33.

² "Analytical Chemistry," 1st Ed., 2 (1904), 66.

³ J. prakt. Chem., 83, 485.

⁴ Z. anal. Chem., 7, 224.

second addition of acid. The ignited lime precipitate was of course free of organic matter prior to the first addition of H_2SO_4 as a result of the ignition as well as the second heating to remove traces of the added alcohol. The only source of organic matter for possible reduction of the sulfate would therefore be the "C. P." acid itself. This objectionable feature of the conversion to sulfate by means of H_2SO_4 led to a study of the substitution of ammonium sulfate for the acid.

PRELIMINARY OBSERVATIONS

Qualitative sulfate conversion tests were made with recrystallized ammonium sulfate without obtaining any indication of the formation of calcium sulfide upon ignition of the chloride. With heavy occurrences of lime it is essential to make the preliminary conversion to the soluble chloride, when effecting the sulfate conversion by means of sulfuric acid. The same idea was at first followed in the substitution of ammonium sulfate. The chloride and sulfate radicals were introduced simultaneously by the use of a mixture of the two ammonium salts. It was thought that the use of the mixture might make possible the use of a smaller excess of sulfate. In further tests it was found that while the use of ammonium chloride in the fusion mixture is to be desired, it is not, however, necessary chemically in that a complete conversion to the sulfate is accomplished by the ammonium sulfate melt without the preliminary conversion to the chloride. The presence of ammonium chloride is particularly justified because of its mechanical effect, more especially in determinations of heavy lime

the crucible. In effecting the conversions of the lime residues to the sulfate, there is, of course, a considerable loss of ammonium sulfate by sublimation. This necessitates the assurance of a workable excess of the ammonium salt. In using the mixture of ammonium salts, it was therefore necessary to determine the excess of sulfate which would constitute a safe working basis. The only reference found, where the use of the solid sulfate is suggested, is that of Fresenius¹ who mentions, without citation, the technic of Schrötter. We have been unable to find the original in order to ascertain whether any specific directions and amounts are given by Schrötter. As a matter of fact the modification was worked out independently and the details perfected before our knowledge of the somewhat obscure reference mentioned by Fresenius, or the indefinite directions given by Crookes.²

In addition to determining the necessary excess of sulfate, it was essential to determine the most desirable proportion of chloride to sulfate in the conversion mixture. The data presented in Tables I and II were obtained in the determination of these points.

DISCUSSION OF RESULTS

The analyses given in Table I were made upon aliquots obtained from an HCl solution of Iceland spar. The results with a constant charge of chloride show that an excess of less than 0.3 g. of sulfate over the 0.2 g. charge of $CaCO_3$ fails to afford a safe working margin for a charge of this amount. The proportion of chloride to sulfate is also shown to be immaterial, insofar as the completeness of the conversion is concerned.

The results given in Table II were secured upon charges of calcium oxalate, which was made in the laboratory from "C. P." chemicals. The salt was dried, but was not heated sufficiently high to dispel the water of crystallization. The results of determinations 1, 2 and 3, made with constant amounts of the mixture, but with increasing amounts of salt, show that the charge is sufficient for the two smaller charges, but that insufficient excess of the mixture is present for conversion of the 0.7500-g. charge. It is evident from the results given in Table II, No. 3, that approximately 0.1 g. of NH_4SO_4 in excess of that theoretically required to convert 0.7500 g. of $(CaCOO)_2$ to sulfate is insufficient for complete conversion. In No. 4 it is shown that the same absolute amount was found insufficient to convert 0.5000 g. of $(CaCOO)_2$ entirely to the sulfate, although in the latter case there is nearly 100 per cent excess of (NH_4SO_4) compared with only about 11 per cent excess in the former case. The results in No. 5 show as outcomes where a 100 per cent excess of (NH_4SO_4) was sufficient. It seems, therefore, that an absolute minimum excess of (NH_4SO_4) is necessary for the successful use of the method. These and additional data have led to the adoption of the amount of the mixture designated in the procedure outlined below.

¹ Quantitative Chemical Analysis, 4 (1908), 212.

² *Ibid.*, 30.

TABLE I.—A STUDY OF THE CONVERSION OF THE IGNITED CALCIUM PRECIPITATE TO CALCIUM SULFATE, AS INFLUENCED BY VARYING RATIOS OF SULFATE AND CHLORIDE

No.	FUSION MIXTURE Charge in Grams NH_4Cl (NH_4SO_4)	Reagent Blank Gram	$CaCO_3$ Gram	FORMATION Theory Gram	Actual* Gram	Conversion Per cent
1.....	1.5	0.3	0.0002	0.2000	0.2721	95.44(0)
2.....	1.5	0.5	0.0003	0.2000	0.2721	96.76
3.....	1.5	0.7	0.0003	0.2000	0.2721	100.00
4.....	0.25	0.7	0.0002	0.2000	0.2721	100.00
5.....	0.5	0.7	0.0003	0.2000	0.2721	100.00
6.....	0.75	0.7	0.0002	0.2000	0.2721	100.07

* Corrected for blank

(a) Test demonstrated presence of $CaCl_2$.

occurrences. When using the ammonium chloride and ammonium sulfate mixture the sulfate melt goes down evenly and there is obtained a skeletal mass which in the most part is readily removed mechanically from

TABLE II.—THE DETERMINATION OF THE MINIMUM EXCESS OF FUSION MIXTURE ESSENTIAL TO THE COMPLETE CONVERSION OF THE IGNITED LIME PRECIPITATE INTO $CaSO_4$

No.	FUSION MIXTURE Charge in Grams NH_4Cl (NH_4SO_4)	Reagent Blank Gram	$CaCO_3$ Gram	GRAVIMETRIC Charge Corrected Gram for Blank	$CaSO_4$ FORMED Gram	PERCENT CONVERSION
1	0.25	0.25	0.0002	0.1500	0.1476	0.1478
2	0.25	0.25	0.0002	0.4500	0.4431	0.1477
3	0.25	0.25	0.0002	0.7500	0.6641	0.1476
4	0.25	0.25	0.0001	0.1500	0.1458	0.1478
5	0.50	0.50	0.0002	0.1500	0.1476	0.1476
6	0.25	0.25	0.0001	0.0750	0.0689	0.1478
				0.0750	0.0690	0.1480
				0.0893	0.1479	

(a) Re-ignited after addition of H_2SO_4 .

TECHNIC OF THE METHOD

The detail of the procedure is as follows: Carefully precipitate the lime as oxalate, reprecipitating, as is usually done, where the magnesium content is appreciable. Ignite in a small platinum dish (or platinum or porcelain crucible) over a Bunsen burner (or in a muffle) until the filter is completely incinerated. For each approximate 0.2 g. of CaCO_3 add enough of an equal part and *finely ground* and *dried* mixture of ammonium sulfate and ammonium chloride to insure an excess of approximately 0.3 g. of sulfate. Effect a thorough mixture of the fusion salts with the lime residue in the crucible by means of a small glass rod, enlarged and flattened at one end. Quantitative comparisons indicate that it is decidedly preferable that the mixing be done in the crucible, rather than by transfer to a mortar. The volatilization of the excess of salts may be efficiently carried out as follows: insert the crucible in a circular opening cut in a piece of asbestos board, placed horizontally. The upper half of the crucible should extend above the upper surface of the asbestos. Direct a nearly horizontal flame from a small Bunsen burner across the surface of the crucible in such a manner as to have the side of the crucible nearest the flame intensely heated. The conducted heat will effect volatilization without spattering.

Should duplicates fail to agree within a few tenths of a milligram, the analyst may verify the results by moistening the ignited CaSO_4 with a few drops of $\text{r} : 10 \text{ H}_2\text{SO}_4$, evaporating excess of water and again igniting.

The above procedure has been tested thoroughly against reagents of known purity and as to ease in close duplication of results in a large number of unknowns, and has given complete satisfaction. We have found the modification to be especially well adapted to high occurrences of lime and to sets containing widely varying percentages.

SUMMARY

I—Though not in general use, the determination of lime as CaSO_4 is authoritatively stated in accepted texts to be accurate.

II—The procedure generally given calls for the use of H_2SO_4 as the converting agency.

III—In addition to loss of weight as a result of the dissociation of sulfate because of high temperature, there occurs a loss due to the reduction of sulfate to sulfide, as induced by the small amount of organic matter contained in "C. P." H_2SO_4 .

IV—The use of recrystallized ammonium sulfate eliminates this objectionable feature.

V—It was found that a mixture of ammonium chloride and ammonium sulfate afforded a very satisfactory conversion mixture which gives very accurate results.

VI—The detail of the procedure, as perfected, is given.

A MODIFIED METHOD FOR THE DETERMINATION OF FLUORINE WITH SPECIAL APPLICATION TO THE ANALYSIS OF PHOSPHATES¹

By CARY R. WAGNER AND WILLIAM H. ROSS

Received September 13, 1917

In the preparation of phosphoric acid from phosphate rock by the sulfuric acid method there may be found as impurities in the acid any of the constituents of the raw materials used. In the volatilization method, however, which consists in smelting the rock with silica and coke in an electric or other furnace, the impurities may be limited to those constituents of the charge which are volatile at the temperature used in the process. The most important of these volatile constituents are the alkalies, sulfur, chlorine and fluorine. The last mentioned is usually the most abundant and is found associated with lime phosphate in all mineral deposits and in the bones of animals.

In the scrubbing tower method of recovering the phosphorus oxide fumes evolved in the heat treatment of phosphate rock no separation of hydrofluoric from the phosphoric acid takes place since both are absorbed in the process. In experiments made in this laboratory it has been shown² that by use of the Cottrell process of electrical precipitation in place of the scrubbing tower method much more efficient and economic recovery of the acid is possible, and in addition a separation of the hydrofluoric acid from the phosphoric acid may be brought about at the same time.

In carrying out this process the phosphorus pentoxide, as it is evolved from the furnace, quickly combines with the moisture driven off from the charge or with that present in the current of air which is passed through the furnace for the oxidation of the evolved phosphorus, and is thus precipitated in the form of a solution of phosphoric acid. If the temperature of precipitation is below 100° the strength of the solution will depend on the amount of moisture associated with the acid. When the precipitation is made at a temperature above 100° , however, the strength of the acid will be independent of the moisture with which it is associated. Under these conditions any excess moisture will remain in the gaseous state while passing through the precipitator pipes and will consequently escape without being precipitated. By use of a proper temperature for precipitation, acid may thus be recovered directly of such a concentration that it will crystallize to a solid mass on cooling.

The same conditions which bring about a recovery of the phosphoric acid in concentrated form also contribute toward its purification from such volatile constituents as hydrofluoric acid with which it is initially associated as it escapes from the furnace. At a temperature above 100° these constituents will remain in the gaseous state in passing through the treater pipes and will therefore undergo no precipitation excepting that portion represented by the solubility of the respective constituents in the phosphoric acid under the conditions of the precipitation. As referred

¹ Published by permission of the Secretary of Agriculture.

² Ross, Carothers and Merz, *This Journal*, 9 (1917), 26.

to in experiments which are to be described more in detail in a later publication complete removal of the hydrofluoric acid or other impurities may subsequently be effected in one of several ways, as by bubbling hot air through the acid, by recrystallization or by chemical means.

In carrying out the work thus outlined on the preparation of crystallized phosphoric acid free from hydrofluoric acid, it was found necessary to make numerous analyses for fluorine when present in phosphoric acid in widely varying amounts. No official method is available for the quantitative determination of fluorine and the methods given in the literature were found to be of limited application. Accordingly an attempt was made to devise a suitable method for the determination of fluorine in the presence of phosphates or phosphoric acid. The object of the present paper is to give an account of the results obtained.

PROPOSED METHODS FOR THE ANALYSIS OF FLUORINE

The various methods which have been proposed for the determination of fluorine may be conveniently divided into four classes as follows:

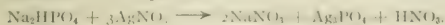
1—*Gravimetric methods*, as the Berzelius-Rose method in which the fluorine is weighed as calcium fluoride.

2—*Etching methods*, in which comparative tests are made of the action of hydrofluoric acid on glass or quartz.

3—*Colorimetric methods*.

4—*Volatilization methods*, as the Offermann method, in which the fluorine is distilled as silicon fluoride and collected in water.

1. GRAVIMETRIC METHODS—In the Berzelius¹ method as modified by Rose² and by Treadwell and Koch,³ the sample is fused with sodium and potassium carbonates, the silica precipitated with ammonium carbonate and ammoniacal zinc oxide, phosphates removed from the neutral solution by silver nitrate, the excess of silver taken out by sodium chloride, and $\text{CaF}_2 + \text{CaCO}_3$ precipitated with a large excess of calcium chloride. Calcium carbonate is dissolved after igniting the mixed precipitate in 1.5 *N* acetic acid and the calcium fluoride weighed. The method gives low results on account of the solubility of calcium fluoride in water and acetic acid. If phosphates are present the solution becomes acid when silver nitrate is added, as indicated in the equation



This acidity prevents complete precipitation of silver phosphate and, furthermore, will cause volatilization of fluorine when the solution is heated, unless the acidity is neutralized. This is a point that seems to have escaped notice in texts on the subject and could easily be overlooked by an analyst working on an unknown sample.

Ditte⁴ and Densen and Kessler⁵ have devised methods depending upon the formation of calcium fluoride in a fusion, the remainder of the melt being removed later by solution. Dim-widdie⁶ proposed precipitation of calcium fluoride with powdered calcium sulfate and treatment of the combined precipitate with sulfuric acid, such a mixture filters much more easily than a calcium fluoride carbonate mixture. Starck⁷ and Thorm⁸ suggested precipitation of calcium fluoride and oxalate.

Heintz¹ precipitated calcium fluoride and phosphate, determined the weight of $\text{Ca}_3(\text{PO}_4)_2$, and got CaF_2 by difference. Kneeland² used Berzelius' method, but determined lime in the precipitate. Jannasch³ distilled hydrofluoric acid from the sample in a platinum retort and then used Berzelius' method on the neutralized distillate. Pisan⁴ claimed excellent results by precipitating $\text{ThF}_4 \cdot 4\text{H}_2\text{O}$ and igniting to thorium dioxide. Starck⁵ precipitated PbFCl with saturated lead chloride solution.

Of the various methods referred to in this class that of Berzelius-Rose is the only one commonly used when phosphates are present. The method, however, is applicable only when the percentage of fluorine with respect to the phosphate present in the sample is not below a certain limiting amount. For the determination of small amounts of fluorine in phosphoric acid, the method was found to be entirely impractical and therefore could not be used in our work.

2. ETCHING METHODS—The methods of this class are dependent upon the corrosive action of hydrofluoric acid on glass or quartz. Carles,⁶ Ost,⁷ and Woodman and Talbot⁸ compared the extent to which a glass surface is attacked with that resulting from the use of a known amount of fluorine. Westberg⁹ and Kobell¹⁰ determined the loss in weight of a watch glass exposed to the action of the hydrofluoric acid evolved from a sample. Many other minor modifications of apparatus and procedure have been proposed but none seem to take into account the effect of silica in the sample.¹¹ When a sample containing silica is treated with acid a greater or less proportion of the fluorine, depending on the amount of silica present, will pass off as silicon fluoride. Therefore unless due precautions are taken for the initial removal of the silica a negative test may frequently be obtained even when considerable fluorine is present. Phosphoric acid prepared by the volatilization method always contains silica and to remove this constituent completely without danger of losing some of the fluorine would be very difficult if not impossible. The use of etching methods for the determination of fluorine in phosphoric acid was therefore considered impractical.

3. COLORIMETRIC METHODS—The Steiger¹²-Merwin¹³ method depends upon the fact that fluorides bleach oxidized titanium solutions. Another method proposed by Gautier and Clausmann¹⁴ depends upon the formation of lead fluoride and its transformation into lead sulfide. The turbidity caused by distilling hydrofluoric acid into a solution of a calcium salt has been recommended by Petersen¹⁵ as a means of determining fluorine.

The method of Steiger and Merwin is the best known of this class and gives good results¹⁶ for the determination of fluorine in the absence of such constituents as phosphoric acid, which have a bleaching effect on the titanium solution. All colorimetric methods, moreover, are applicable only when working with small amounts of fluorine and are therefore not of convenient application to the analysis of phosphate materials containing varying amounts of fluorine.

4. VOLATILIZATION METHODS—In this class are to be found a

¹ *Proc. Am. Chem. Soc.*, **77**, 6.

² *Trans. Am. Chem. Soc.*, **80** (1858), 111.

³ *Z. anal. Chem.*, **9**, 185.

⁴ *Compt. rend.*, **108** (1916), 791.

⁵ *Z. anal. Chem.*, **70** (1911), 100.

⁶ *Compt. rend.*, **144** (1907), 37.

⁷ *Ann.*, **26** (1858), 131.

⁸ *Z. anal. Chem.*, **28** (1899), 133.

⁹ *Ann.*, **26** (1858), 131.

¹⁰ *Z. anal. Chem.*, **192** (1913), 384.

¹¹ The authors have found that the method of Petersen, based on the reaction of titanium with hydrofluoric acid, is not reliable for the determination of fluorine in phosphoric acid. Methods of Chemical Analysis.

¹² *J. Am. Chem. Soc.*, **30** (1908), 111. See also H. Position, *J. Am. Chem. Soc.*, **33** (1911), 111.

¹³ *J. Am. Chem. Soc.*, **33** (1911), 111.

¹⁴ *J. Am. Chem. Soc.*, **36** (1914), 585.

¹⁵ *J. Am. Chem. Soc.*, **37** (1915), 585.

¹ *Proc. Am. Chem. Soc.*, **15** (1893), 426.

² *Leibig's Ann.*, **72** (1851), 343; *ibid.*, **79**, 115.

³ *Z. anal. Chem.*, **43** (1904), 469.

⁴ *Compt. rend.*, **80** (1875), 561.

⁵ *Monatsh. Chem.*, **28** (1906), 153.

⁶ *J. Am. Chem. Soc.*, **42** (1920), 463.

⁷ *Z. anal. Chem.*, **61** (1912), 14.

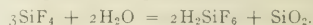
large number of methods and modifications dependent on the volatilization of fluorine as silicon fluoride. Oettel¹ measured the volume of silicon fluoride formed. Fresenius² observed the gain in weight of a tube filled with moist pumice when silicon fluoride was passed through it. Wöhler³ recommended volatilizing the silicon fluoride and noting the loss in weight of the flask and contents. Daniel's⁴ method is a combination of the two. Penfield⁵ distilled silicon fluoride into water, added potassium chloride and alcohol, and titrated with ammonia the hydrochloric acid set free. Offermann⁶ titrated the aqueous solution with potassium hydroxide using phenolphthalein. Offermann's method has been modified somewhat in the manner of procedure by Drawe,⁷ Hileman⁸ and Adolph.⁹ Browning¹⁰ suggested decomposing silicon fluoride on moist black paper and noting the amount of silica formed. Korovaef,¹¹ Städeler¹² and Weinland¹³ observed the loss in weight due to volatilization of silicon fluoride. Carnot¹⁴ passed silicon fluoride into a solution of potassium fluoride and weighed the precipitate of potassium silico-fluoride. Carnot's method was modified in some respects by Prost and Balthasar¹⁵ and by Burk.¹⁶ Somewhat similar methods had been proposed previously by Stolba,¹⁷ Liversidge¹⁸ and Tammann.¹⁹ Bein²⁰ collected and weighed the silica formed when silicon fluoride is decomposed by water. Lasne²¹ and Schneider²² distilled silicon fluoride into water and after removing silica precipitated $\text{CaF}_2 + \text{CaCO}_3$ and weighed the CaF_2 . Hileman²³ made use of an entirely different action of H_2SiF_6 when he titrated the iodine liberated in a solution of $\text{KI} + \text{KIO}_3$ by fluosilicic acid.²⁴

EXPERIMENTAL

The volatilization methods, unlike the methods of the preceding classes, are all applicable to the analysis of phosphates as well as other materials. The methods of this class, however, which are based on a determination of loss in weight due to the volatilization of silicon fluoride, are not suited to the analysis of material containing a low percentage of fluorine. The principle of all the remaining methods consists in passing the volatilized silicon fluoride into water and then determining, either volumetrically or gravimetrically, the amount of hydrofluosilicic acid formed. This procedure should be applicable to the determination of fluorine in amounts varying between rather wide

limits. A comparative study was accordingly undertaken to ascertain the most satisfactory details to be followed in the determination of fluorine according to this general scheme.

In carrying out these experiments use was made of a special double-trapped generating flask, designed by the Victor Chemical Co., for the volatilization of silicon fluoride. This flask (C), shown in Fig. 1, was called to our attention by Dr. H. E. Patten of the Bureau of Chemistry. The remainder of the equipment and the procedure followed in the preliminary experiments were in principle the same as that used by Offermann,¹ Adolph,¹ and others. The sample to be analyzed was mixed with a small proportion of ground quartz and then treated in the generating flask with 08.5 per cent sulfuric acid. A current of carbon dioxide washed with sulfuric acid served to carry the silicon fluoride evolved in the generating flask through a U-tube filled with glass beads, to remove accompanying fumes of sulfur trioxide, and then through water in a large test-tube, where decomposition of the silicon fluoride took place as represented in the equation



The solution thus obtained was boiled to expel dissolved carbon dioxide and sulfur dioxide, and the hydrofluosilicic acid determined both volumetrically by titrating with standard sodium hydroxide, using phenolphthalein as indicator, and gravimetrically by precipitating with saturated lead chloride solution.

Satisfactory results were sometimes obtained by this procedure, but, as a rule, and particularly when working with small amounts of fluorine, the values obtained were very greatly in error. After numerous tests had been made, the principal sources of error were ascertained to be as follows:

(1) Glass beads were found to be only moderately efficient in removing the sulfur trioxide fumes carried over from the generating flask. The result is that a portion of the fumes which escape passes into solution in the absorbing tube and thus gives high results whether the hydrofluosilicic acid is determined volumetrically or gravimetrically.

(2) Sulfur dioxide, which also escapes from the generating flask, is partly taken up by the solution in the absorbing tube and a portion there undergoes oxidation to sulfuric acid. This gives high results in the same way as with sulfur trioxide.

(3) When the solution of hydrofluosilicic acid was boiled to expel carbon dioxide and sulfur dioxide preparatory to the determination of the fluorine either gravimetrically or volumetrically, loss of fluorine was found to result when using the volume of solution ordinarily specified.

(4) Any chlorides or nitrates in the sample analyzed will result in the evolution of the corresponding acid and its absorption in the solution of hydrofluosilicic acid. This will give high results when the fluorine is determined volumetrically.

METHODS FOR THE ABSORPTION OF SULFUR TRIOXIDE IN FLUORINE ANALYSIS—When the sulfuric acid is boiled in the generating flask sulfur trioxide is carried

¹ *Z. anal. Chem.*, **25** (1886), 505.

² *Ibid.*, **5** (1866), 190.

³ *Pogg. Ann.*, **48** (1839), 87.

⁴ *Z. anorg. Chem.*, **38** (1904), 257.

⁵ *Am. Chem. J.*, **1** (1879), 27; *Z. anal. Chem.*, **21** (1882), 120.

⁶ *Z. angew. Chem.*, **3** (1890), 615.

⁷ *Ibid.*, **26** (1912), 1371.

⁸ *Z. anorg. Chem.*, **51** (1906), 157; *Am. J. Sci.*, [4] **22** (1906), 329.

⁹ *Loc. cit.*

¹⁰ *Am. J. Sci.*, [4] **32** (1911), 249.

¹¹ *J. prakt. Chem.*, [1] **85** (1862), 442.

¹² *Ibid.*, [1] **99** (1866), 66.

¹³ *Z. anorg. Chem.*, **21** (1899), 45.

¹⁴ *Bull. soc. chim.*, [3] **9**, 71; *Z. anal. Chem.*, **35** (1896), 580; *Compt. rend.*, **114** (1892), 750.

¹⁵ *Bull. assoc. belg. chim.*, **13** (1899), 453.

¹⁶ *J. Am. Chem. Soc.*, **23** (1901), 825.

¹⁷ *J. prakt. Chem.*, [1] **89** (1863), 129.

¹⁸ *Chem. News*, **24** (1871), 226.

¹⁹ *Z. anal. Chem.*, **24** (1885), 328; *Z. physiol. Chem.*, **12** (1888), 322.

²⁰ *Z. anal. Chem.*, **26** (1887), 733.

²¹ *Ann. chim. anal.*, **2** (1897), 182.

²² *Oesterr. Z. Berg.-Hüttenw.*, **61**, 365; *C. A.*, **7** (1913), 3582.

²³ *Am. J. Sci.*, [4] **22** (1906), 383.

²⁴ A volumetric method, belonging to none of these four classes, developed by Guyot [*Compt. rend.*, **71** (1870), 274; **73** (1871), 273] and Greef [*Ber.*, **46** (1913), 2511] depends on the precipitation of Na_2SiF_6 in neutral solution by standard FeCl_3 . As modified by Bellucci [*Ann. chim. applicata*, **1** (1914), 441], it gives good results for soluble fluorides, but is not applicable to the analysis of phosphates, since FePO_4 would be precipitated along with the fluorine compound.

¹ *Loc. cit.*

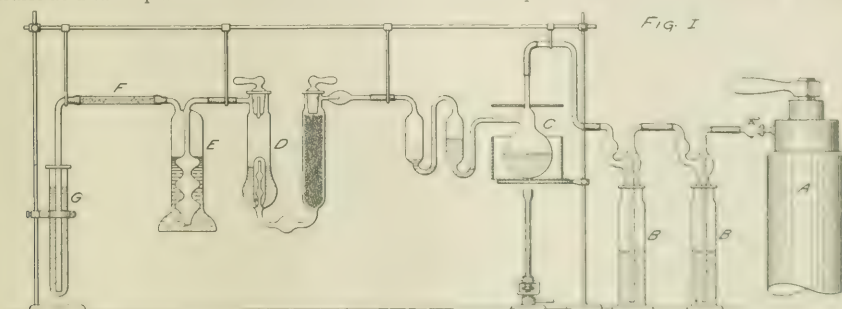
over as a white fume which is difficult to condense. The proportion retained by the glass beads in the U-tube will depend on the rate at which the carbon dioxide is passed through the apparatus, but even when the flow of gas is as slow as it is expedient to use, a white fume may still be seen to issue from the end of the tube containing the glass beads. It was found, however, that complete absorption of the fumes could be effected by joining in the apparatus, in addition to the tube containing glass beads, a straight piece of glass tubing (*F*), filled with glass wool as shown in Fig. I. A perceptible coloration of the glass wool on heating to 100–130° will indicate the depth to which the fumes have permeated. Care should be taken to replace the tube before the glass wool becomes completely saturated.

METHODS FOR THE ABSORPTION OF SULFUR DIOXIDE IN FLUORINE ANALYSIS—When the fluorine treated in the generating flask is considerable, the greater part of it passes over before the acid in the flask begins to boil and before an appreciable dissociation of the sulfuric acid takes place. It was also noted that

hydrochloric acid were used. Table I shows some results, obtained when using the volumetric method of determining the hydrofluosilicic acid.

It was observed, however, that when organic matter to the extent of 0.1 gram or more is contained in the sample analyzed, sulfuric acid then appears in the solution after boiling out dissolved gases, even though hydrochloric acid had previously been added. So much sulfur dioxide is evolved under these conditions that the hydrochloric acid present cannot prevent the oxidation of a part of it. It is well known that solutions of sulfur dioxide are rapidly oxidized by exposure to air and some work has been done on preventive measures. Thus Saillard¹ found that a solution of sucrose exerted an inhibitive effect on this oxidation. Accordingly 30 per cent and 60 per cent sucrose solutions were made up and used in place of water in the absorption tube. The effect was very much less than that produced by hydrochloric acid.

An oxidizing solution² was then prepared consisting of chromium trioxide in 98.5 per cent sulfuric acid. This was placed with an excess of the trioxide in the



when using pure samples of sodium fluoride in the generating flask, little or no sulfuric acid was formed in the absorbing tube when the fluorine taken amounted to 0.015 gram or more. From these observations it was thought possible that the hydrogen-ion concentration affected the oxidation of the sulfur dioxide. This would be expected if the oxidation depends on

TABLE I—RETARDATION OF THE OXIDATION OF SULFUR DIOXIDE IN ACID SOLUTIONS

Grams NaF Taken	Ce N/10 HCl Added to Absorption Tube	Ce N/10 NaOH—Equivalent of HCl Required	H ₂ SO ₄ Formed Expressed as Ce. of N/10 Solution
None	None	0.75	0.75
None	1.00	1.65	0.65
None	3.00	3.30	0.30
None	5.00	5.15	0.15
None	10.00	10.01	0.01
None	10.00	10.00	0.06
0.0046	10.00	18.24	0.07
0.0194	10.00	14.62	None

the amount of SO_2^{+} present, for sulfurous acid is very slightly dissociated into $\text{H}^+ + \text{SO}_3^{+}$. The larger part of it is in the form of $\text{H}^+ + \text{HSO}_3^+$ and the presence of an acid would therefore force back the dissociation of $\text{HSO}_3^+ \rightarrow \text{H}^+ + \text{SO}_3^{+}$. Several determinations were run using varying quantities of *N/10* hydrochloric acid in the absorption tube. It was found that the amount of sulfuric acid formed decreased steadily with increasing amounts of acid until practically none was formed when 10 cc. of *N/10*

Bowen potash bulb (*E*, Fig. I). When no organic matter was used in the generating flask the quantity of sulfur dioxide that escaped was found to undergo such complete oxidation in the trioxide solution that the amount carried over was too small to give rise to any appreciable quantity of sulfuric acid in the absorption tube. When the sample analyzed contains a large proportion of organic matter, however, so much sulfur dioxide is then evolved that quick reduction of the trioxide takes place. In this case the most convenient procedure is first to remove the greater part of the organic matter by heating at a temperature below the melting point of the material. The complete combustion of certain phosphoric materials is, however, sometimes difficult and if in such cases some carbonaceous material remains unburned in the sample, the sulfur dioxide evolved may be sufficiently great to cause complete absorption in the chromium solution. In the analysis of such materials standard hydrochloric acid solution should be used in the absorption tube as an added precaution. The effectiveness of the chromium trioxide solution in the absorption of sulfur dioxide is shown by the results given in Table II.

TABLE II.—ABSORPTION OF SULFUR DIOXIDE IN SULFURIC ACID SOLUTION OF CHROMIUM TRIOXIDE

SAMPLE TAKEN AT	Cc. N/10 HCl		Cc. N/10 NaOH		H ₂ SO ₄ FORMED	
	Added to Abs. Tube	NaF + HCl	Required + Cc. H ₂ O	No CrO ₃	(Cc. N/10 Solution) + CrO ₃	No CrO ₃
None	None	None	None	0.75	None	0.75
0.0214 g. Na ₂ SiF ₆	None	16.82	16.80	...	None	..
0.0050 g. NaF	None	1.19	...	2.00	..	0.81
NaF + Starch (ignited)	10.00	10.84	10.87	...	0.03	..
	10.00	10.84	...	11.30	..	0.46

LOSS OF FLUORINE IN BOILING SOLUTIONS OF HYDROFLUOSILICIC ACID—When proper precautions were taken to prevent the formation of sulfuric acid in the absorption tube, low results for fluorine were frequently obtained, as Adolph¹ observed in his experiments with the Offermann method. This was finally traced to a loss of fluorine on boiling the hydrofluosilicic acid solution to expel dissolved carbon dioxide and sulfur dioxide. As the volume of the solution was increased, the loss of fluorine decreased, and beyond a *N*/1000 concentration of the hydrofluosilicic acid no loss of fluorine took place, as shown by the results given in Table III:

TABLE III.—LOSS OF FLUORINE ON BOILING A SOLUTION OF HYDROFLUOSILICIC ACID

Cc. Acid Solution Taken	Boiling Period Min.	Cc. N/10 NaOH	
		Equivalent to H ₂ SiF ₆ Taken	Required
100	10	11.14	10.95
100	15	11.14	10.85
100	20	11.14	10.75
150	20	11.20	10.96
175	20	11.20	11.13
250	20	11.20	11.18

DETERMINATION OF FLUORINE IN PRESENCE OF CHLORIDES AND NITRATES—In most phosphatic materials a limited amount of chlorides is usually present. On treating such material in the generating flask hydrochloric acid would be evolved along with the silicon fluoride and would be taken up by the solution in the absorption tube. This would interfere with the volumetric determination of the hydrofluosilicic acid. With a view to preventing any hydrochloric acid reaching the absorption tube, the gases from the generating flask were made to pass through a Schmitz tube (*D*, Fig. I) containing a solution of silver sulfate in 98.5 per cent sulfuric acid. Glass beads were placed in the small arm of the tube and as thus equipped it took the place of the U-tube used in the preliminary experiments. That a solution of silver sulfate in sulfuric acid is able to absorb effectively any hydrochloric acid given off from the generating flask without interfering in any way with the determination of fluorine is shown by the results given in Table IV. In carrying out these experiments the acidity of the solution in the absorption tube was determined volumetrically after the precautions already noted were taken to prevent the formation of sulfuric acid or loss of fluorine through boiling.

When nitrates are present in the sample analyzed,

TABLE IV.—DETERMINATION OF FLUORINE IN PRESENCE OF CHLORIDES AND NITRATES

NaF	GRAMS REAGENT TAKEN		Cc. N/10 NaOH	
	NaCl	NaNO ₃	Equivalent to NaF Taken	Required
None	0.2	None	None	0.05
0.0093	0.05	None	2.21	2.22
None	None	0.2	None	0.0
0.0050	None	0.5	1.19	1.20

¹ Loc. cit.

nitric acid will be evolved at first, but as the temperature is raised, this will decompose to give nitrogen dioxide. In either case the product evolved will be taken up by the solutions in the Schmitz and Bowen tubes and consequently no nitric acid will be formed in the absorption tube as shown by the results given in Table IV.

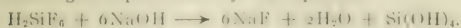
DETAILS OF PROCEDURE IN THE MODIFIED METHOD OF DETERMINING FLUORINE

APPARATUS—The equipment finally adopted in the analysis of fluorine is represented in Fig. I. *A* is a cylinder of compressed carbon dioxide or nitrogen fitted with a reducing valve or other safety device for regulating the flow of gas. *BB* are wash bottles containing concentrated sulfuric acid for washing the gas. *C* is a generating flask of 250 cc. capacity provided with 2 traps containing 98.5 per cent sulfuric acid, that next the flask being half full while the acid in the second is just sufficient to make a seal. *D* is a Schmitz tube having a 10 per cent solution of silver sulfate in 98.5 per cent sulfuric acid in the bulb of the tube and glass beads in the other. *E* is a Bowen bulb containing a saturated solution of chromium trioxide in 98.5 per cent sulfuric acid. *F* is a straight piece of glass tubing filled with glass wool. *G* is an absorption tube consisting of a large test-tube containing about 50 cc. of water.

On account of the pressure that must be generated in the apparatus to cause a flow of gas against the head of sulfuric acid, great care must be taken in assembling the apparatus to make all joints tight. Ends of glass tubing must be brought together and the rubber tubing used should be a good grade of heavy-walled gum tubing. As a precaution against diffusion of gas through the joints the rubber tubing may be covered with a good coating of shellac. Glass stopcocks should be paraffined also. An asbestos screen may be used under the flask and to minimize the danger of breaking the flask a ring of asbestos paper should be placed around it for protection against cold air currents. A mantle of asbestos over the bulb of the flask must also be used to prevent burning the rubber connection at the top of the flask. The exclusion of every trace of water from all parts of the apparatus is essential. The following additional reagents are required:

- (1) Anhydrous copper sulfate.
- (2) Ground quartz.
- (3) 98.5 per cent sulfuric acid prepared by boiling *C. P.* concentrated sulfuric acid for about 20 minutes in an open vessel.
- (4) A 10 per cent solution of silver sulfate in 98.5 per cent sulfuric acid. The silver sulfate should be ignited with an excess of sulfuric acid before using to drive off any volatile acids present.
- (5) A saturated solution of chromium trioxide in 98.5 per cent sulfuric acid.
- (6) *N*/10 sodium hydroxide, preferably standardized chemically pure sodium fluosilicate.
- (7) *N*/10 hydrochloric acid, carefully standardized against the *N*/10 sodium hydroxide.

DETERMINATION—The sample to be analyzed must be carefully dried. A quantity containing between 0.001 and 0.1 g. of fluorine is weighed into the generating flask with 0.1–1.0 g. of silica and 5 g. of anhydrous copper sulfate: 100 cc. of 98.5 per cent sulfuric acid are then added, allowing the first portions to run into the traps, and the flask quickly connected to the source of carbon dioxide. The valve of the carbon dioxide cylinder is adjusted to give a flow of gas through the absorption bulbs at a rate of about 2 or 3 bubbles per sec., and this rate should be maintained the same throughout the course of the experiment. The contents of the flask are shaken until well mixed and then heated gradually to boiling. At this point a white scum indicating fluorine will appear on the inside of the flask. The flame under the flask should then be adjusted so that the condensing sulfuric acid will wash this scum freely and completely into the first trap. Care should be taken, however, to avoid heating so strongly that white fumes will be evolved in noticeable quantity, nor should the acid in the first trap be made to boil. When the second trap is half full of acid the heating is discontinued. On turning off the flame, particular pains must be taken to regulate the flow of gas so that the relatively cool acid from the traps does not flow back into the flask and thus cause it to break. The valve in the carbon dioxide cylinder must therefore be sensitive enough to admit of quick adjustment. After a minute or two of adjustment the valve may be set to give as before a uniform flow of carbon dioxide, which is continued from 25 to 30 minutes, so as to wash all silicon fluoride into the absorption tube. The latter is then removed, its contents transferred to a 350 cc. Erlenmeyer flask, the solution made up to 200–250 cc. and boiled gently for 10 to 15 minutes to expel dissolved gases. This operation should consume as little time as possible, because any prolonged exposure to the air before boiling leads to oxidation of the sulfur dioxide in solution. The solution is allowed to cool somewhat and then titrated with *N*/10 sodium hydroxide, using phenolphthalein as indicator. The end-point must be approached slowly but is fairly sharp when the fluorine present amounts to less than 0.02 g. The reaction occurring is represented by the equation



It will require about an hour to make one determination.

If an appreciable amount of organic matter is present in the sample to be analyzed, it must first be removed by burning. This is done by adding sufficient sodium carbonate to make the material alkaline and then igniting in a muffle furnace at a dull red heat until a white, or nearly white, ash remains. Care must be taken that the temperature does not get high enough at any time to melt the material or to volatilize sodium fluoride.

In the determination of fluorine in phosphoric acid the latter must first be prepared for analysis by making neutral to phenolphthalein with sodium hydroxide and then drying.

In the analysis of samples free from organic matter,

it will be found unnecessary to add standard hydrochloric acid to the water in the absorption tube, providing the fluorine in the sample is equivalent to 10 cc. or more of *N*/10 acid. If the fluorine taken is less than this, or if there is any possibility of organic matter being present, then 10 cc. of *N*/10 hydrochloric acid should be added as a precaution against oxidation of sulfur dioxide to sulfuric acid. To insure that no error has been introduced from this source, the solution, after titrating, may be concentrated to about 50 cc., acidified with hydrochloric acid and a small amount of barium chloride solution added. In case a precipitate of barium sulfate occurs, this may be filtered off, ignited and weighed, and the proper deduction made from the volume of sodium hydroxide required.

When undertaking a second determination, a portion of the acid in the trap equivalent to that which distilled over in the preceding determination must be returned to the flask. This may be done by removing the stopper in the Schmitz tube and simply lowering the flask into the proper position. Whether or not the contents of the flask should be changed with each determination will depend on the character of the sample taken for analysis. Using samples containing little carbon and weighing 2 g. or less, the same acid may be used in making several determinations. In this case the sample to be analyzed, mixed with the proper amount of silica, is placed in a thin-walled glass capsule, dropped into the flask and the latter then quickly connected with the source of carbon dioxide as before. In this way little time is lost between successive determinations. The copper sulfate may be renewed with each change of acid. Its purpose is to serve as a dehydrating agent and to prevent bumping.

The accuracy of the method described and its range of application is shown by the results given in Table V. For the sake of comparison some results obtained with the Berzelius-Rose method are also given.

TABLE V.—RESULTS OBTAINED IN THE ANALYSIS OF FLUORINE COMPOUNDS

Sample Used	Grams Taken	CC. <i>N</i> /10 HCl Used in Absorption Tubes	PER CENT FLUORINE IN SAMPLE	
			Modified Berzelius Method	as Calculated
NaF.....	0.0376	10.00	48.63	48.74
	0.1037	10.00	44.49	45.24
	0.0000	None	45.06	45.24
	0.2000	...	43.21	45.24
	0.2000	...	42.95	45.24
NaF + CaF ₂	0.4644	10.00	4.48	4.52
	0.4220	10.00	4.52	4.52
	0.5000	None	4.54	4.52
	0.5000	None	4.43	4.52
	1.0000	...	2.92	4.52
	1.0000	...	2.62	4.52
	1.1035	10.00	0.438	0.452
	1.1610	10.00	0.434	0.452
	1.0000	...	0.30	0.452
	1.0000	...	0.18	0.452
	5.0000	10.00	0.037	0.045
	10.0000	10.00	0.015	0.045
Na ₂ SiF ₆ + 1 Calc. Fluorine	0.0441	10.00	0.67	0.68
	0.0441	10.00	0.68	0.68

In Table VI are given some results obtained separately by each of us in the analysis of some commercial materials which normally are supposed to offer special difficulty in the determination of fluorine.

An examination of the results given in Tables V and VI will show values obtained for the fluorine in different materials ranging from 0.01 to 4.1 per cent.

tirely free from other acid constituents. By titrating this solution with standard sodium hydroxide, using phenolphthalein as indicator, closely agreeing results for the fluorine in the samples analyzed may be obtained. In the case of samples freed from water and from organic matter (by burning) a complete analysis by this procedure may be made in the course of an hour. The method is applicable to the analysis of material having a fluorine content as low as 0.01 per cent.

BUREAU OF SOILS
U. S. DEPARTMENT OF AGRICULTURE
WASHINGTON, D. C.

A WOOL FAT (LANOLIN) SUBSTITUTE AND THE PREPARATION OF CETYLIC ALCOHOL

By SOL. AXELRAD
Received October 17, 1917

The question of substitutes for various materials has been one of prime importance during these war times, especially those substances and chemicals used in medicine and pharmacy. A year and a half ago the supply of wool fat was very limited and the price asked was four times more than that under normal conditions. A substitute called "Eucerin" imported from Germany was also scarce and the agency for this product had only four ounces left. It was claimed that "Eucerin" was made from the washings obtained in the manufacture of wool fat. The uses of lanolin are many, especially in pharmacy; as a vehicle for ointments, in the preparation of bougies, suppositories, cold creams and plasters of various kinds, etc.

This investigation on a wool fat substitute was undertaken with the idea of making a fatty composition which would have all of the desirable properties of lanolin, such as body, tenacity, power of absorbing water readily, taking up solutions of various chemicals used in pharmacy, dry powders, etc., etc.

Liebreich claimed that the absorbing power of wool fat was due to the cholesterin ethers it contained. Lifschuetz¹ isolated the cholesterin ethers of Liebreich and proved that they had very little power of absorbing water. He concluded from his experiments that the absorbing power of wool fat was due to the fatty alcohols of iso and oxycholesterols. He separated from the alkaline washings of partially saponified wool fat two saturated alcohols and one unsaturated alcohol. His experiments further proved that the more purified lanolin was, the lower was its power to absorb water, owing to the fact that during its purification the iso and oxycholesterols were partly removed.

Unna,² in his paper "Ointment Bases," states that "Eucerin" is a mixture of alcohols of the iso and oxycholesterin group with petrolatum. He does not, however, give a commercial method for the preparation of these alcohols. The absorbing power of "Eucerin" is due to these alcohols, but Roemer (see below) claims that with the employment of cholesterol for ointment bases, hydrocarbons, such as mineral oil, benzol, etc., are essential, for it is due to them in combination that the absorbing property is imparted. Roemer,³ in his

paper on "The Pharmacy of the Oxycholesterine Ointment Bases," confirms to a certain extent the work of Unna, but he also fails to give a method for the preparation of the alcohols.

Unna¹ states that "Eucerin" has been used in skin preparations in Germany, especially in pure form, for ichthyosis. According to the U. S. Dispensatory, 19th Edition, page 97, experiments have been carried on in reference to the absorption of wool fat by the skin. Patschkowski and Kaspar claim that the skin readily absorbs lanolin, but Ritter and Pfeiffer in a long series of experiments were unable to verify these results. Grimm² recommends, in his paper "Ueber die Verwendung von Aethyl in der Hautpflege," cetyl alcohol, $C_{16}H_{31}OH$, for skin preparations on account of its absorption by the skin and he further states that he has found it useful in the treatment of prurigo, weeping eczema and other skin infections.

In view of the fact that Unna and Roemer have written about the cholesterol, which are aliphatic higher alcohols, and Grimm has given a favorable report on the use of cetyl alcohol, the writer came to the conclusion that the use of this alcohol was advantageous in a substitute for wool fat.

A review of the literature failed to show any commercial method for the preparation of cetyl alcohol. There were many references as to its preparation from spermaceti by saponification with caustic potash and shaking the aqueous soap solution with petroleum ether, this being analogous to the extraction of unsaponifiable matter. Spermaceti is essentially the cetyl ester of palmitic acid. Chevreul in 1818 isolated the alcohol by the above method. Krafft³ prepared this substance by the reduction of palmitic acid to the aldehyde and heating it with barium formate. He also made the alcohol⁴ and by heating the palmitic aldehyde with zinc dust and acetic acid and hydrolyzing the acetate formed.

Levene⁵ made this alcohol by the reduction of ethyl palmitate with sodium and absolute alcohol. Schorlemmer⁶ distilled a dry mixture of barium oxide with sebacic acid. A method given in several text books for the preparation of cetyl alcohol was the saponification of spermaceti with alcoholic potash, evaporating the alcohol, taking up the residue with water, adding calcium chloride solution to form calcium soap and extracting with suitable solvents. The above methods are useful for preparing small quantities of cetyl alcohol, but for commercial quantities these methods fall down for obvious reasons.

The method of Schorlemmer was found impracticable on account of extreme acid not being a commercial substance. The extracted product contains a considerable loss of the desired alcohol and formation of triethylamine compound.

It has been found that cetyl alcohol distils at about 330 to 340° C. without decomposition and the writer's

¹ *Ibid.*, 29, 2890.

² *J. Am. Pharm. Assoc.*, 1, 673.

³ *Ibid.*, 2, 971.

⁴ *Ann. Chem. Phys.*, 1911, 1913, p. 108.

⁵ *Ann. Chem. Phys.*, 6, 108.

⁶ *Ibid.*, 13, 1416.

⁷ *Ibid.*, 16, 17, 18.

⁸ *Ann. Chem. Phys.*, 20, 131.

⁹ *Ibid.*, 3, 100.



FIG. I—HYDROUS LANOLIN $\times 100$
(WOOL FAT WITH 30 PER CENT WATER)
Average cost per pound 40 cents



FIG. II—WOOL FAT SUBSTITUTE $\times 100$
55 to 75 Per Cent Cheaper than Hydrous Lanolin

method is based upon the distillation of the calcium soap of spermaceti. Various experiments were performed with the following purposes in view.

- 1—Greatest yield of cetyl alcohol.
- 2—Cheapest process.
- 3—Most practical method.

EXPERIMENT I—Spermaceti (20 grams) was saponified with alcoholic potash, the alcohol evaporated and the residue heated in a distilling flask to 340°C .

EXPERIMENT II—Spermaceti (20 grams) was saponified with alcoholic potash, the alcohol evaporated and the soap dissolved in water. To the soap solution was added an excess of a 10 per cent calcium chloride solution. The calcium soap was separated and dried at 100°C . and finally distilled at 340°C .

EXPERIMENT III—The method employed was the same as in Experiment II, except that the soap solution was saturated with sodium chloride. The soap was filtered, dried at 100° and distilled. Many minor experiments were performed by this method but they did not show results of such value as to warrant their description.

EXPERIMENT IV—Twenty grams of calcium oxide containing about 5 per cent water were added to 15 grams of melted spermaceti. The mixture was heated for about 6 hours, with occasional stirring. When cooled, the mass assumed a brown-yellow color. On distilling same, frothing occurred at 100°C . due to the escape of water. When the water had all been driven off the temperature was raised to 340° when the cetyl alcohol distilled as white fumes and on cooling formed oily drops, which became pure white upon solidification, the melting point being 49.5°C . The yield obtained was over 6 grams, this being over 40 per cent of the actual spermaceti taken. The theoretical yield (calculated) was about 45 per cent.

This method gave a larger yield than the other three preceding methods, and, calculating the cost of the

alcohol obtained on a 40 per cent basis, was also cheaper than the others. The ideal temperature for the distillation of cetyl alcohol is 330 to 350° , as above this temperature a yellow liquid distills, being strongly acid and having a pungent odor; its value commercially will be investigated at a later date.

A copper still, manufactured by Sargent & Co., Chicago, for the distillation of oils, etc., at high temperatures, was found to be of most service. Glass stills are apt to crack, due to the "caking" of the residue which can readily be removed from the copper still after each distillation.

Mixtures were made having different quantities of base, cetyl alcohol, lanolin and water. The formula finally selected as being the best suitable for pharmaceutical compounding, was the following: 70 parts petrolatum, 20 parts paraffin, (m. p. about 60°C .), 10 parts cetyl alcohol, 5 parts lanolin (anhydrous), 100 parts water. This preparation stood in the laboratory for 17 months with absolutely no change in appearance or working qualities. The properties of this mixture are the same as wool fat; *viz.*, taking up solutions of salts, powders, etc., etc. The advantage over wool fat is that it will not become rancid and is considerably cheaper. The reason for using 5 parts of lanolin in the mixture was to have the "unctuous" property of wool fat. This, however, is a minor physical property.

A cold cream having very desirable properties can be made by using the above formula except for the addition of 250 parts of water instead of 100. The method of mixing the various substances is of prime importance. The petrolatum, alcohol, lanolin and paraffin are melted together. The water is warmed to the same temperature as the melted fats and added slowly with constant grinding so as to get a smooth mixture.

Microphotographs of hydrous wool fat, the substitute

and cold cream have been taken and are shown in Figs. I, II and III.

The writer believes that the wool fat substitute described in this paper will stand competition with wool fat and "Eucerin," both now and under normal conditions.

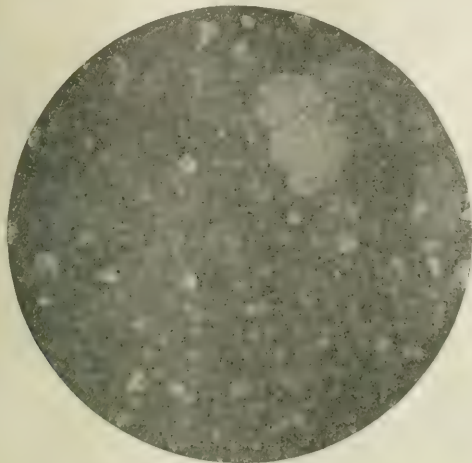


FIG. III—COLD CREAM X 100
80 to 90 Per Cent Cheaper than Hydrous Lanolin

A further investigation is under way to determine the value in the preparation of a wool fat substitute, of ceryl alcohol, $C_{27}H_{56}OH$, from Chinese wax and myricyl alcohol, $C_{30}H_{61}OH$, from Carnauba wax.

In conclusion, due credit is hereby given to Mr. Sol. Bernstein, who spent considerable time in performing experiments and assisting in general to bring this paper to a successful issue.

OTHER REFERENCES

- "Technology of Oils and Fats," Lewkowitsch, 239.
Allen's "Organic Analysis," 4th Ed., 479.
Jahresberichte, 1862, 413.
J. prakt. Chem., 9, 321; 43, 148.
Ann., 131, 283; 83, 16.
Ber., 28, 1335; 29, 618, 1474; 31, 97, 1122.
Apoth. Zeil., 20, 857.
J. Soc. Chem. Ind., 11, 134; 15, 14.

HIGHEST-STATE LABORATORIES
227 FRONT ST., NEW YORK CITY

THE RENNATIC PROPERTIES OF PEPSIN

By HOWARD T. GRAHAM

Received August 29, 1917

Physiological chemists teach us that the gastric juice consists of hydrochloric acid, inorganic chlorides and phosphates, together with mucin and the enzymes pepsin, gastric lipase and gastric rennin.

The theory as to the source of the proteolytic activity and the milk curdling property of the juice has not been explained satisfactorily so as to be acceptable to all.

Some physiologists claim that these two properties reside in a single substance and that the milk-curdling and protein-hydrolyzing activities are present in definite and distinct side chains of a single mammoth molecule; others claim that the two properties are due to two definite and distinct enzymes secreted by separate and distinct glands.

The scarcity of the calf rennet, both in extract and powder forms, due to the foreign situation, made it imperative that a substitute be obtained if the cheese-making industry were to be perpetuated. It was natural to turn to pepsin from the hog stomach for such a substitute. The first experiments were somewhat disappointing. Our custom had been, in the assaying of the calf rennet,¹ to determine the amount of rennet necessary to curdle a definite quantity of sweet, unpasteurized milk in a definite period of time at a definite temperature.

When this same technique was applied to the assay of pepsin for its rennetic power, it was found that our results were not comparable. A pepsin solution which has a rennetic value of 100 per cent by our arbitrary standard did not have a strength of 50 per cent when it was diluted 50 per cent with distilled water, and in like manner a pepsin scale having a power of 100 per cent, diluted 50 per cent with milk sugar or other similar diluent, did not possess a rennetic power of 50 per cent its original strength.

This was contrary to the action of the calf rennin, which always showed an activity in proportion to its dilution.

Inasmuch as acid is an activator for the proteolytic hydrolyzing power of pepsin, it was natural to assume that our lack of uniformity in our rennetic assays was due to variations in the acid concentrations of the solutions being assayed. Experiments proved this theory correct and it was found that when the pepsin dilutions were brought back to the original acidity of the undiluted solutions our results became more concordant. The next step was to consider the reaction of the milk and to adjust it to a definite acid concentration. When this precaution was taken, the results proved to be as comparable for judging the rennetic property of pepsin as for calf rennet.

The technique observed now in judging a sample of pepsin for its milk coagulative power is the same as previously published for rennet, with the addition that the acidity of the sweet, unpasteurized milk is brought to 0.185 by the addition of q. s. pure lactic acid.

To illustrate the above points, I have appended the following experiments. These experiments include the determination of the E. M. F. and pH values, as well as the acid titrations, of the sweet and adjusted milk, together with the period of coagulation.

EXPERIMENT 1.—The milk had developed a high state of acidity before reaching the laboratory. The acidity 0.204 developed during a thunderstorm while the milk was held in the ice box.

SWEET (UNADJUSTED OR UNNEUTERIZED MILK)					MILK ADJUSTED			
No.	Date 1916	pH	Acidity Per cent	μ_a	Strength	Coag. in Min.	Coag. in Min.	pH
1.....	9/7	5.277	0.22	4415 No. 2	1: 3000	3.75	3.75	...
2.....	9/8	6.581	0.16	4479 No. 4	1: 3000	2.75	2.0	...
3.....	9/15	6.56	0.135	4893 No. 1	1: 10,000	0.9	0.5	6.21
4.....	9/18	6.33	0.1425	4893 No. 2	1: 3000	2.8	1.5	...
5.....	9/19	6.49	0.1475	5532	1: 3000	Inert	4.0	...
6.....	9/20	6.41	0.15	5528 No. 2	1: 3000	Inert	1.75	0.17
7.....	9/22	5.70	0.1525	5470	1: 3000	Inert	2.0	6.34
8.....	10/2	6.3	0.14	Elix. Pepsin	1: 3000	Inert	1.25	...
9.....	10/4	Elix. Pepsin	1: 3000	Inert	2.0	...
10.....	10/6	...	0.13	Elix. Pepsin	1: 3000	Inert	1.5	0.1975
11.....	10/20	...	0.145	Scale, No. 1	1: 3000	Inert	1.0	5.857
				Elix. 5446	1: 3000	Inert	0.75	...
				Elix. 5447	1: 3000	Inert	2.75	6.04
				5579	1: 3000	Inert	3.5	...
				5580	1: 3000	Inert	1.5	0.2075
				4422 No. 6	1: 3000	Inert	6.25	6.17
				4420 No. 3	1: 3000	Inert	1.25	...
				5520 No. 7	1: 3000	Inert	1.0	0.2075
				No. 8	1: 3000	Inert	2.25	5.784
				4420 No. 3	1: 3000	Inert	2.5	...
				4422 No. 6	1: 3000	Inert	1.0	5.5
				5808 No. 2	1: 3000	Inert	1.0	...
				5627	1: 3000	Inert	14.5	...
				5579	1: 3000	Inert	6.5	...
				Sol. No. 1	1: 3000	Inert	9.25	...
				No. 2	1: 3000	Inert	Less than 1	0.20
				No. 3	1: 3000	Inert	Less than 1	...
				No. 4	1: 3000	Inert	Less than 1	...
				4420 No. 3	1: 3000	Inert	1.75	...
				No. 4	1: 3000	Inert	2.25	0.18

EXPERIMENT 2—This test illustrates the question of dilution. When the 1:10,000 pepsin was diluted with 7 parts milk sugar, it was apparently inert when tested on sweet milk of 0.16 per cent acidity, but when the same milk was brought to an acid concentration of 0.19 per cent lactic acid the pepsin dilution was found to test 1/8 as strong as the original.

EXPERIMENT 3—In this assay the three scales were apparently inert in milk of 0.135 per cent acidity, also one fluid drachm of the elixir failed to coagulate one quart of milk. When the acidity of the milk was brought to 0.17 per cent, coagulation readily took place.

STRENGTHS OF MIXTURES USED

- EXP. 2. Rx 4893 No. 1=1 part 4893 + 2 parts Milk Sugar
 Rx 4893 No. 2=1 part 4893 + 7 parts Milk Sugar
 EXPS. 3, 4 AND 10. Elixir Pepsin=1 fluid drachm contains 2.5 grs. 1: 3000 Pepsin.
 EXP. 6. Rx 5580=1 part 1: 10,000 Pepsin + 7 parts Milk Sugar.
 EXP. 11. Rx 4420 No. 4=1 part 4420 No. 3 + 4 parts Milk Sugar

CONCLUSIONS

The foregoing experiments seem to indicate that the substance which gives the rennetic property to pepsin is not the same substance which gives this property to the calf rennin. It has been shown that it is necessary to activate the pepsin by means of acid before it shows its rennetic power in its proper degree. The adjustment of the milk to a definite acid concentration also aids the coagulation by calf rennet, but the great difference between pepsin and calf rennin in this respect is that calf rennin never fails to coagulate sweet milk or to give comparable results upon dilution, while pepsin fails more often than it produces coagulation on perfectly sweet milk. Another great difference is that pepsin acts best on very ripe milk, even to an acidity of 0.2 per cent or more, while rennin is not favored by such a high acid concentration.

Considering the above facts, together with the additional notation that in pepsin these two properties, the milk-curdling and proteid-hydrolyzing, have never been isolated, so that we have in the one case an

enzyme of high curdling power with no proteolytic strength, and in the other a high proteolytic power with no coagulative strength leads me to accept the theory that these two activities are closely bound in a single molecule, and that under the proper conditions of temperature, etc., it is only necessary for this large molecule (pepsin) to come in contact with milk and acid, or protein and acid when the respective activities of milk coagulation or protein hydrolysis takes place.

RESEARCH LABORATORY
 DIGESTIVE FERMENTS COMPANY
 DETROIT, MICHIGAN

A METHOD FOR THE DETERMINATION OF ALCOHOL

By C. J. HAINES AND J. W. MARDEN

Received June 21, 1917

The fact that so many methods have been suggested for the determination of alcohol is indicative of much to be desired in the speed and ease with which determinations can be made. The specific gravity method with which accurate results can be attained and which is most popular cannot in general be applied to liquids other than pure alcoholic solutions. This paper has been prepared suggesting a method which does not require in many cases the distillation necessary to specific gravity determinations, in the hope that the results may be of value in analytical chemistry.

Frary¹ and others have observed that potassium fluoride or potassium carbonate when added to alcoholic solutions will cause the alcohol to separate from the remainder of the solution, that is, that aqueous solutions of potassium fluoride or potassium carbonate are immiscible with alcohol. Frary has suggested a method based on these observations for the determination of ethyl alcohol by the use of potassium fluoride. The method is to add sufficient of the salt (carefully weighed out) to an alcoholic solution in a glass-stoppered cylinder to cause the alcohol to separate, add an in-

¹ "Studies in Chemistry, No. I." University of Minnesota, 1913.

dicator (phenolphthalein) which colors the alcoholic solution and then gradually add water with frequent shaking till the two layers just disappear and the two liquids become completely miscible. From the weight of liquid (which is then determined) and the weight of the salt, Frary finds the percentage of alcohol from a table which he has prepared. He finds that the separation of the alcohol by means of potassium fluoride is apparently quite independent of ordinary laboratory temperature conditions.

There are various objections to this method. The potassium fluoride must be perfectly dry and pure. Also, after the analyst has made such a titration as is suggested above, made the weighings and used the table he has consumed much time. It seemed at the outset of the present work that, if the salting out of the alcohol was quantitative, the entire volume of the alcohol could be separated and that the process would be much simpler if the percentage by volume were read off directly.

METHOD OF DETERMINATION

The determinations were made at first in graduated tubes of 15 cc. capacity which had been prepared by cutting off 50-cc. gasometer tubes and later in centrifuge tubes of the same capacity. The tubes were all graduated to 0.1 cc. and before use were carefully calibrated with water. In every case the readings were estimated to 0.01 cc. In a determination, 10 cc. of alcoholic solution at 15.6° were used where the concentration was less than about 50 per cent, but where the concentrations of alcohol were greater than this, 5 cc. were taken and the volume made up to 10 cc. in the tube. Potassium fluoride was then added till the tube read about 13 cc. It was found by trial that this gave sufficient of the salt to saturate the solution. A small crystal of malachite green was dropped in which served to color the alcohol layer so that the volume could be easily read. Various substances could be used for this purpose such as a small piece of phenolphthalein, iodine, etc., but the malachite green proved quite satisfactory giving no color to the aqueous potassium fluoride solution. The tubes were then closed with a tight-fitting stopper and shaken vigorously for perhaps 2 minutes. If the potassium fluoride is dry the solution warms up but when placed in the centrifuge for 2 or 3 minutes, cools down to about room temperature. The alcohol separates in the upper layer while the excess of solid salt settles to the bottom of the tube. From the volume of alcohol observed and the volume of alcoholic liquid used for the determination, the percentage of alcohol by volume is readily found. Since one cc. of this alcohol changes about 0.005 cc. per degree Centigrade at room temperatures, the volume can be corrected to 15.6° if so desired. It was found by experiment that the potassium fluoride did not precipitate quite the last traces of alcohol and when the readings were made from the bottom of the meniscus it was necessary to add 0.1 cc. to observed readings to allow for this and the amount of alcohol adhering to the sides of the tube.

ANALYTICAL RESULTS

Tables I and II are given to show the results obtained by this method of analysis. The first series of determinations was made on pure aqueous alcoholic solutions, the concentrations of which had been carefully determined by the specific gravity method at 15.6°, Table I. A one per cent alcoholic solution just shows the presence of alcohol by this method.

TABLE I—ALCOHOL DETERMINATIONS IN AQUEOUS SOLUTIONS BY POTASSIUM FLUORIDE METHOD CORRECTED TO 15.6° C.

No.	Strength % by volume	Alcohol Actual Cc.	100% ALCOHOL FOUND		PER CENT ALCOHOL FOUND
			Used	Found	
1.....	95.34	5 cc.	4.77	4.71	-0.06
2.....	82.0	5 cc.	4.10	4.11	+0.01
3.....	75.71	5 cc.	3.79	3.87	+0.08
4.....	67.69	5 cc.	3.38	3.40	+0.02
5.....	57.84	5 cc.	2.89	2.84	-0.05
6.....	41.84	5 cc.	2.09	2.07	-0.02
7.....	30.4	10 cc.	3.04	3.09	+0.05
8.....	18.48	10 cc.	1.85	1.88	+0.03
9.....	12.4	10 cc.	1.24	1.28	+0.04
10.....	5.0	10 cc.	0.50	0.53	+0.03
11.....	1.26	10 cc.	0.12	0.15	+0.03

Values read from bottom of meniscus and 0.15 cc. added.

Table II shows the analysis of various substances for alcohol. In nearly all cases the alcohol was determined directly, but in several analyses precipitates were formed when the fluoride was added. In such cases the alcohol was distilled and the determinations made on the distillates. Whiskey was successfully analyzed after clarifying with alumina cream.

TABLE II ALCOHOL DETERMINATION IN DIFFERENT SUBSTANCES CORRECTED TO 15.6° C.

No.	SUBSTANCE ANALYZED	Cc. Used	100% ALCOHOL FOUND		Sp. Gr. by vol.	Difference Per cent
			Used	Found		
1	Alcohol (denatured).....	5	4.7	94.0		
2	Beer (a).....	10	0.43	3.3	1.1	+0.2
3	Beer (a).....	10	0.45	4.5	4.2	+0.3
4	Cider (a).....	10	0.50	5.0	5.28	+0.28
5	Bar tonic (a).....	5	1.45	2.0	29.4	+0.4
6	Tincture of Iodine (a).....	5	4.55	91.0		
7	" " ".....	5	4.73	94.6	98.0	+0.4
8	" " ".....	10	4.74	47.4	47.5	+0.1
9	" " ".....	10	2.85	23.8	23.75	-0.25
10	Tincture of Iron (a).....	5	4.73	94.6	98.0	+0.4
11	" " ".....	10	4.74	47.4	47.5	+0.1
12	Vanilla Extract (a).....	5	1.35	27.0	27.65	+0.65
13	Whiskey (a).....	5	2.50	50.0		
14	Whiskey (a).....	5	2.50	50.0	50.0	

(a) After distillation. (b) Before distillation.

CONCLUSIONS

I—A method has been proposed for the easy, rapid determination of ethyl alcohol which, if care is observed in reading the tubes, gives a fair degree of accuracy. The potassium fluoride used is inexpensive and need not be purified. It is best to dry this substance but small amounts of moisture in it do not affect the results.

II—The method cannot be used for solutions containing less than 1 or 2 per cent of alcohol or where other organic liquids are present such as acetone, essential oils, etc.

It might be pointed out, however, that in a solution such as the tincture of iodine the determination is very simple. The yellow solution is placed in the tube, the potassium fluoride added, the tube shaken, resealed, and the volume of the alcohol which remains the yellow in solution read. The iodine in the solution seems to have little effect on the volume of the alcohol.

ADDRESSES

"DOING OUR BIT"

By BERNHARD C. HESSE

The American chemist, in common with all other good Americans, has his "bit" to do not only during the period of the war but also when peace returns. It is more than likely that we shall find new conditions when this war is over and to meet them we chemists will have to work along lines quite different from those to which we had theretofore been accustomed. Therefore, it can be only prudence and good policy to discuss now, in a more or less general way, just what these conditions may be and what may be the general modes of meeting them, and it is with this problem that we are now concerned.

THE PUBLIC AND SCIENCE

The general public has now realized as never before the important part that can be and in fact is played in matters of national aggression and of national defense by those who create, disseminate and apply science. There is hardly a single one of the many divisions and subdivisions of our Council of National Defense and of our National Research Council that does not call for a new application of some branch of science in one form or another. Every branch of our varied activities which pertains to the transporting, housing, feeding and equipping of our soldiers

TABLE I—ORGANIZATION OF THE NATIONAL COUNCIL OF DEFENSE AND THE ADVISORY COMMISSION

COUNCIL OF NATIONAL DEFENSE		ADVISORY COMMISSION	
DIRECTOR OF COUNCIL AND COMMISSION			
Sections and Boards of the Council		Divisions of Advisory Commission	
GENERAL MUNITIONS BOARD		TRANSPORTATION AND COMMUNICATION	
MUNITIONS STANDARDS BOARD		MUNITIONS	
AIRCRAFT PRODUCTION BOARD		ENGINEERING AND EDUCATION	
MEDICAL SECTION		SUPPLIES	
COMMERCIAL ECONOMY BOARD		RAW MATERIALS	
INTERDEPARTMENTAL ADVISORY COMMITTEE		Alcohol	Lumber
COÖPERATIVE COMMITTEES ON PURCHASE OF ARMY SUPPLIES		Alumina	Mica
(U. S. CHAMBER OF COMMERCE)		Asbestos, Magnesite and Roofing	Nickel
INVENTIONS (NAVAL CONSULTING BOARD)		Brass	Oil
NATIONAL RESEARCH COUNCIL		Cement	Rubber
COMMITTEE ON SHIPPING		Chemicals	Steel and Steel Products
COMMITTEE ON WOMEN'S DEFENSE WORK		Coal-Tar By-Products	Sulfur
COMMITTEE ON COAL PRODUCTION		Copper	Wool
SECTION ON COÖPERATION WITH STATES		Lead	Zinc
		LABOR	
		MEDICINE AND SURGERY	

both here and abroad has to meet new and untried conditions; many of these are themselves the direct offspring of scientific knowledge, and have to make a demand upon sciences not only in their applied forms but in many cases in their pure forms; among the sciences so called upon, chemistry has been prominent.

It is inevitable that when peace does return, this new realization of the general public will not be at once laid aside. Further, it is inconceivable that, impressed as it now is with the potential and actual power of science in war, the public will not conclude that science must have equally great potential beneficial effect on peace-time pursuits and development and demand the full realization of those potentialities. This attitude of the public mind is of great importance and is something which should not be permitted to perish or to fall into decay. Unless those of us who are engaged in creating or in disseminating or in applying science make every effort to realize these fundamentally correct expectations of the public we can hardly expect their continuance, and the result will be that sooner or later and, as a nation, we shall be at a disadvantage with respect to those peoples who are not remiss in that direction.

¹ Address before the Chemical Society, Massachusetts Institute of Technology, Boston, Mass., November 22, 1917.

PUBLIC OPINION AND NATIONAL EFFORT

In our democratic government public opinion is, in general and usually, the source and fountain-head of all our governmental and national activities; whatever governmental machinery we have is here for the benefit of the public and the public is not at all here for the benefit of any of our governmental machinery. Except in times of stress we do not take orders from our government; it is our habit to give orders to our government.

We can give orders only if we have a well grounded and well founded public opinion upon which to base them and by which to give those orders force and effect.

The public is now in more sympathetic attitude towards science than ever before and it has singled out the science of chemistry as one of its especial hopes and supports, both in war and in peace. Every one of us must take hold with a will and do his level best to the end that this valuable national asset of a sympathetic public opinion and a favorable public attitude of mind be not withdrawn from us. We are the custodians of a most valuable trust and our responsibilities are co-extensive with our opportunities.

THE CHEMIST IN THE LIFE OF THE NATION

Impressed as we are with the magnitude of our task and with

the seriousness of our responsibilities let us consider the situation in some detail. Now as to the problem and its scope.

In the first place, what is our position in the general scheme of affairs of our nation? The diagram of the early organization of the Council of National Defense is probably the most complete, authoritative and effective answer we can to-day obtain. A skeleton of it is given in Table I.

In the second place, what is the general position of the chemist in the industrial activities of our nation? Broadly and fairly speaking it can be said that the chemists make up about *one ten-thousandth* of our population and that in their various industrial activities they are connected with industries that employ roughly *one-sixth* of our industrial wage-earners, produce about *one-fourth* of the value of our manufactured products and about *one-fifth* of the value added by manufacture; in our foreign trade in 1913 with Germany alone in products of and for chemical industries these made up *one-twentieth* of our total international trade and provided *one-seventh* of our balance of trade.

To take only a very few from a great many striking examples of the chemist's activities it may be said that he has added between \$10 and \$12 to the value of each bale of cotton grown, has invented or discovered, made and marketed over 100 different

commercial products from corn and for these he uses as much corn as is produced in North Carolina or is produced by the nine states of Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, Connecticut, New York, New Jersey and Delaware combined.

Many industries flourished for centuries before chemical knowledge and chemical treatment, as we understand them to-day, were applied to them and these are to-day brought to an efficiency, economy and diversity of production by the chemist, which without the chemist would have been impossible; such are those of leather, soap, iron, copper, textiles of all kinds, paints, varnishes, fats, paper, glass, stoneware and porcelain; there is also a large number of industries which were literally created by the chemist during the past 75 years, such as artificial fertilizers, fuel-gases, gas-lighting, photography, explosives, illuminating oils, carbide, aluminum, carborundum, dyes, medicines and in all but a very few of these the American chemist has taken a leading part and there is no reason why he should not keep right at it.

What the limits of chemical industry are, must in the very nature of things be vague but nevertheless more or less closely following that undefined thing called usage. One thing is certain, it does not include every industry making or using products of chemical change for that would include almost all human activities; it can no more be so inclusive than could every industry that employs or profits by the use of arithmetic be called a mathematical industry. Of course, there are many different accepted usages, but for present purposes the usage of the United States Census will be followed.

Coming now to more precise matters and taking the classification of the U. S. Census for 1909 as a criterion of what constitutes chemicals and allied products we find that these are nine in number, namely:

- 1—PAINT AND VARNISH
- 2—CHEMICALS
- 3—FERTILIZERS
- 4—EXPLOSIVES
- 5—DYESTUFFS AND EXTRACTS
- 6—SULFURIC, NITRIC AND MIXED ACIDS
- 7—WOOD DISTILLATION (NOT INCLUDING ROSIN AND TURPENTINE)
- 8—ESSENTIAL OILS
- 9—BONE, CARBON AND LAMPBLACK

From the 1909 census data it appears¹ that "if we compare the average chemical plant with the average plant in all domestic industries that the average chemical plant, when so contrasted, costs 330 per cent of that general average, employs 144 per cent as many persons of which the salaried employees are 264 per cent of the general average and the wage earners 134 per cent; the output value is 261 per cent of the general average and its enhancement in value is 248 per cent. Therefore, as a unit, the average domestic chemical plant costs more, produces more, enhances more, employs more salaried persons and more wage earners than the average industrial plant.

"A dollar invested in our chemical industries is not so productive as in our industries as a whole; it spends less for wages, salaries and materials and produces less product-value and less enhancement value.

"Per \$100 of product, the general average and the average domestic chemical plant, respectively, expend \$16.58 and \$9.09 for wages, \$4.54 and \$5.65 for salaries, or \$21.12 and \$14.74 for services.

"Per individual wage earner the annual output of product is \$3.125 for the general average and \$6.035 for the average domestic chemical plant.

"Per individual salaried employee, the annual output of product is \$96.157 for the general average and \$25.733 for the average domestic chemical plant.

"The average salaries are \$1.188 and \$14.55, respectively, for our

industries as a whole and our domestic chemical industries; the average wages are \$5.18 and \$5.49, respectively; in the industries as a whole there are 8 wage earners to each salaried employee and in our chemical industries there are 4 wage earners to each salaried employee.

"Relatively, our chemical establishments are 0.79 per cent of all our industrial establishments and the number of persons employed is 1.15 per cent of all persons employed in manufacture.

"Hence while an average chemical plant, as such, is of greater importance to the community than the average industrial plant, yet the capital so invested is not so productive as in the average industries."

PEACE TIME GROWTH OF OUR CHEMICAL INDUSTRIES

That these nine branches of the U. S. industries of chemicals and allied products are increasing actually as well as relatively to our entire industrial activities as a whole is one of the gratifying facts shown by the U. S. Census figures for 1914 only recently available. The actual figures are given in Table II; the growth is evidenced by the percentages.

Another gratifying disclosure of the 1914 census is that the groups of chemicals and allied products have been increased in number and scope and to the nine groups above enumerated and considered the following 17 have been added:

- 1—Baking Powders and Yeast
- 2—Blacking, Stains and Dressings
- 3—Bluing
- 4—Candles
- 5—Cleansing and Polishing Preparations
- 6—Coke (not including Gas-house Coke)
- 7—Drugs (including Drug Grinding, Druggists' Preparations, Patent Medicines and Compounds, Perfumery and Cosmetics)
- 8—Gas, Illuminating and Heating
- 9—Glue, not elsewhere specified
- 10—Greases (including Grease and Tallow, Lubricating Greases and Soap Stock)
- 11—Printing Ink
- 12—Writing Ink
- 13—Cottonseed Oil and Cake, Linseed Oil, Fish Oils, Oleo and all other oils have been added to Essential Oils
- 14—Petroleum, refining
- 15—Salt
- 16—Soap
- 17—Turpentine and Rosin

This is a very gratifying state of affairs particularly if we bear in mind that the 1914 census covers the fiscal year ending with June 30, 1914, or about one month before the present war broke out. It shows that domestic capital before the war was taking more to these chemical and allied industries than to our industries in general; that the compilers of the census have become convinced that the chemical and allied industries had therefore been too narrowly defined. That can only mean that prior to this war we had obtained greater official and hence public recognition of the chemist's influence in the nation's business and that domestic capital had of its own accord increased its confidence in our business as a business.

To give an idea of what this classification-expansion of "Chemical Industries" means to the U. S. statistical position of the "Chemical Industries," Table III has been compiled.

Because of the absence of information as authentic and as carefully checked, sifted and arranged as are these figures from the U. S. Census reports no profitable effort can now be made to measure the present effect of the war on these industries, to do so we must wait until such data are available.

ONE EFFECT OF THE WAR

Since the outbreak of the war, in addition to the many departments of the Federal Government which previously were engaged in applying and developing chemistry and our chemical industries for national benefit, there have been created a number of Federal agencies of national scope whose aim is, among others, to bring out promptly and efficiently the whole of our chemical science

¹ THIS JOURNAL, 9 (1916), 1050.

TABLE II—GROWTH OF AMERICAN CHEMICAL INDUSTRIES 1909 TO 1914

ITEM	ALL INDUSTRIES		CHEMICAL AND ALLIED PRODUCTS		PER CENT INCREASE 1914 OVER 1909		Per cent of the Whole in Chemicals & Allied Products		Per cent Increase in 1914 over 1909 of Per cent of Whole in Chemical & Allied Products in 1909	
	1909	1914	1909	1914	Index	Chemical & Allied Products	1909	1914		
1 No. of Establishments.....	268,491	275,791	2,140	2,461	3	15	0.79	0.89		13
2 No. of Wage Earners (Av.)...	6,615,046	7,036,337	70,426	86,788	6	23	1.06	1.23		16
3 Capital.....	\$18,428,269,706	\$22,790,979,937	\$483,729,410	\$722,989,000	4	49	2.62	3.17		21
4 Wages.....	3,427,047,884	4,078,332,433	38,658,201	53,021,000	9	37	1.13	1.30		15
5 Materials.....	12,142,790,878	14,368,088,831	258,115,975	340,218,000	18	32	2.13	2.37		11
6 Value of Products.....	20,672,051,870	26,246,434,724	425,084,540	547,802,000	17	29	2.06	2.09		1
7 Value Added by Manufacture (Item 6 less Item 5).....	8,530,261,000	9,878,345,893	166,968,565	206,864,000	16	24	1.96	2.10		7
Column.....	A	B	C	D	E	F	G	H		J
NOTE—Percentages given above were obtained as follows:										
$E = \frac{(B - A) \times 100}{A}$ $F = \frac{(D - C) \times 100}{C}$ $G = \frac{C \times 100}{A}$ $H = \frac{D \times 100}{B}$ $J = \frac{(H - G) \times 100}{G}$										

and industries for the good and the safety of the nation. Among these are the National Defense Council, the National Research Council, the Naval Consulting Board, the War Trade Board, the Tariff Commission and others all supplied with chemical advisers, while all the earlier Federal agencies have intensified their efforts and enlarged their scope. In addition thereto, members of the chemical faculties of almost every one of our universities, technical schools and colleges are working with governmental departments and with industrial enterprises in positions and on subjects and in a manner heretofore never known and the American chemist is to-day in better position than ever before to obtain sympathetic interest and action in any proposition he may have that looks toward national benefit. Most, if not all, of our states, and many of our cities, have similarly provided for intensified chemical aid. We have therefore, through this war, progressed along the line of cooperation between our governmental agencies, Federal, state and municipal, our universities and our industries to an extent almost inconceivable in its power for national welfare.

CHEMICAL SOCIETIES AND THE GOVERNMENT

On the other hand, all our chemical and allied associations and societies, whether business, scientific or technical in their aims and objects, have whole-heartedly placed all their resources and information at the disposal of our various governmental agencies; not the least among these societies is the AMERICAN CHEMICAL SOCIETY with a membership well beyond 10,000, meeting in 53 Local Sections throughout the country and conducting its affairs in 8 technical and similar Divisions. In order to assure as far as possible that in such a multitude of organizations there shall be a minimum of duplication of effort and lost motion the AMERICAN CHEMICAL SOCIETY has recently created a special committee to direct the participation of that Society in all matters of national scope and with this committee the expectation is that the President of the American Chemical Society will be in better position than otherwise to give prompt effect to any meritorious suggestions that may be made to him. There are therefore many avenues through which the individual American chemist can get national action on his suggestions. Other societies have made similar provision.

Thus it is clear that not only did we have in 1914 a wider public recognition and a greater confidence of capital in us than in 1909 and that both have grown greatly since the outbreak of the war but also that all our governmental and private agencies have since then immensely increased the points of contact and the avenues of communication between the chemist, the public and our governmental agencies. As individuals we also have added machinery in our hands wherewith to direct and shape the course of events and to prevent what might ultimately become, first, a chemical bureaucracy and finally a chemical autocracy in this country. We thus have each of us our clear and well-defined duties, responsibilities and opportunities.

PROMPTNESS AND EFFICIENCY

All of our efforts are, however, bound to be vitiated if we are not at all times mindful of the fact that unless we and each of us do our share promptly and efficiently that the whole national effort cannot fully succeed; the net result can hardly be better than its poorest component nor completed faster than its slowest part. Hence, our watchword should be at all times: "Accuracy, Completeness and Despatch." The student in the classroom is no more exempt from it than is the faculty-member, the corporation head or the government official; in that respect we are each and all of us in the very same boat.

Having thus briefly summarized the position of the chemist in the public mind, in the government's view, in the view of domestic capital and in our national industrial life and having described the avenues through which the chemist can work and the agencies upon which he can draw, what is he to do? What is the problem?

"OUR BIT"

For the period of the war all our national activities will be directed toward immediate national needs largely, with only relatively small attention to after-the-war matters, and for these sufficient directing machinery exists and it is merely a question of selecting the right means.

In the period after the war and in the rush and stress of rebuilding and making up for lost opportunities in the multitudinous directions offered, the chemist is likely to be lost sight of unless he systematically and continuously plans ahead and prepares accordingly. Broadly considered, our future activities can be classified as relating to:

- 1—Matters of national defense.
- 2—Development of our natural resources.
- 3—The highest national independence possible in chemicals and allied products.

KEEPING PUBLIC INTEREST ALIVE

In order to accomplish the above-mentioned ends we must make sure that we do not lose our place in public opinion nor the confidence of capital nor the helpful attitude of our governmental agencies, legislative as well as administrative. To retain our place in public opinion we must take the public into our confidence much more than we have heretofore, and in this delinquency we are not alone; other countries and other sciences have been afflicted with the same shortsightedness. We must inform the public of such of our problems as are of public bearing in language as free from technicalities as possible and as a very valuable aid in that direction we now have through the PRESS AND PUBLICITY COMMITTEE OF THE AMERICAN CHEMICAL SOCIETY the interested attention of a great many influential daily and other papers. Our scientific and technical societies everywhere should make an effort as does the AMERICAN CHEMICAL SOCIETY to have at least one meeting a year at which technical topics of interest to that ubiquitous and powerful person "the man-in-the-street"

TABLE III

		1914 RETURNS		INCREASE	
		Based on Classification of 1909	1914	Due to New Classification	
				Actual	Per cent
1	No. of Establishments.....	2,461	12,374	9,913	403
2	No. of Wage Earners (Av.).....	86,788	299,569	212,781	245
3	Capital.....	\$722,989,000	\$3,034,209,000	\$2,311,220,000	320
4	Wages.....	53,021,000	167,494,000	114,473,000	216
5	Cost of Materials.....	340,218,000	1,289,348,000	949,130,000	279
6	Value of Products.....	547,802,000	2,001,634,000	1,453,834,000	265
7	Value Added by Manufacture.....	206,864,000	712,286,000	505,422,000	244

are presented in such a way as to receive and to hold his attention, and a readable digest of those proceedings will no doubt be very welcome in the editorial offices of most newspapers; if they are not welcome then there must be something wrong with the meeting, with the digest or with both, and the only thing to do is to go at it again.

Now, telling a technical story in non-technical language or thought is no easy matter, but all of us should endeavor so to frame our technical stories that they are free from such matter because we can none of us tell when we may be in position to render good service by such a story told in such a way. Personally, I very much suspect that we have not really mastered a technical subject unless and until we can make it understood by the willing but non-technical "average man." That ability is indispensable in creating and in holding public interest in any technical subject like ours, and since public opinion is formed wherever there is a public it behooves all of us to cultivate that ability to our utmost since we can never know when or where we can make it tell. For example, at any one of the National Expositions of the Chemical Industries, which promise to become a fixture in New York City every September, large opportunities of legitimately and helpfully adding to the public understanding and appreciation of the chemist's efforts are offered and the cumulative effect of such additions, if sound and clearly made, cannot help but be advantageous. Each of us in our ordinary routine has almost daily opportunity to aid the public thought in these matters. It should be our aim to prevent recurrence of any public apathy like that in England towards the dangers of synthetic indigo to the British indigo growing interests or in our own country when we were appraised in 1912 of foreign advances in fixing atmospheric nitrogen. This is merely preventing the chemist from crawling into his shell, *i. e.*, keeping him a human.

RETAINING THE CONFIDENCE OF CAPITAL

We shall retain the confidence of capital so long as we do not indulge in any wild schemes, so long as we keep our promises, promise no more than we can do, expose and condemn hare-brained schemes, of which there are plenty, and in general behave in a level headed but optimistic and perhaps even enthusiastic manner. Most business ventures contain hazards but there are reasonable and unreasonable hazards, and we must exercise good judgment there; so long as we do that, capital, that is desirable capital, will not withdraw the confidence it has now given us. This is merely common sense behavior.

OUR GOVERNMENTAL AGENCIES

Having public opinion calling for a complete and independent domestic chemical industry and capital in good standing behind us, with a fair and frank approach to them, our standing with our various governmental agencies, legislative and administrative, ought not and will not be a matter of conjecture. This is merely civic candor.

These sound trite and sophomoric, and no doubt they are. I should not have made these statements if, as a matter of fact, it had not taken the colossal nightmare of a war to shake us all awake and to bring us to our senses. We thought the public to blame and the public and we were to blame. Perhaps both were right. However, if we as a body refrain from acting along these simple general lines we need not be surprised

if sooner or later the old conditions return. It is our job to make the public take an interest in us; that, to my mind, is one of these war-lessons we should never forget; we have paid too high a price ever to let it get away. As I see it, it is of the greatest importance that, even in our college days, we should lay the foundations for these view-points and these rules of conduct.

THE NEED OF A COMPREHENSIVE PLAN

But all this will be of no avail unless we show vision, imagination, foresight, initiative, enterprise and strength of purpose on our own account. We shall have to inform ourselves very thoroughly of the country's requirements of chemicals and the like in war and in peace as to quantities and values and their uses and also their modes of manufacture and their needful raw materials; further, of our suitable natural resources, their nature, extent and location whether of vegetable, animal or mineral origin. Then we must plan wisely for the most efficient development and set about it. Sounds simple, does it not? But it is one of the tallest orders 10,000 men ever had handed to them.

A start has been made in the Norton Dyestuff Census published a year ago by the Department of Commerce. That tells us about the amounts, values and kinds of coal-tar dyestuffs and puts us in the way of getting at their raw materials and their uses. The reasonable expectation is that, through the initiative of the AMERICAN CHEMICAL SOCIETY, in about six months or a year from now we shall have a printed compilation giving us the names, quantities and values of every chemical other than coal-tar dyes imported into the United States from any country during the fiscal year ending with June 30, 1914, the last peace year before the present war. Then comes the rest of it, the manufacturing methods, the needful raw materials and where they are located in this country and elsewhere, and in what industries these chemicals are used. Through the initiative of the AMERICAN CHEMICAL SOCIETY it is expected that this will also be completed within a reasonable additional time. After that, plans have to be made as to how, when and where these various things shall be made, and in deciding that there comes in the further question as to the importance of the individual chemicals to the nation's welfare, their arrangement in the order of their importance, and an efficient plan of making them at home. That is going to take some "midnight electricity."

GOVERNMENTAL HELP

Further, it is not inconceivable that some of these important things will not be made without added governmental help, as, for example, by means of tariff protection. This will not be as difficult as heretofore for the very important reason that both principal political parties, Republican and Democratic, have by enacting the present diversified tariff emphatically affirmed, sweeping, and let us hope lasting, changes in their heretofore views of tariff legislation. The Republicans have in the past refused to help themselves because they did not employ enough labor to become their product were raw materials, for many industries that stood well in the eyes of that party largely because they did employ much labor. Now the Republicans admit that there are industries which are "key industries" because their products are "raw materials" for many industries and hence they should be made in the country and protected by tariff if need be. The Democrats, by leaving for, I believe, the first time, a tariff unscathed for the purpose of creating an industry in this country.

and necessarily thus potentially depriving the U. S. Treasury of a corresponding amount of revenue have also endorsed the "key industry" view-point.

But right in this comparative ease is where difficulties are going to come for us chemists. "Key-industries" is a new expression; just exactly and precisely where it begins and ends, no one yet knows. Merely because the Republicans and the Democrats have agreed that because coal-tar dyes constitute a "key-industry" and hence should be protected is a very long way from saying that they have agreed that every "key-industry" should be so protected, but it is a very tempting inference. It would be a peculiar kind of a product, chemical or otherwise, for which a more or less plausible argument of "key industry" could not be constructed. Unless we are very cautious we may find this "key-industry" notion a very unwholesome and treacherous thing. In presenting to Congress or to the Tariff Commission the "key-industry" claims of any particular thing, we shall have to be very circumspect and very frank and straightforward. I very much suspect that there may be times when this will be a severe test of our civic candor. Whenever we are sure that any such product really, or fairly so, is a "key-industry" in the sense of coal-tar dyes and in the manner that the 64th Congress viewed them then we must have sufficient strength of purpose to keep at Congress or the Tariff Commission or at both until they "see the light," for surely that is what public opinion now wants. When we believe that the country's welfare, as viewed by that public opinion, demands our industry and there is opposition to it, we must seek out that opposition and bring it down; that is not merely our privilege, it is our civic and professional duty.

THINKING IN TERMS OF THE NATION

In this same connection we shall all have to learn to think in terms of the Nation and have the map of the world in our minds as we study our chemistry and apply it to our industries. In order to do that our publications will have to make a change. None of our chemical journals systematically and in a form that lends itself to preservation, presents its readers with world-information, both detail and general, at any stated periods or in any correlated or coördinated way. In that respect we have much to learn from foreign chemical journals and particularly the German journals which, while they did it far better than others, still left a very great deal to be desired. Then, after our journals have made such a change you and I and all the rest of us will have to learn to read those statements. They are dry; but there is no help for it. It is a new language and a new job, but we have simply got to master it. Perhaps the AMERICAN CHEMICAL SOCIETY may be able to find a way to sugar-coat that pill and if it does, more of us may be induced to take it.

The Superintendent of Documents, Government Printing Office, Washington, D. C., will supply for cash or money order (stamps will not be received) any of the Government publications dealing with our domestic and foreign commerce. For domestic production the 714-page cloth-bound publication, entitled "Abstract of the Census of Manufactures—1914" (price, 65 cents); for our foreign import business, the 90-page paper-bound publication, known as "Summary Table No. 9 of the Annual Report on Commerce and Navigation" (15 cents) and for all the U. S. activities and as a whole the 749-page paper-bound publication entitled "Statistical Abstract of the United States" (50 cents) make a good starting point, not only for individual study in college or after, but for the majority of our chemical publications as well. If then we apply only a very small fraction of the industry we usually put on the statistics of our baseball players we ought very soon to show a marked increase in our knowledge and appreciation of the place chemical industry holds in the business and economic affairs of our Nation and of the world. All our publications must more systematically than heretofore help to disseminate in coördinated and more readily appreciated and preserved

form the vast amount of fundamental and valuable information collected by our Government. The Government cannot do it all; we as individuals have a share to perform.

OUR EDUCATIONAL INSTITUTIONS

But even with all this our task is not yet done. All these efforts will be of short life, from the point of view of the Nation, if we overlook or fail to encourage the science of chemistry in its purest forms as well as in its applied forms at our universities, colleges, and technical schools or if we overlook keeping them in the very forefront of educational efficiency. We must test and examine every scientific advance made anywhere as to its potential value for, or harm to, this country and act accordingly. It goes without saying that our chemical industries must each and all have their own research laboratories, whether individually or in groups, and these must be as well equipped and manned as any for it is not inconceivable that publication of research results in foreign countries hereafter may not be as unrestricted as it was before the war. Chemical fellowships like those of the Chemists' Club will, no doubt, be a welcome help in this direction.

OUR GOVERNMENT OFFICIALS

Nor would we be fully utilizing our opportunities of aid and help were we to overlook the various Federal governmental departments or committees of the AMERICAN CHEMICAL SOCIETY or other chemical societies that coöperate with them. Our Federal officials are more than ready at all times to help the Nation and if they have not in times past done all that we now think they should have done the blame for that rests squarely on our own shoulders—we simply have not told them, and perhaps have not even tried to tell them, how they could help or where and in what way we needed help in any such fashion as to make help on their part practical or practicable.

Successful chemical industry calls for dependable labor and therefore labor laws, workmen's compensation acts and the like will call for a good deal of our attention. Should we also have an eye on export business additional competent chemical members of our foreign trade and consular service will also be required.

COÖPERATION THE ONLY WAY

From this, of necessity sketchy and fragmentary outline, it is obvious that the American chemist has and will have a multitude of new things to engage his attention and that the only practicable way of handling them is through coöperation. Unless all signs fail there will be more of national coöperative effort throughout the world than ever before and we must shape our course accordingly. As a first-step student chemical societies like this one at "Tech" are to be highly commended and supported either as independent organizations or as sections of the AMERICAN CHEMICAL SOCIETY which has done so much to coördinate the efforts of American chemists in so many different ways and which is the best organized and the largest chemical society in the world. The trial now being made by the section of the AMERICAN CHEMICAL SOCIETY at Buffalo, New York, of affiliating and meeting with other local technical societies is a step forward and in the right direction. We should also seek out opportunities for coöperative effort with our educational and governmental institutions as well as with strictly commercial organizations such as Boards of Trade, Chambers of Commerce, Merchants' Associations, and the like, of local, state, national and of international scope. We must widen our horizon in every direction and we can do that only through coöperative effort, intelligent and persistent.

"THERE ARE OTHERS"

It must not be forgotten that the chemist is not the only one who was shown to be behindhand as a result of this war. A very good index of that is supplied by a recent and dependable statement that of the some 650 British enemy-owned patents under which license to operate had been granted British manufacturers under the British Trading-with-the-Enemy Act, only "some

scores" applied to the dyeing industry, while the remainder dealt with the following twenty arts, namely: leather substitutes; sewing machines for boots, etc.; wood impregnation; taximeters; turbine compressors and pumps; explosive engines; magnetic separators; treatment of waste paper and fibrous materials; reduction of ores; aluminum alloys; speed indicators; electric ignition apparatus; incandescent gas lamps; elastic bandages; embroidering machines; calculating machines; electricity meters; talking machines; internal combustion engines and printing machines. Quite a formidable list. It will be most instructive similarly to follow the course of events under our own recently enacted Trading-with-the-Enemy Law.

PATENTS AND INVENTIONS

The proper lesson for us to learn from this seems to me to be that whenever a foreigner patents anything anywhere we should really invent and make something better or just as good ourselves. It may, and no doubt will be expensive, but will it be more expensive to the Nation than our present situation has turned out to be? I say decidedly not. And this applies to others besides us chemists. It will certainly be better than tinkering with our patent laws. The proper answer to an invention is another invention and not a hamstringing or a boomeranging change in our patent laws.

CONCLUSION

This, then, presents, in rough outline, as I at present see it, our future and the work it holds for us; our work may fairly be said to be stupendous and it is made so wholly by the national complacency, not to say indifference, of our entire country's past. We must all make up for lost time and for lost opportunity. With an enlightened public opinion and a truly national spirit in our Federal legislation, the American chemist can safely and confidently be depended upon to do his full share, and more, toward making this country as independent of any other nation on earth as it is possible to be, and toward making our democratic government lastingly as efficient and as far-sighted as any autocratic government ever dreamed of being.

25 BROAD STREET
NEW YORK CITY

MERCHANDISE CONTROL LABORATORIES

By ELLWOOD HENDRICK

Received September 5, 1917

An episode in the history of the Bureau of Chemistry of the U. S. Department of Agriculture may throw a little light on the progress and workings of private laboratories in the few mercantile concerns that have adopted chemical control.

The Pure Food Law was passed and it was necessary to have means to enforce it. The law and the courts were in existence but other machinery was needed. In the Bureau of Chemistry more inspectors were appointed, happily under civil service rules, for at the first examination for inspectors only 16 out of 1400 applicants passed. They then went about collecting samples and brought them into the department for analysis. They looked for breaches of the law and they found them, found them with increasing facility as they developed the art of search. Convictions were frequent. The question then arose whether increasing the number of convictions was the best and most useful work that the Bureau could do. The conclusion was reached that while this was a necessary part it was not the whole duty of the Department of Chemistry in the interest of general welfare. Various industries were studied from the standpoint of chemical control and producers of foods were informed how to avoid error and how to get the best results. Vigilant inspection makes adulteration dangerous while chemical supervision and aid improves the product. The government is not the enemy of honest producers but rather their friend. Chemical control goes far beyond police duty.

Now the introduction of chemical aid in mercantile establishments seems to develop in a similar manner as time and experience enrich their laboratory records. Foods and drugs are standardized by law; they are already under chemical control and we shall not even discuss the pharmaceutical trade for the obvious reason that it is already established in chemical technology. The same holds good in regard to the preparation and handling of meats, the great packing houses being models of efficiency in the administration of materials. The fisheries are in sore need of chemistry but the possibilities in the utilization of these products would not be within the scope of an article on merchandising.

In order to determine what advances have been made in this respect a number of large, progressive houses were visited. Of these several were entirely willing to display their laboratories and methods in the interest of science, but insisted that no special praise be accorded them for their accomplishments on the ground that it would smack of gratuitous advertising. I shall therefore make the record as impersonal as possible.

Foods, drugs and insecticides are under government supervision while most other merchandise is not, but as we proceed, I think it will be borne out that wherever efficient chemical control is instituted, there it stays, law or no law; and that those who maintain it would not do without it. A guaranty is a good thing in its way; it is a kind of free insurance policy thrown in with the goods. What is wanted of it is that it shall be passive, for, as a general rule, the better a guaranty is the less frequently is it brought into action. It is always an endorsement and therefore a liability. Chemical control on the other hand determines the status of the goods warranted; it fixes credit by the establishment of fact and it is therefore an asset.

A leading wholesale grocery house was good enough to give me the following outline of the functions of their laboratory, which speaks for itself:

1—Without a competently conducted laboratory we should not of our own knowledge know what we are selling.

2—Our laboratory is maintained for the protection of our customers, and in order to keep our qualities uniform.

3—Raw materials differ greatly in percentages of essential parts, so that to buy intelligently the make-up of each lot must be studied.

4—The greatest function of the laboratory is to safeguard purity and wholesomeness. The enforcement of Federal and State Food Laws must necessarily be based upon standards and these cannot but be of a technical nature. We must be certain that all food products meet legal requirements and thus conform with the iron-clad guaranty of the house that all its goods comply with all Food Laws. With a laboratory any contaminations are discovered.

5—The laboratory does creative work. New food products are constantly sought and many good ones are discovered. These are both simple and complex. In the latter class various food substances are mixed together. During the past three years several very successful combinations have been worked out.

6—The laboratory maintains records of all our drug supplies. The value of this is shown by a recent instance. A physician in a small town purchased of a customer several half pint bottles of Castor Oil. He complained that it was not U. S. P. From the markings on the bottle labels the lot was traced back to the identical original producer but which there was complete analysis. This analysis was submitted to the physician with the assurance that he also analyze the oil, and make a comparison. The result was a complete vindication of the producer.

7—Another instance showing the value of the laboratory is the case of a customer who claimed to be able to produce Pure Black Pepper at a considerably lower price than we were quoting. A sample was measured and analyzed and the comparison made to count in large part of Pure Pepper instead of Pure Mustard. On our laboratory report the business of this customer was retained.

The creative or synthetic work calls for various degrees of scientific application. To mix up fruits and spices into a sweet meat is achieved that concerns a successful only may be more the job of a candy man than of a chemist, but you never can

tell. The line is hard to draw. It requires a chemist to prepare a permanent mayonnaise dressing in which the oil does not separate out, of which great quantities are now sold for salads as well as a substitute for butter for making sandwiches and the like in hotels and restaurants. Thirty-five cents worth of this mayonnaise has the spreading value of seventy cents worth of butter.

ADVANTAGES OF CHEMICAL CONTROL

Chemical control saves the day occasionally. A very large order for vanilla powder was given by a consumer who buys on specification and analyzes the product. For good measure and safety the goods were made up a little above specification in vanilla, but the whole shipment was declined on the ground that it was not up to standard. Details were not available except that analysis showed that the powder failed to reach specifications, but the refusal was very clear. A visit by the chemist to the purchaser's chemist and investigation into his methods brought out the fact that he had made the test for sucrose and let it go at that. The discovery that the vanilla content was above specification made the delivery acceptable.

Maple syrup, jams, preserves, olive oil and many other goods require constant supervision to substantiate guarantees and make them not only acceptable to the purchaser but profitable to the seller. One firm is planning to print the food value in calories on every package.

A good control laboratory is usually available for consultation to all department heads in addition to routine work in testing those classes of merchandise that may be accidentally or intentionally adulterated. To a concern that does a jobbing business, chemical control is of signal value.

Most manufacturers are conscientious and do the best they can, but the presence of the laboratory is like the policeman on the block; the occasional crook is more likely to try a house in some other locality than where the policeman is stationed.

A first-class house is very jealous of its good name and would rather spend a large sum than have its goods confiscated for deficiency in standard. The value of the laboratory comes in time and again to provide for the avoidance of this. For instance, whether an added chemical preservative is deleterious or not is not the question; if the label does not state that a parcel of goods contains it, it must not be present. In a certain state not long ago the charge was made of the presence of borax in mince meat and under the rigid control exercised it was known that none had gone in. The Commissioner held to his point. The analysis was followed up and the trace of borax proved, but the cause was found to be the raisins which were grown in an alkali soil in California, and such raisins are not taboo. The house demonstrated that borax had not been used as a preservative and avoided the penalty.

A good laboratory also works the other way. Last Spring the demand for macaroni was not only high but rampant. The market was bare. A manufacturer offered some for sale that had just the color of durum wheat, but alas, analysis showed coloring matter that does not grow in that cereal. The manufacturer knew better, and, being an emotional man, he offered to jump out of a seventh story window if the presence of foreign coloring matter could be proved to him. He was urged to spare his life while this factory was investigated. His foreman finally acknowledged that he had "just tried out a little color" on that particular batch.

Maple sugar is a stormy petrel in groceries but it has greatly improved since the Pure Food Law went into effect. The ash is characteristic, the acid is malic and the base is lime, but it can be imitated through the use of sucrose, glucose, burnt corn cobs and commercial maple flavoring extract. Grape juice calls for testing for added sucrose, glucose, preservatives and water. A few pails of water in a barrel of grape juice is easy money.

It has been found profitable to keep very complete records of analyses to meet a certain shortening of the memory from which some retailers occasionally suffer, when, under attacks of absent-mindedness, unsatisfactory goods are returned that were procured from other sources.

While the standard of 25,000,000 per cc. has been fixed as the bacterial count for tomato products by the Department of Agriculture, the ordinances stop here. It seemed wise to one organization in particular to get ahead of the game and apply laboratory cleanliness to their own manufacture of preserves, jams and jellies. Few manufacturers are clean in the laboratory sense. A good kitchen standard is as high as most of them reach, and spores multiply. The result of this forward step has been salutary. The factory staff now knows and understands moulds and ferments as it never did before; the quality of the goods has markedly improved and certain economies have been established. Figs, for instance, ferment so easily and persistently that large stocks of this raw fruit are never carried. Fruits are generally bought in season and placed in cold storage, but the demand can never be gauged with sufficient accuracy to determine whether the stock will last through the season or be used up by Christmas. It has been observed also that fruits change as the season progresses, even in cold storage, which has an important bearing on the making of jellies. A jelly that grows fluid is sure to be returned, whereas if it is too hard the housewife is very likely to refuse it on the ground that it is made with gelatin even though it does not contain gelatin. Control of this factor based on research enables jellies to be made and shipped within 24 hours and by freight at that, with all the rough handling that goes with it. The absolute control of jellies is thus an accomplished fact.

Research plays an important part in meeting legislative whimsies as well as in matters of general importance. For instance, when bone-dry laws came into force, soft drinks were suspect, being made with alcoholic flavors. In the present temper of the public mind one molecule of alcohol will almost ring the alarm. The 0.25 per cent content of alcohol in ginger ale might have been a tragedy. So the whole list from sarsaparilla to harvest-pop has had to be worked out to stand bone-dry laws.

From the foregoing it will be observed that the wholesale grocery trade is already acquainted with chemical control, though the practice is by no means general. Many large houses depend upon occasional analyses or the guarantees of manufacturers. But of those with which I am acquainted and which have established laboratories with competent men in them, not one could be induced to do without such laboratories. Let us note, then, that there is legal protection to the purchaser of foods and drugs, that the Pure Food Law makes it difficult for manufacturers to escape its searchings and that under it, dealers have recourse against manufacturers; nevertheless dealers of the first rank in foods and drugs find it profitable to maintain chemical control. Observe also, however, that other merchandise knows no law and everything goes. The manufacturer produces and "finishes" his wares, an agent sells them, a wholesaler buys them, a jobber distributes them and a retailer guarantees them. In hard, soft, wet and dry goods, trade is pretty wild and the real nature of the materials is known only when the articles are worn out or used up instead of when it should be known, at the time of purchase. Here is where chemical control comes in and it is a new thing, far from its complete development, but it bids fair to call for a large number of chemists as soon as standards are established. Until then, any chemist who overguesses his own knowledge in such an undertaking is likely to do more harm than a hundred good men can repair.

The only general trade into which chemical control appears to have entered is that of certain mail order houses and these have indeed blazed the trail in scientific merchandizing. Mail order houses claim to sell to the consumer at approximately

jobbers' prices plus transportation and the free return of unsatisfactory goods is a necessary condition of successful merchandizing by mail. If a customer returns merchandise the transaction is more expensive to a mail order house than an unsuccessful sale made over the counter is to a local retailer. If a mail order customer is dissatisfied he is likely to remain so because he is too far away to be jollied around. It is therefore of very great importance that dealers who sell by catalogue be able to make descriptions of their wares that shall be correct.

OPERATION OF MAIL ORDER LABORATORIES

The arrangement of a laboratory for general merchandise control would be hard to determine without specifications, but the following division of the work is employed in the laboratory of a house that sells nearly everything:

- I—Textiles of all kinds, Furs, Paper, Dyes.
- II—Foods, Drugs, Insecticides, Cosmetics, Detergents.
- III—Feeds, Fertilizer Materials.
- IV—Iron and Steel, Non-ferrous Metals and Alloys, Physical Testing and Metallography.
- V—Oils, Paints, Varnishes, Japans, Asphalts.
- VI—Miscellaneous Products (including Rubber, Leather, Wood, Earthenware, Glue, etc.) and Experimental.

Another arrangement that is in successful operation with staff consisting of a chief chemist and a corps of assistants is:

- I—Textiles.
- II—Foods.
- III—Drugs.
- IV—Metals.
- V—General (including paper, leather, shoes, etc.).

Physical tests are very important in determining the endurance of mechanical devices, and apparatus are required for testing the hardness, elasticity, and tensile, transverse and torsional strengths of materials. The range of materials that come under observation is very wide and extends from cotton tape to canvas belting, from thread to hemp rope and from piano wire to steel cable.

Of special value is metallographical and metallurgical control in relation to agricultural and mechanical implements and tools. Steel is chemically tested, its tensile strength and bending strain taken and its true nature determined under the microscope. Or, specifications are made for the various parts of tools and machinery to ensure the greatest measure of strength and endurance in accordance with customs in vogue among progressive manufacturers.

Food control we have already considered. Mail order houses are large distributors of foods and the operation of their laboratories in this connection is similar to that of wholesale grocers.

Rubber goods, more particularly boots and overshoes, are usually appraised as to quality by the price charged. This is not a satisfactory practice. From a chemical standpoint the problem is not simple save to the man with experience, and yet it is very important for the seller to know whether a pair of rubbers that he offers contain a sufficient quantity of good gum or is filled in, under a finished exterior, with an excess of substitutes. The buyer has an interest in this too, but usually neither of them knows. The advantage of this general control to customers is very marked.

Specifications for many kinds of goods are required of general merchandise control laboratories. An important item, for instance, is paints, because the average house owner is more particular about the enduring qualities of the dress for his home and barn than he is of almost any other purchase. His grief is said to be more poignant and his lamentations more piteous when he has any cause to complain. And no paint is everlasting, although sometimes this seems expected.

TEXTILE FABRICS NEED LABORATORY CONTROL

A subject of vast importance is that of textile fabrics. Cloth is one of those half-way things: its chemical aspect is important and so is its physical nature and again, from another standpoint, it travels on its looks. The chief chemist of a great establishment told me that the first thing he did on entering upon his engagement was to look out for weak spots as, for instance, in the men's clothing department, where goods supposed to be all wool were sometimes not. His first professional interview with a woolen goods buyer resulted in a resolution on the part of that gentleman never to travel without a microscope again. I can do no better than quote liberally from a paper on "Laboratory Control of Textile Merchandise," read by Mr. D. M. Nelson before the Chicago Section of the American Chemical Society.

"In making a selection between a number of fabrics for sale, the buyer for a distributing house is guided chiefly by appearance or price. Under appearance he considers the pattern, color, weave and finish and the clearness or brightness of the sample, as well as the firmness of the weave, the draping qualities and the softness of the feel. The determination of these characteristics can be made only by the experienced buyer, who has in mind the customer. Usually the customer buys for appearance alone, having little knowledge of the composition of the stuff and relying principally on his confidence in the retailer or manufacturer for the service he expects. The responsibility of the distributor ceases only when the customer gets the service he has a right to expect, and here the laboratory inspection may be a large factor in supplementing the buyer's off-hand examination. The buyer, through long experience, is able to judge with surprising accuracy, but it is possible to fool the most experienced in this respect."

The accuracy of the buyer is surprising because he guesses; if he were a chemist and his guess as to the content were taken as an analysis he would not be praised at all.

The situation in regard to textiles is probably less orderly and less reliable than anything else that is sold. There are no standards. A thing may be all wool and yet be mostly felted dust, or sold as wool and be 2 to 100 per cent cotton. "Manufacturing routine in the textile industry," said Mr. Nelson, "is largely carried on by rule of thumb and is conducted with the idea of giving the fabric as good an appearance and as good handle as possible, even at the expense of quality if need be." We must not blame the manufacturer for this. The trouble is with the rest of us who are so dead set after style that we will have none of his goods unless he gives them an imitation million dollar look. On the other hand, "manufacturers are able by expert finishing to disguise the cheaper fibres and make very successful imitations of more expensive fabrics that almost defy detection in an off-hand examination." How true this is!

A chemist in one of the laboratories visited observed that mercerized cotton is strengthened by the process although the primary demand for it is because of its look, that is because of its lustre and its smoothness. "Now mercerization may be cleverly imitated by calendering, but the first washing will destroy the lustre produced by the process whereas the true mercerized cotton will retain it. The same holds good for imitation in regard to alkali content. Unwashed alkali has a far better lustre and sheen after washing than has weighted alkali. Appraisers, which are usually of primary value to textile trade, do not discover the laboratory as they frequently do deceive the senses."

These laboratory reports on the nature and content of textile fabrics mark a distinct step in advance in merchandising. I know of no dry goods house or department store that maintains this control although I speak with very slight knowledge of their practices. In preliminary correspondence in regard to this article one firm reported that they are now opening a laboratory

but that it was not yet in working order. Two great mail order houses at least have established themselves in advance of the times in this respect and they certainly have found it profitable. On the basis of an off-hand examination, no buyer alive can be sure of the precise content of every piece of goods. His guess is indefinite. The laboratory report is definite. On the other hand, without more experience than is available today, the laboratory report will not take the place of knowledge and experience as a complete guide to wearing qualities. The merchant with a good buyer and no laboratory control is better off than the one with a dunderhead for a buyer and a good laboratory. The two must work together, as men of successful experience, insist and repeat and then insist again. The use to which goods are to be put is another factor which must be known, and here again experience is needed until standards are established. It is doubtful if all the Nobel Prize chemists together could pass satisfactory judgment on the wearing requirements of women's dress goods.

An old established house dealing in various kinds of merchandise whether in wholesale, retail or mail order trade will naturally go right on whether there is a laboratory upstairs or not. Buyers have grown up in the business and they do not care to have somebody who is not as well informed as they are, criticize their transactions. But the expert buyer cannot go below the surface of things. Of values, of demand and selling qualities, he knows a hundredfold more than the chemist; but the chemist can impart to him information of the greatest value, and surprise him time and again.

Right here we meet a psychological turn that has nothing whatever to do with chemistry, except that it has the power to make chemical control possible or to kill it. If the buyers come to the chemist asking information all is well and good; together they will know far more than either would know alone. If the chemist criticizes the buyers and condemns their purchases against their own judgment, there will be trouble in the air and chemical control of that establishment is likely to enter into eclipse. I have yet to meet a successful chemist in a mercantile establishment who does not insist that he must work in harmony with buyers so that the wisdom of both may be available to the house.

Another point that needs emphasis is the possible development of a practice that is certain to end in failure: we refer to over-advertising or false advertising of the laboratory control of merchandise. It cannot be too strongly stated that the art of laboratory control is not far enough advanced to be exploited in the manner customary among many writers of advertisements. Its purpose is to protect the merchant, to substantiate his guaranty and to bring his customer into more intimate understanding of the wares sold, but it is of no value whatever in aiding the sale of defective merchandise.

To return to Mr. Nelson's paper, he proposes a more elaborate examination than has been reached yet for textiles, and with definite standards fixed for various purposes the ability to purchase according to quality should be greatly augmented.

I—MICROSCOPIC

- 1 IDENTITY OF FIBERS
 - a*—Length of fibres
- 2 QUALITY OF STOCK
 - b*—Diameter of fibres
 - c*—Uniformity of fibres

II—CHEMICAL

- 1 PERCENTAGE COMPOSITION
 - a*—Fibre composition
 - b*—Weighting or sizing
- FASTNESS OF DYESTUFF
 - a*—Washing
 - b*—Light
 - c*—Rubbing
 - d*—Special uses

III—PHYSICAL

- 1 BREAKING STRENGTH AND ELONGATION
- 2—WEIGHT PER YARD OF A SPECIFIED WIDTH
- 3—PICKS AND ENDS PER INCH
- 4—YARN STRUCTURE
 - a*—Single or double
 - b*—Amount and character of twist
- 5—COUNT OR SIZE OF YARN
- 6—SHRINKAGE IN SPONGING OR WASHING

In made-up goods it is sometimes difficult to distinguish exact qualities of material, as, for instance, in wool, to know quantitatively the fleece, pulled wool or shoddy in the stock. The composition of a fabric as to different kinds of fibre is in most cases easily determined. Cotton and wool are quickly separated by boiling in a 5 per cent sodium hydroxide solution. A simple way to determine silk is by ravelling out and weighing.

In fastness of dyestuffs again, the use of the fabric determines the quality of fastness needed. In millinery goods, for instance, it is especially fastness to light that is desired while rubbing and washing tests are negligible. In all goods the nature of the test is indicated by their prospective uses.

Breaking strength and elongation are factors that throw most light on the question of durability, although here again we lack standards. The results are comparative rather than absolute. But minimum breaking strengths can be established which will serve to draw the line between what is desirable and what is not. The test is of special value in checking deliveries from factories because a decrease in strength indicates a lower quality of stock or less care in manufacture. The moisture content of the sample plays a very important role, but 40 per cent increase in relative humidity will increase the tensile strength of cotton yarns 16 per cent and decrease that of woolen yarns about 18 per cent. More research on this subject is needed. Mr. Nelson noted two general methods of controlling the moisture factor: to break the sample bone dry and to break it in a standard atmosphere of constant humidity and temperature; the latter more nearly approximates usual conditions, but is more difficult to control. The type of apparatus, the speed of moving jaws and the length of test sample between jaws are all factors that affect the result of the test.

In conversation with Mr. Yundt, he noted the special value of the thread count in silk or linen dress goods in determining quality. The only method of determining shoddy content is by microscopic examination and the nearest one can conveniently come is an estimate. Dye tests are for fastness to light, wash and spotting from mud and rain. Exposure is the best with regard to light but the peroxide test will give an indication in a hurry. The mud test Mr. Yundt makes with lime water and the wash test with soap. Silks are tested for weighting as well as for quality and whether natural or artificial. The artificial fabric, generally speaking, breaks more easily than the natural product.

In this connection the value of the microscope and a trained eye is of leading importance. Indeed, although the man in the laboratory must have a sound chemical training to pass on textile goods, he must also have training as a textile microscopist. Thus he can gain rapid and wide information from a small clipping from the seam of a suit or a shirt. Recovered wool may show fraying ends, possibly indicative of brittleness due to improper carbonization or more likely to the tearing apart of the fibres in milled goods. Pulled wool will show the roots of the fibres in raw stock. In manufacturing the roots are usually torn off. Lamb's wool shows the natural end, which is easily distinguishable from the wool of a sheep that has been sheared.

It occurs with increasing frequency that jobbers take the reports of these mail order house laboratories when they have earnest and serious questions to ask of manufacturers. The case was related of a linen manufacturer who bought his yarns and guaranteed his products to be all linen. He was an honest man

and a good manufacturer, nevertheless his product was half cotton. He couldn't and wouldn't believe it until he saw the test, and even then he could hardly believe his own eyes. It proved that his yarn, that he bought for all linen, was only half of flaxen origin. The rest was cotton. He had been buying it and guaranteeing it for years.

In the extensions under way in the laboratories of the mail order houses examined, provision is made for the separation of the respective departments, with a view to greater efficiency. Under pressure of work a man from one department may be assigned to work in another but the chief chemists are unanimous in favor of this separation and are resolved upon it.

The proof of the pudding is in the eating. A question directed to any one of the establishments visited as to the value of chemical control would bring but one kind of reply. "The trouble," as one chemist says, speaking of the use of the laboratory by the many departments of the concern with which he is connected, "is to hold them back." Chemical and technical control do not come ready made. But their value is beyond measuring. It discounts the trademark premium on goods in buying. It strengthens and augments guaranties, because, as we have already intimated, if it is known that a merchant knows what he is selling, his guaranty is better than if it is merely an assurance of "your money back if dissatisfied." Usually, when one makes a purchase, he does not want his money back but he does want to be satisfied.

SUCCESS OF CONTROL LABORATORIES NOW ESTABLISHED

In proof of the value of a well-conducted laboratory by the right man, I am permitted to go behind the scenes a little and quote parts of a letter written by a general manager to another officer of the same company in regard to a proposal that their laboratory facilities be increased and extended.

"I am very much impressed with the good that has come and can come from the fact that we have a complete laboratory and our merchandise gets a thorough examination from a scientific standpoint before we make any claim in our catalogue as to its qualifications. There is no question in my mind that in time there will be legislation on textile merchandise somewhat similar to the Pure Food Laws, making it necessary that we state of every article whether it be made from cotton, wool, etc., and if made from a mixture of cotton and wool, just how much cotton and how much wool it contains. It is a known fact that the statement that an article is pure wool has been much abused, and I am sure it is only a question of time when legislation of a national nature will control this condition.

"I believe we should anticipate this; the nature of our business should compel us to do so. I positively believe we should not put any article in our catalogue, no matter what its nature, without having it go through our laboratory to be passed on scientifically; in other words, we should not take the word of salesmen or manufacturers, but should obtain an absolute knowledge of it ourselves before making any claims.

"I further believe you cannot put a dollar and cent value on the good that will result from this work; it is work along lines so good and wholesome that it cannot help but make our future assured."

ACKNOWLEDGMENT

In conclusion, and despite the stipulation of certain houses visited that this article be prepared in the interest of chemistry and that it in no wise partake of the nature of that quality of publicity which is akin to advertising, candor and chemical conscience require that I make the following acknowledgment.

I am indebted to Messrs. Austin, Nichols & Co., of New York, and Messrs. Sears, Roebuck & Co., Montgomery Ward & Co., and Sprague Warner & Co., of Chicago (in the order visited), and to their respective chief chemists, Dr. J. A. Riche, Messrs. A. V. H. More, C. R. Yumbt, and Dr. Paul D. Potter for a great deal of the information above set forth.

THE PRODUCTION OF SCIENTIFIC KNOWLEDGE¹

By C. E. KENNETH MEES

The great value of scientific research both to the industries and to the nations at large is now generally recognized throughout the world and in the last few years there has been a remarkable increase in the efforts made to stimulate the production of scientific knowledge. In 1914 the American Association for the Advancement of Science appointed a Committee of One Hundred to inquire into the steps which should be taken for the increase of scientific research in the United States and the work of this committee has been continued and expanded by the National Research Council. Among the European nations there is a great awakening to the national value of scientific research. The British government has appointed a Department of the Privy Council to deal with the subject, while it is announced that in France a new national laboratory on a very large scale has been projected. In Australia the government has appointed a special department to consider what steps should be taken for the organization and development of research work in the Commonwealth, and in Canada the matter has been the subject of government inquiry and solicitude.

The increase of scientific knowledge can be divided into three steps:

I—The production of new knowledge by means of laboratory research.

II—The publication of this knowledge in the form of papers and abstracts of papers.

III—The digestion of the new knowledge and its absorption into the general mass of information by critical comparison with other experiments on the same or similar subjects.

The whole process, in fact, may be likened to the process of thought. We have first the perception by means of the senses. The precept is then stored in the memory and in the mind is compared with other previously stored precepts, and finally forms with them a conception.

I desire in this paper to consider the methods by which these three sections of the production of knowledge may be carried on, to suggest an arrangement of laboratories to produce experimental results dealing with any branch of science, then to consider how the knowledge so obtained may best be stored and classified and finally the methods to be employed to make the results of scientific research available for application.

1.—RESEARCH WORK

The agencies engaged in scientific research are of several kinds. The traditional home of research work is in the university, and the bulk of the scientific production of the world comes from institutions connected with teaching. The industries are more and more supporting research laboratories, a large number of which contribute to the general fund of scientific knowledge by publishing the results which they obtain, and some of which are engaged upon purely scientific work not of menial order. Consulting and technical laboratories engaged in industrial work make frequent contributions to science, and there are some very important laboratories engaged in pure research work which are supported by philanthropic foundations.

The classification of research laboratories is not altogether an easy task. They may obviously be classified according to the source of the funds which support them; if, we may classify them as university laboratories, industrial laboratories, government laboratories, institution laboratories, and so on, but if we look at them simply as the result of the research undertaken, this does not seem to be altogether a based classification since there is little distinction between the work done in some university laboratories and in some industrial laboratories, and the work of the government and institution laboratories, each overlap that of the two former classes.

The University of Pittsburgh, for instance, has an industrial

¹ Address before the Research Council of that Association, at America, October 23, 1915.

laboratory where definitely technical problems are dealt with. The research work on photometry done at Nela Park and at Cornell University would seem to be similar in kind, and work on physical chemistry or on the structure of chemical compounds is of the same type, requires the same class of workers, and produces the same results, whether it be done in a university, in a laboratory of the Carnegie Institution or in such an industrial laboratory as that of the General Electric Company. It is equally difficult to classify laboratories according to the purpose for which researches are avowedly carried on. Most university laboratories are willing to undertake work of industrial value, and, indeed, some specialize in such problems; while many industrial laboratories are quite willing to carry out a research of purely academic and theoretical interest provided the problems involved bear a relation to the general work of the laboratory.

A useful classification of laboratories can, however, be obtained if we consider whether the problems investigated in a laboratory are all connected with one common subject or whether the problems are of many kinds, having no connecting bond of interest.

problems carried on in the same laboratory are not necessarily related in any way whatever.

The greater number of university and industrial laboratories are necessarily of this type. It would be a disadvantage for a university laboratory, whose primary business is training students, to be too narrowly specialized. Specialized university laboratories are only desirable in the case of post-graduate students, and it would be very inadvisable to allow the laboratories responsible for the general training of scientific men to specialize in one branch of science, since as a result the students would acquire a proper acquaintance with only a limited portion of their subject.

Industrial laboratories, on the other hand, must necessarily be prepared to deal with any problems presented by the works, and as these will be of all kinds, covering generally the whole field of physics, chemistry and engineering, it is impossible for the usual works laboratory to specialize except in so far as it deals with the works processes themselves.

In the "convergent" laboratories, however, although the

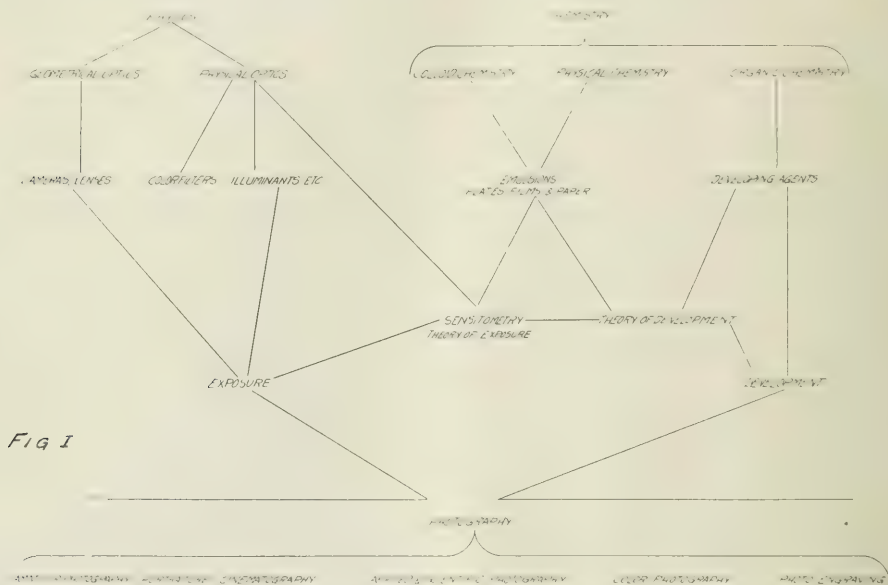


FIG 1

I would suggest that the first type of laboratory might be called "convergent" laboratories and the second "divergent."

In the "divergent" group of laboratories are included all those research institutions which are interested in science in general or in science as applied to industry and which will attack any problem which may seem to promise progress in knowledge or, in the case of an industrial laboratory, financial return. Most university laboratories are of this type. When they devote themselves to special problems it is usually because of the predilection of some professor, and as a general rule a student or instructor may choose any problem in the whole field of the science in which he is working and may carry out an investigation on that problem if he be interested in it without regard to the relation of his work to the other work which is carried on in the same laboratory.

Correspondingly, in most industrial laboratories the problems investigated are those which present themselves as a result of factory experiences or of suggestions from the men working in the laboratory and which promise financial return, and the different

actual investigations may cover as great a range of science as those undertaken in a "divergent" laboratory, yet all those investigations are directed toward a common end; that is, towards the elucidation of associated problems related to one subject. Thus, the staff of the Geophysical Laboratory, which includes physicists, geologists, crystallographers, mineralogists and chemists, works on the structure of the rocks, and although the field of the actual investigations range from high temperature photometry to the physical chemistry of the phase rule, yet the results of all the work carried out are converged on the problem of the structure and the origin of the earth's crust.

The Nela Park Laboratory, in the same way, is studying the production, distribution and measurement of illumination, and all its work, which may involve physiology, physics and chemistry, is related to that one subject. Such convergent laboratories sometimes develop in universities owing to the intense interest of a professor in a single subject and to the enthusiasm which inspires students and assistants to collaborate with him and to concentrate all their energies on the same group of problems.

There are many examples of such laboratories, such as the laboratories dealing with radioactivity, and those which are concerned chiefly with spectroscopy. Among others may be mentioned the Cavendish Laboratory at Cambridge and several of the larger university laboratories which deal with the physical chemistry of solutions.

But these university laboratories are rarely able to concentrate onto the group of problems which they are studying, specialists from such different branches of science as are available for similar laboratories outside the universities, owing to the fact that it is very difficult to obtain inter-departmental cooperation in research in a university. In a specialized laboratory, on the other hand, workers in all branches of science may well collaborate in the investigation of problems representing different points of view of one general subject.

In addition to the examples of industrial and institutional laboratories mentioned above I should like to illustrate the structure of a convergent laboratory, if I may be forgiven for doing so, by referring to the organization of the research laboratory with which I am connected—that of the Eastman Kodak Company.

The purpose of this laboratory is the investigation of the scientific foundations of photography and its applications, everything relating to photography in all its branches and applications being of interest. The branches of science which are of chief importance in photographic problems are those of optics in physics and of the colloidal, physical and organic branches of chemistry, and the relation of these sciences to photographic problems are shown in graphic form in Fig. I.

Optics deals on its geometrical side with the materials used in photography—cameras, lenses, shutters, etc.—and on its physical side with such materials as color filters and illuminants, but especially with the study of the relation of the photographic image to the light by means of which it was produced—a study which is known by the name of sensitometry. The manufacture of the sensitive material itself, which in the case of modern photographic plates, films and paper is called the emulsion, is a province of colloid and physical chemistry, colloid chemistry dealing with the precipitation and nature of the sensitive silver salts formed in their gelatine layer, while physical chemistry informs us as to the nature of the reactions which go on, both in the formation of the sensitive substance and in its subsequent development after exposure.

The organic chemist prepares the reducing agents required for development and the dyes by which color sensitiveness is given to the photographic materials and by which the art of color photography can be carried on, and while the physicist therefore deals with sensitometry and the theory of exposure, the chemist must deal at the same time with the theory of development and with the conditions relating to the development of photographic images.

A laboratory, therefore, for the study of photographic problems must be arranged with a number of sections such as are shown in Fig. II. In physics we require department dealing with sensitometry and with illumination, reflection and absorption, colorimetry, spectroscopy and geometrical optics. We need a department of colloid chemistry, one of physical chemistry, one of organic chemistry, one of photochemistry to deal with the action of light upon the plate, and finally a number of photographic departments, dealing with photographic chemistry, with portraiture, color photography, photo-engraving, motion picture work and X-ray work, and all these departments are converged together upon first, the theory, and then upon the practice, of photography.

Each research specialist in the laboratory is given work corresponding to a limited field of science, so that while his special attention is devoted to that one department his field of activity just overlaps that of the departments on each side of him, while

his general knowledge of the subject should, of course, cover a much wider range. It is important that each man should have his own special field of work and that overlapping should not be complete since such complete overlapping will inevitably produce friction destructive of cooperation and harmony. The way in which such a subdivision is arranged may perhaps be best illustrated by Fig. III, which shows the range of the specific investigations of those who in our laboratory cover the range of research work between sensitometry and pure physical chemistry. There are five workers in this range; the first, *A*, being a pure physicist; *B*, a physicist with a considerable experience of chemistry; *C*, a physical chemist who has specialized in photography; *D*, a physical chemist who has specialized in photographic theory; and *E*, a pure physical chemist. The interest of each of these workers overlaps the field of the other workers but nevertheless each of them has his own specific problem, his own equipment and apparatus. Thus, *A* and *B* use sensitometric apparatus chiefly; *C*, both sensitometric apparatus and the thermostatic and electrical equipment of physical chemistry; *D*, microscopic apparatus and chemical apparatus dealing with the precipitation of silver salts; and *E*, the analytical and solubility apparatus of chemistry.

The whole of this range is also connected with colloid chemistry and especially the overlap of the different sections involves colloid problems, so that we can consider colloid chemistry as dealing with the inter-relations of the different sections of photographic chemistry and can represent its province in the diagram by shading the overlapping areas. The colloid division of the laboratory will therefore be interested in the work of each of the specific investigators and will be of assistance to all of them.

These charts, prepared for a photographic laboratory, are equally applicable in form for almost any other convergent laboratory, so that if we have to work out the organization of a research laboratory which is to study any inter-related group of problems, we can do it by the construction of charts similar to these. Thus, considering Fig. I, we place first at the bottom of the chart the general subject considered and its various branches and then above these the scientific problems involved, separating out on opposite sides of the chart those problems which would involve different branches of pure science. Thus, we can place on one side biological problems, then physical problems, then chemical problems, and so on, thus reconstructing a chart similar to Fig. I from the bottom up until at the top we have the various branches of pure science involved, subdividing these branches until each subdivision represents the work capable of being handled by one man in the laboratory.

It will now be possible to draw Fig. II, showing on the circumference the different sections of the laboratory for which accommodation, apparatus and men must be provided and showing the relation of these sections to the problem as a whole, and having worked this out it is easy to find the amount of space and the number of men who will be required for which the funds available will allow for each part of the work.

Specialized laboratories may originate in various ways, but it seems clear that with an increasing total amount of research and with an increasing realization of the importance of research more laboratories will be developed and no doubt laboratories which originally were of the divergent type will split their growth and to split into a fixed group of convergent laboratories. Consider, for instance, a very large industrial research laboratory covering a wide field of research and dealing with many different types of problems. There are two types of organization possible to such a laboratory. It might be divided according to the branches of science in which the workers work problems. It might have, for instance, a chemical division, physical division, and so on, but if the grouped problems dealt with were sufficiently numerous in their number it would more probably develop into a group of sections or laboratories in which men are placed knowing of general chemistry, physics, and so on, worked

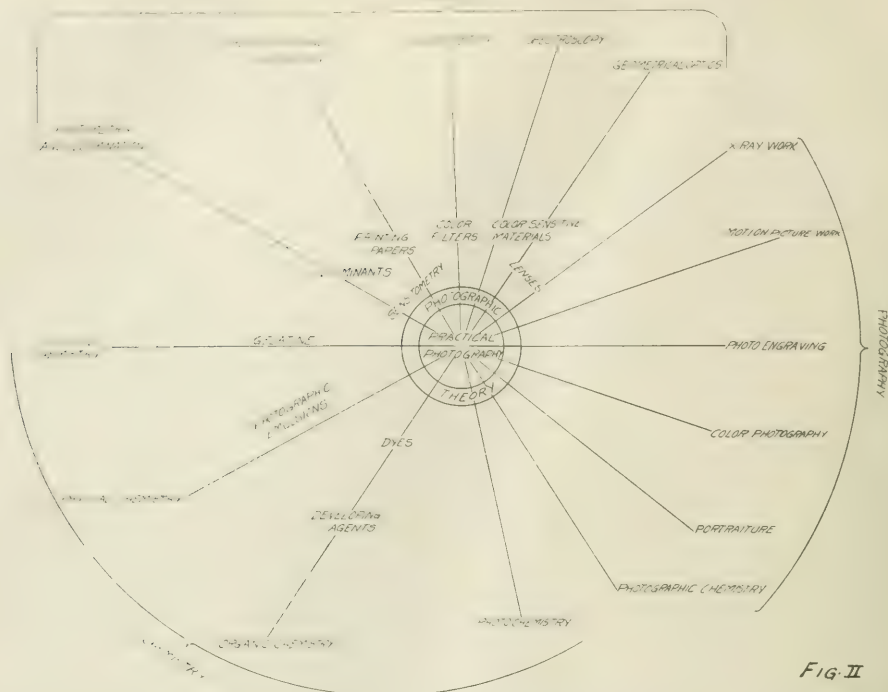


FIG. II

together (and probably even had their working places in proximity) because they were working on the same general problem. Any national laboratory which is developed for industrial research, for instance, should almost certainly be organized as a group of convergent laboratories rather than as a group of separate physical, chemical, engineering, etc., laboratories.

We may expect then that the general organization of scientific research will tend towards the production of numbers of specialized laboratories, each of which will be working on an inter-related group of problems and attacking it from various standpoints.

Some of the questions relating to the internal organization suitable for these convergent laboratories have already been discussed in a former paper¹ and I need add here only that the "conference" system described there as a method of actually carrying on the scientific work of the research laboratory has continued to prove quite satisfactory.

II THE CLASSIFICATION OF SCIENTIFIC KNOWLEDGE

The work of the research laboratories is published by various methods in the form of scientific papers, and with the increasing amount of research done the number of technical journals is increasing steadily, so that the workers in most branches of science find it difficult to keep up adequately with the current literature and especially those who become interested in the light thrown upon their own problem by other branches of science find it a task of great magnitude to acquaint themselves adequately with the literature. In order to meet this difficulty the various scientific societies publish journals giving abstracts, in a conveniently indexed form, of all the important papers published; these abstract journals are of great value in searching for information on special subjects.

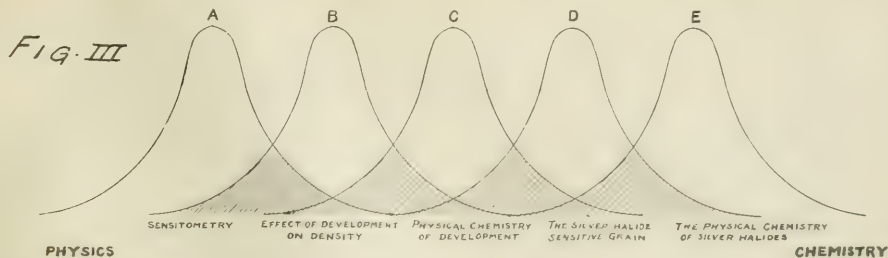
¹ "The Organization of Industrial Scientific Research," *Science*, 1916, 763.

In spite of these abstract journals the task of obtaining all the references to the literature on a given subject is still a formidable one and might be very much simplified by the adoption of some radical changes in the organization of the abstraction and classification of scientific knowledge.

In the first place, there seems to be no reason why abstracts of scientific papers should be prepared by the national societies. At present, for instance, there are at least four complete sets of abstracts of chemical papers prepared in different countries, together with a number of less complete sets, and this represents a great overlapping and duplication of effort. On the other hand, sciences which have not so many or so wealthy workers as chemistry cannot afford to produce any complete abstract journals, so that in these sciences reference to the literature is much more difficult. There seems to be no reason why an interchange of abstracts between different countries could not be arranged and, indeed, it might be the best method of obtaining abstracts to have the author of a paper supply an abstract suitable in form and length for the abstract journal at the same time that he sends his paper in to the journal which publishes it. The editor of that journal could suggest modifications in the abstract which in his opinion were desirable and forward both the corrected and uncorrected abstract to the editor of the abstract office, where it would be re-edited for insertion in the international abstract journals and these journals would, of course, be supported by subscriptions, either through the societies or by individuals in the same way as the abstract journals which are at present published.

Whether such an ambitious scheme of international scientific abstracts is capable of realization or not, reference to the abstract journals would be made much simpler if some method of numerical classification could be adopted.

In this connection, an experiment has been made in the last



two years at the laboratory of the Eastman Kodak Company which has proved successful and which seems to be worth trying on a larger scale. The laboratory publishes each month for the use of the employees of the company an abstract bulletin of the photographic journals, including also abstracts from other scientific journals which have any relation to photographic problems or manufacture, the abstracts being made by the laboratory staff, and attached to each abstract is a reference number. These numbers refer to a numerical classification of photography based somewhat on a decimal system but adapted to the special needs of the subject. Each month as the bulletin is issued the abstracts are clipped out, pasted on cards and filed under the number printed on them in numerical order so that each recipient of the bulletin can prepare for himself a file either of all photographic literature or of any portion of it in which he may be specially interested. For example, in the classification, photographic apparatus commences with the number "2", and if any particular worker is not interested in anything but apparatus, if he has no interest in materials or in photographic processes or in applications of photography, then he need file only the cards starting with "2", while, if his interests are even more limited, if, for instance, he is interested only in photographic shutters, he can file the cards starting with "262" thus obtaining only a very limited file which is, however, complete for the subject in which his interest lies.

If the abstract journals would print such a numerical classification attached to each abstract, adopting as their basis either the numerical classifications of the international catalogue of scientific literature, which have proved themselves satisfactory after trial, or some different classification adopted after due consideration, then each recipient of the abstract journals could prepare for himself card index files of the scientific literature in which he was interested.

To prepare a card index of all science or even a complete index of one large branch of science in this way would be too formidable an undertaking either for an individual or even for a small library, but it should certainly be possible for large libraries such as those of the scientific societies or of large cities to keep such numerically indexed files to which reference could be made by correspondence from any research worker. Thus, adopting the classification of the international catalogue, a worker who became interested in questions, *e. g.*, of catalysis, could apply for a copy of the reference cards on this subject, which would include all those indexed under 7000, and could be supplied with a complete file or with a partial file covering any period of time; the copies could easily be made by photographing the cards with such a camera as the "Photostat."

III. THE UTILIZATION OF SCIENTIFIC KNOWLEDGE

The actual application of science to industry is so vast a subject that it cannot be considered here, but it is not satisfactory to leave the results of research at the point where they are published in papers and filed in the abstract journals. In order to make them available as a part of scientific knowledge the new information as it is obtained must be incorporated in books.

There are three classes of books dealing with scientific work which require separate consideration. The first class comprises the dictionaries, in which almost all the progress in some branches of science can conveniently be summarized. Beilstein's "Handbook of Organic Chemistry" is a good example of the way in which almost all the facts of a science can be absorbed in a classified form and made available for ready reference. These dictionaries, in fact, represent the critical and discriminating summary of the scientific publications on the subjects with which they deal and the preparation of such dictionaries should be ensured by international coöperation of the national societies.

Other sciences, however, do not by their nature lend themselves to the convenient preparation of dictionaries and what is wanted in this case are critical and well arranged handbooks covering the whole science and resuming impartially but critically the various additions which are made from time to time in the different branches of the subject. These handbooks, as well as the dictionaries, would, of course, require the addition of supplementary volumes from time to time and occasional complete revision.

The preparation of both dictionaries and handbooks would, of course, be greatly facilitated by the existence of a numerically classified card index to the literature concerned, and the preparation and revision of such books might well be undertaken in connection with the large libraries having in their possession the complete classified card indexes.

On the other hand, for the assistance of advanced students of science, what is required is a steady supply of monographs correlating critically and comprehensively all the literature in a special field, and these must be brought up-to-date from time to time. Such monographs are especially required in connection with rapidly developing new branches of science; it is difficult to overestimate the importance and value for progress in research of such a book as Bragg's "X-Rays and Crystal Structure" for instance, and while nothing should be done to hinder individual initiative in publishing such books, it would seem that when it was apparent that some branch of science required such a monograph a national society might very well approach well-known workers in the field and request them to write such a book, offering its assistance in the matter of bibliography and also offering to arrange for the publication of the manuscript. The initiative in indicating the need for such a book might come in the form of suggestions from members of the Society or other scientific men. It is quite true that at the present time the scientific publishers are extremely active in searching for notable books to publish, but nevertheless they must consider the probable demand rather than the actual need for a book, and this leads to an overproduction of books dealing with those fields of science which have a large following, and an insufficient supply of books in those fields where the workers are few, though the progress the more sparsely worked fields would seem to require almost as much representation in literature as those which are of wider interest.

PUBLISHED FOR THE EDITOR
BY THE EASTMAN KODAK COMPANY
ROCHESTER, NEW YORK

FRANCE AND AMERICA IN SCIENTIFIC UNION

On the evening of October 19, 1917, honorary membership in The Chemists' Club of New York City was conferred upon Prof. Victor Grignard of the French Mission. The ceremony took place at the regular joint meeting of the New York Sections of the Society of Chemical Industry, American Chemical Society and the American Electrochemical Society. Dr. M. C. Whitaker, president of the Club, introduced Dr. L. H. Baekeland who officially informed Prof. Grignard of the action of the Club. In accepting the honor, Prof. Grignard replied in French. Dr. Baekeland has prepared a translation of the address, which follows.—[EDITOR.]

ADDRESS

By PROF. VICTOR GRIGNARD

GENTLEMEN—I feel truly perplexed before all the marks of sympathy, all the honors, which have come to me like an avalanche since I put my feet on this beautiful land of America.

From the moment I arrived, even on the ship itself, already two of your eminent representatives, Dr. Baekeland and Professor Bogert, kindly put themselves at the disposal of Mr. Engel and myself and offered the hospitality of this House.

Since then, everywhere we present ourselves, we have encountered the same enthusiastic welcome, the same sincere desire of being of service to us.

Then again, at the beginning of the month of August, a charming and unforgettable banquet, even more touching by its intimate cordiality than any great official galas which often are more arranged for the gallery than for the participants, brought us together in this same place.

Then again, that important meeting in Boston where Professor Stieglitz announced so kindly the great honor which was conferred upon me by the American Chemical Society and which has been appreciated as much as it was unexpected.

And, to-day, gentlemen, you open to me all the big doors of your Great House, you welcome me in the intimacy of your Home, in a word, you adopt me as a member of your great family.

Let me tell you that this honor impresses me even more than the preceding ones because there is in this something which touches me more particularly in a personal way.

Undoubtedly, I am happy and proud to have been for you an occasion to manifest your sympathies, even your admiration, for France in general and for French chemistry in particular. But, believe me, I would be less impressed when bringing home from here honor certificates and diplomas, if I did not know I am taking home to my country also somewhat of your hearts.

This ceremony proves to me that I am not mistaken in this. Therefore, gentlemen, I desire to express more particularly my profound gratitude, my great happiness, to have been able, notwithstanding my lack of knowledge of the English language, to bring to you the impression that, in spite of the sorrows of the present hour, French chemistry, like all France, lives and works; and only desires to live and work still more and we look upon our big American sister as particularly qualified to help us in this work of reconstruction.

Indeed, gentlemen, you possess all that is necessary for this. Thanks to the immensity of your magnificent territory, you have natural forces and mineral riches of the most varied nature, of greatest abundance and of the most precious kind which nature has been able to give to any people.

You have the confidence and enthusiasm of youth; you have also the audacity thereof, and fortune, which loves the audacious, smiles upon you. Have you not shown excellent proof of this in the creation and the prosperity of the Chemists' Club? You

have banking organizations which know how to favor beginning enterprises; you do not let yourself be held back by timid men or by skeptics, and you know how to look forward on a large scale—large like your beautiful land.

Many of your projects surpass by their audacity the limits of our immediate comprehension. Thus it has frequently happened in France, at least in certain circles, to try to class such enterprises by saying, "It is American bluff." But, nothing of the kind. We have to admit it. The bluff resides merely in our imagination. It is not in yours; you look at the world in all the boldness of your imagination and you dream of realities which sometimes seem to surpass the possibilities of the moment. You have the vision of *grandeurs* of the future—that is all. But do not let us call this bluff; let us admire it.

What can your older little sister bring you to complete such a powerful ensemble? Truly, very little, but, nevertheless, something: A finer sense of truly scientific ways, due to a tradition and an education of older duration; after all, the privilege of seniority is not always enviable, but it may often render its services.

France owes it to this that in many directions, and more particularly in chemistry, she was an innovatrix, and this privilege would have been still more obvious, even to the minds of those who are less informed, if our laboratory men, if our engineers, had had behind them sufficient backing, well equipped laboratories, more elastic budgets, well informed manufacturers, daring capitalists.

Many new ideas which germinated in France might have grown up there and might have contributed to make the halo of French science still more brilliant.

For instance, to speak of a question of burning actuality, the synthesis of ammonia which at this moment preoccupies all the Allies, the so-called Haber process, is called thus because it has been studied and put in shape in the laboratory of Haber by a Frenchman, Rossignol. It is probable that if Rossignol had possessed in France a laboratory which commanded the resources of that of Haber, France would not be, at this moment, anxious to procure ammonia and Germany might, perhaps, have been short of it long ago. Furthermore, the principle of this process, that is to say, the combination of nitrogen and hydrogen under pressure at a sufficiently high temperature and in presence of a catalyzer, was discovered a long time ago in Paris by our eminent chemist Le Châtelier.

Unfortunately, the gaseous mixture at one of the tests was ill-prepared and still contained oxygen, and caused the explosion of the apparatus and the experiments did not go further. We should not think, of course, that when an apparatus blows up, it is the French scientist who retreats. No, alas, it is simply his budget which blows up!

And thus it was that the synthesis of ammonia, which ought to have been a French conquest, has taken the aspect of a German discovery.

Well! We know at present in what soil we shall have to plant the good seed; whenever the old French humus will no longer be deep nor rich enough to permit a rapid and powerful growth, do not let us lose our way among our rapacious eastern neighbors, who are always on the alert for some new plunder; let us take it to you where we shall find the confidence, the daring perseverance, with all the material and financial resources which can assure success.

In this way, long ago, the inventor of the triple effect evaporator, when he was misunderstood in his own country, brought to your sugar refiners his ingenious discovery, which since then has had a splendid development in many industries. It is necessary that a close coöperation on scientific and industrial lines should be organized more and more between our two countries.

The horrible war which has been imposed upon us, has already made a big step in that direction.

In order to save the world from Prussian hegemony, in order to stop the grasping hand of Germany over every liberal thought and generous instinct, we cannot have enough of the support of the United States alongside that of the European Allies. And this brotherhood of our armies has made indispensable, more particularly between our two countries, the scientific and industrial alliance which is necessary to conduct this war, —a war more scientific than anyone ever might have imagined.

Without citing too many examples, our metallurgists have already brought to you precious improvements in the manufacture of steel; from your side, you bring us a solution, and perhaps two solutions, to the worrying nitric acid problem.

This fecund collaboration should continue after our victory.

Yesterday we exchanged professors; to-morrow we shall exchange students. Thanks to the zeal of my devoted collaborator, Engel, thanks to the friendly efforts of some among you, quite a number of American chemists have already subscribed their names for membership in the Société de Chimie Industrielle which recently has been founded in Paris, and I hope that at our return in France, we shall be able to reciprocate and to increase the number of members of the American Chemical Society.

In this way, the field shall have been well prepared for the exchange of ideas which will precede our common efforts.

In their own turn, other elements of intimate collaboration will present themselves to reinforce all that exists already, and if I am enabled, within a few years, to visit again your beautiful land, I have the firm conviction that I shall be able to bring then the greetings of a newer France to a still greater America.

CURRENT INDUSTRIAL NEWS

ESTIMATION OF TIN IN LOW-GRADE STUFF

Mr. A. Adair contributes to a recent issue of the *South African Mining Journal* a method of estimating tin in low-grade ores, tailings and slimes. The method is stated to have been devised on account of the difficulty which the sodium peroxide and other fusion methods present, owing to the trouble experienced in separating the tin from the excessive amounts of gelatinous silica produced, for, in practice, evaporation with hydrochloric acid to render the silica insoluble results in large losses of tin as stannic chloride. The method described depends on converting the stannic oxide into its phosphide without fluxing the gangue. The metal is then dissolved and readily separated from the non-gelatinous silica. The ore is roasted or treated with nitric acid and washed free from pyrites. It is then ground to impalpability and mixed with 0.4 its weight of dry ammonium phosphate and 0.2 charcoal, both ground finely and well mixed. For 5 g. ore take an annealing cup and grind a lid to it till it closes all around. The inside is wetted and rubbed with a little black lead to get a good coating for polishing when dry. A kerosene blast lamp and jacket are used, first heating gently for 20 min. and then at a red heat for one-half hour, cooling off with the vapor of the lamp. Any charcoal remaining is blown off and the ignition transferred to a porcelain crucible and ground to the finest powder. It is transferred to a flask and wetted with alcohol. 25 cc. of boiled hydrochloric acid are added and the mixture left in a warm place over night, by which time the tin is in solution and easily filtered from the gangue and charcoal. Results on a sample of ore containing 1.5 per cent stannic oxide, from seven successive tests, gave an average value of 1.21 per cent.—A. McMillan.

COCONUT INDUSTRY

From a recent report it would appear that the coconut industry of Trinidad and Tobago, which has been affected by prolonged droughts in previous years, has now recovered. The export figures for 1916 show an increase of 3,000,000 nuts above the number exported in 1915. On the other hand, however, the export of copra has decreased by about 1,000,000 lbs., which works out at about 2,500,000 nuts, so that the real increase for 1916 is only 500,000 nuts. The cultivation is being rapidly extended. The following figures show the distribution of the coconuts among the various countries:

	Tons	Copra, lbs.
United States	10,000,000	2,750,000
United Kingdom	10,000,000	2,750,000
Canada	100,000	275,000
British West Indies	1,000,000	275,000
Other Colonies	2,844	
TOTAL	11,000,000	5,750,000
VALUE	\$481,000	\$208,000

STARCH SUBSTITUTES IN GERMANY

In all countries, says the *Oil and Color Trade Journal*, 52 (1917), 985, articles which were quite common prior to the war have now had to be replaced by others, either because the importation of the necessary raw materials from foreign countries has ceased or because such raw materials are being employed for other purposes to better advantage. Some interesting data regarding starch substitutes have recently been published by Dr. R. Koenig, who has investigated several types. At the beginning of the war starch substitutes in Germany consisted chiefly of potato flour mixed with chalk ground as fine as possible. When potato flour was no longer available, admixtures of powdered gelatine, white glue and fine white chalk were used. The percentage of chalk increased very rapidly as gelatine advanced in price so that in one instance it was found that the percentage of chalk increased from 20 to 35 per cent in 14 days. Although these products, as long as the glue was not of a yellowish color, were fairly satisfactory, still their price was generally out of all proportion to their actual value. Other preparations placed on the market consisted of crystallized bitter or "cat" salts, water and burnt magnesia. The latter was afterwards sold as "fatless" washing medium. This contained 70 per cent bitter salt, 23 per cent water and 70 per cent magnesia. The salt was dissolved in water and the magnesia thoroughly stirred in till dissolved, whereupon it was allowed to stand in moulds for some hours till it stiffened through the formation of oxysulfate.—M.

SALTPETER PRODUCTION IN INDIA

From the bulletin issued by the Agricultural Institute, Pusa, it would appear that, subject to certain conditions being realized, there is a good opportunity for developing the production of saltpeter in India. The general conclusions arrived at are as follows. (1) The present sources of saltpeter are not fully utilized on account of the drawbacks at present associated with the *gobar's* business and the low price of crude saltpeter. (2) Artificial methods, on account of the favorable soil and climatic conditions in India would probably form a much added source of saltpeter. (3) The present methods do not allow of recovery of all the nitrate present in the earth worked. It is to be determined whether a better method of extraction could be devised capable of being carried out and whether the efficiency of the method would sufficiently depend upon some reduction or revision of the restrictions at present imposed by the salt department. (4) The present conditions of trade in this commodity require examination to determine whether a grant of license for Indian saltpeter would result from increased efforts to improve them such as the discovery of the conditions and the standard reduction of the product itself.—M.

CERAMICS

In an instructive paper on "Ceramic Objects of Pure Materials" published in *Zeitschrift für angewandte Chemie*, the author insists on the finest subdivision of the materials when it is intended to prepare "tun-walled" refractory objects. His materials are the rare earths, magnesia, alumina, carbides, silica, etc., and especially also the nitrides of boron and titanium which he has been studying. The calcined materials should be crushed to grains of 1 mm. and then ground down in steel mills to powders of particles of from 0.001 to 0.005 mm. Though this extreme subdivision seems to undo what has been gained by calcination of the briquetted materials, he considers that the uniformity obtained increases the strength of the objects and reduces the tendency to shrinkage. As binding materials, he recommends water, colophony, oils of turpentine, celloidin in amyl acetate, bakelite varnish, glycerine, and caramel. The last two he prefers, for example, for thoria, and describes how zirconia can be provided with a glazing of thoria. The preparation of boron nitride from boric anhydride and, similarly, of titanium nitride, is an elaborate process. The oxide turns into the nitride when heated at 1200° C. in an atmosphere of ammonia, but the presence of water, which is difficult to expel, interferes with the reaction and the first formed superficial coating of nitride prevents further access of ammonia; high pressure also accelerates the reaction. Mixed with paraffin, the nitride can be squirted into threads 0.1 mm. in diameter. The resulting nitride stands 2,000° C. quite well, and is used for making the tubes in which granular carbon resistances are baked. The boron nitride, density 1.92, does not melt in the arc burning in an atmosphere of nitrogen: it is, however, attacked by oxygen and also by boiling water, especially if a little boron anhydride should still be left in it.—M.

BRITISH BOARD OF TRADE

During the month of September the British Board of Trade received inquiries from firms in the United Kingdom and abroad regarding sources of supply for the following articles. Firms which may be able to supply information regarding these things are requested to communicate with the Director of the Commercial Intelligence Branch, Board of Trade, 73 Basinghall St., London, E. C.

CHEMICALS:

Aluminate of soda
Chromic acid
Monochloronaphthalene
Sodium sulfide

MACHINERY AND PLANT:

Complete cork preparing plant
For making plough chains
For manufacturing fret saws
For peeling lemons
For making toy marbles
Flexible shaft-driven portable tools
Machines for cutting cleft gears
Articles for West African native trade
Buckle frames, metal or cardboard
Celluloid marking rings for pigeons
Chain coat-hangers

Chamois leather
Curling irons, cheap
Electric driven machinery for floor-polishing
Eucalyptus red gum
Glove makers' waste
Leather waste, i. e., bucks, chamois, suede, etc.
Manioc flour
Paper knives, bone and ivory
Piercing saws for metal
Powder for making beer
Skins, kid
Soap boxes, metal
Synthetic essential oil of mustard
Thimbles, steel and silvered
Wood preservative not containing coal-tar oils
Wooden shovels for margarine factories

—M.

MANGANESE STEEL

A catalog issued by Allen & Co., of Sheffield, England, relates to their Imperial manganese steel and to its use, especially for parts of dredgers, crushing machines and conveyors where great resistance to wear and abrasion are required. This steel is so hard that it cannot be machined and must be finished by grinding and, at the same time, is so tough that it may be bent double while cold without fracture. It has a tensile strength of 55 tons per sq. in., or over, with an elongation of about 40 per cent in 4 in., and is non-magnetic. It is supplied in castings, rolled bars, sheets, forgings and patent rolled rails.—M.

HARDENING OF ALUMINUM BRONZE

According to an article in the *Giesseri Zeitung* for June 1, aluminum bronzes can be improved by thermal treatment. When they contain less than 7 per cent copper, the thermal treatment will not affect the properties much. Higher grade bronzes can be hardened, however, and by the further addition of iron, silicon and other elements, the mechanical properties of the alloys can be much varied. Thus, e. g., bronzes can be prepared having a Brinell hardness of 100 without being brittle. An aluminum bronze resembling in its mechanical properties a 0.35 carbon Swedish steel was given hardness values ranging from 100 to 260 by various thermal treatments; such bronzes of great hardness will answer as bearing metals even for high speeds. The following figures are given as to the properties of a 10 per cent aluminum bronze containing some titanium, the percentage of which is not quoted:

	Bronze as cast	Quenched Bronze	After Thermal Treatment at Different Temperatures
Limit of Elasticity...	9.6	19.8	27.7 to 19.2 kg. per cm ² .
Tensile Strength....	51.8	73.6	67.7 to 64 kg. per cm ² .
Elongation	19.5	1.0	5.5 to 1.4 per cent
Contraction of Area	33.7	0.8	9 to 18.5 per cent
Brinell Hardness...	100	262	158 to 140

—M

POTASH FROM FLUE DUST

A recent article by Mr. H. T. Cranfield in the *Journal of the Board of Agriculture* deals with the extraction of potash salts from blast furnace flue dust. The number of furnaces in full blast in Britain, the author reckons to be 300, and the quantity of flue dust produced per week works out at 20 tons black dust, 5 tons red and 1 ton cream colored. On the assumption that the black dust contains 2.5 per cent, the red 7 per cent, and the cream 10 per cent, each furnace would yield about 50 tons of potash per annum, giving an annual production of 15,000 tons. At least 50 per cent of this would represent soluble potash. From these figures, this may be regarded as an important source of potash and until arrangements can be made and plant erected for the extraction of the water-soluble potash salts, Mr. Cranfield suggests that the raw flue dust might be used on land deficient in potash in the past two years.—M.

A NEW TEST PAPER

A very delicate test paper has been prepared in Japan from the fruit of the Tama-tsubaki, which has a violet color and is turned to greenish blue by a mere trace of alkali and to red by an extremely dilute acid solution. The plant is also known in Japan as Nezumimochi or Teratsubaki. The inventor noticed that the color of its fruits never fades, while the color of the flowers quickly fades. He squeezed the fruit and dyed a filter paper with the juice which gave a violet shade.—M.

FERRO-CONCRETE SHIPS

During the past three months, says the *Times Engineering Supplement*, No. 515, the Committee of Lloyd's Register of Shipping have approved plans for the construction in ferro-concrete of a number of non-propelled barges, some designed to carry 500 tons dead weight, and also of a motor vessel. These vessels will be built in the United Kingdom and in Norway, under the inspection of the Society's surveyors, and are intended for the British and Scandinavian coastal trade. Plans of other ferro-concrete vessels of larger capacity for certain sea trades are at present under consideration. One of the society's principal surveyors recently made a tour of inspection in Scandinavia, where, owing to circumstances arising from the war and other causes, the use of ferro-concrete for ship construction has so far been most developed and the report of his visit has naturally placed the Committee of Lloyd's Register in possession of valuable data on the subject.—M.

RUSSIAN COTTONSEED OIL INDUSTRY

The Russian cottonseed oil industry is established for the most part in the Ferghana, Murgal and Merw districts. The cottonseed from the first-named district contains a high percentage of oil specially suitable for refining. It is stated, says the *Chemical Trade Journal*, that in the Ferghana mills there are more than thirty 16-in. hydraulic presses, seven 12-in. presses and several small ones. The total quantity of cottonseed formerly treated was about 144,000 tons per annum, the working year being 250 days. The yield of oil was approximately 21,600 tons in addition to 48,000 tons oil-cake. Just lately, two new mills have been established and the old mills have been enlarged. The output, therefore, is considerably increased and the total quantity of cottonseed dealt with is now about 192,000 tons. The export of cottonseed from Turkestan in 1913 was about 20-320 tons. It is said that 36 lbs. cottonseed of first quality yield 18 per cent unrefined cottonseed oil, 40 per cent oil-cake and 50 per cent husks, the remainder consisting of linters and other waste.—M.

JAPANESE PAPER-MAKING INDUSTRY

Among the trades in which Japan is sure to make great efforts to maintain a permanent position after the war is the manufacture of "European" paper, says the *Chamber of Commerce Journal*. Before the war a heavy import duty compelled most publishers to use Japanese-made paper although it was both dear and bad and export was hardly dreamed of. Now a large part of the Asiatic trade is in Japan's hands and the new energy put into the business may bring it up to European level. Saghalien makes important pulp contributions—a welcome sign of development of a rather neglected territory. Without the war, it is doubtful whether paper manufacture would ever have been a success, but extraordinary circumstances have justified this and various other protected industries. They have, however, a time of severe trial before them, for in many cases they are far from working as cheaply as Europe in spite of low wages.

The Japanese demand for paper in 1915 was 145,000 tons, of which 60,000 tons were ground pulp and 85,000 tons chemical pulp. The ground pulp was chiefly supplied by home producers, only a small portion being imported. Of chemical pulp about 60,000 tons came from abroad, the home production being limited to 25,000 tons of lower grade material and 7,500 tons of superior grade. The total cessation of imports to Japan since the war began and the enormous rise in prices have stimulated the Japanese pulp industry. Many producers are now exploiting the timber resources of the Saghalien forests and several chemical paper factories have been established recently in Saghalien. With a view to encouraging the pulp industry in Japan, the Japanese Investigation Committee suggests that timber for pulp-making should be supplied at the lowest possible price, and that all possible facilities, for the transport of material, timber and pulp, should be given to producers.—M.

APPLICATION OF RADIO-ACTIVE SUBSTANCES FOR BATTERIES

A recent French patent is concerned with the use of radio-active material for the purpose of facilitating the chemical action taking place in accumulators. For this purpose radium borium sulfate is used. The material is insoluble in the electrolyte and does not appear to enter into chemical action with the lead oxide or the metallic lead of the plates. Its presence is assumed to render the chemical action more complete during charge and discharge, otherwise the process is normal. About 0.2 microgram of radium per lb. of lead oxide is used, the radium compound being merely incorporated in the oxide used on the grid of the plates. M.

LINING WHITE METAL BEARINGS

In order to ensure uniformity of composition in white metal alloys used for lining bearings the Monometer Manufacturing Company of Aston, Birmingham, has introduced a melting furnace which is provided with a device for thoroughly mixing the components of white Babbitt and similar alloys. This device takes the form of a propeller, carried on ball bearings to reduce friction, the blades of which are rotated in the melting pot by means of a handle. The alloy is drawn off from the melting pot, which is enclosed, through an outlet at the bottom controlled by a screw valve, and a thermostatic regulator, which acts on the fuel supply and can be set to suit any particular alloy, maintains the metal at the proper temperature for running into the bearings. An oven for heating the shells of the bearings before they are tinned, made by the same firm, is fitted with a similar automatic controller which keeps the temperature at the correct point for tinning, and the shells need simply to be rubbed with a stick of tin as they are withdrawn. Automatic temperature control is also provided in a die-casting machine for use in connection with small bearings.—M.

ARTIFICIAL WOOD

The Austrian paper, *Kunststoffe*, states that leaves are now being used for the production of artificial wood, which has for some time been manufactured from sawdust, subjected to high pressure either with or without a binding material. The leaves are dried and boiled in water or lye, mixed with a binding material such as glue, resin, waterglass, etc., and squeezed into blocks under a pressure of 300 to 400 atmospheres. Any desired color can be obtained by appropriate additions. It is claimed that artificial wood so produced can be worked like natural wood and can be used for the most varied purposes.—M.

PAINTS AND VARNISHES FOR SIAM

Siam is a prosperous country, says a contemporary, and the bountiful rice crop, the staple product, which has been recently gathered in, should be favorable to the import of manufactured goods. There is a growing demand among the people of Siam for paints and varnishes for the decoration of their houses. These goods are not made in the country and the trade should be noted by manufacturers of these articles. The sending of catalogues and price lists to the leading importers in Bangkok is recommended, but a better means of gaining a business connection would undoubtedly be the visit of a representative. M.

COTTON TRADE IN JAPAN

The British Attaché at Yokohama writes, drawing attention to schemes which are being devised for the amalgamation on a large scale of the various cotton spinning interests in Japan with a view to consolidating the position of the cotton textile industry in that country and enabling the mills to retain their hold of British, American and German goods which will, no doubt, supervene at the close of the war. A recent meeting has been gained by Japanese manufacturers in many oriental markets which were considered to be the permanent markets of British or German goods. It is therefore necessary to improve the financial position of the industry to retain this hold. Not only spinning mills but weaving, printing, bleaching and dyeing mills will be included in the combination. One such amalgamation, it is said, will have a total of 400,000 spindles in operation. The report also states that the cotton industry in Japan is the best organized in Japan and that the amalgamation of these large concerns will certainly tend to reduce expenses and obviate needless competition. M.

NOTES AND CORRESPONDENCE

HYDROGENATION OF OIL

[The following opinion was rendered Oct. 3, 1917, by Judge Augustus N. Hand, of the U. S. District Court (Southern District of N. Y.) on the Burchenal Patent No. 1,135,351 in case of Proctor and Gamble Co. (Complainant) vs. Berlin Mills Co. (Defendant). Kerr, Page, Cooper and Hayward were Solicitors for the Complainant with Alfred N. Allen, Livingston Gifford and Thomas B. Kerr as Counsel. For the Defendant, John C. Pennie was Solicitor, with Marcus B. May and Mr. Pennie as Counsel.]

This suit is for infringement of patent No. 1,135,351, granted to the Complainant as assignee of John J. Burchenal, on April 13, 1915. The application for the patent was filed November 10, 1910. The specification states that the invention is for a food product consisting of a vegetable oil, preferably cottonseed oil, partially hydrogenized and hardened to a homogeneous white or yellowish semi-solid clearly simulating lard.

Claims 1 and 2 alone are in issue and read as follows:

1—A homogeneous lard-like food product consisting of an incompletely hydrogenized vegetable oil.

2—A homogeneous lard-like food product consisting of incompletely hydrogenized cottonseed oil.

The special object of the invention is, according to the specification:

* * * to provide a new food product for a shortening in cooking in which the liability to become rancid is minimized and in which the components of such vegetable oils which are inferior and detrimental to use as such a food product have been to a large extent converted into a higher and more wholesome form. All such vegetable oils contain glycerids of unsaturated fatty acids and among these notable quantities of fatty glycerids of lower saturation than olein. It is the presence of these glycerids of lower saturation that seriously affects the rancidity of the material. Oxidation is largely the cause of rancidity, which oxidation weakens the fat at the point of absorption at the double bonds, and these glycerids of lesser saturation readily absorb oxygen from the air at ordinary temperatures while the more highly saturated glycerids, as olein, only absorb oxygen at elevated temperatures. It is evident, therefore, that oils or fats containing notable quantities of glycerids of linolic acid or of lesser saturation are distinctly inferior as an edible product to those containing a minimum of these glycerids with a larger per cent of olein. On the other hand, while it is important to get rid of the readily oxidizable glycerids of lower saturation, it is also important not to supply too large a per cent of fully saturated glycerids.

* * * In manufacturing this product, cottonseed or other vegetable oil is caused to chemically absorb a limited amount of hydrogen by reacting on the oil with hydrogen in the presence of a catalytic agent and at an elevated temperature. The oil is preferably agitated in a closed vessel in the presence of an atmosphere of compressed hydrogen, a catalyzer of finely-divided nickel carried by kieselguhr being maintained in suspension in the oil and its temperature being raised to about 155° C.

According to the present invention, the amount of hydrogen absorbed is carefully regulated and limited. In practice, the operation is stopped when the oil has been converted into a product which cools to a white or yellowish semi-solid more closely resembling lard than do the commercial mixtures of cottonseed oil and animal oleo-stearin while in many respects the product is superior to the best leaf lard as a shortening. It is not so liable to become rancid and the product can be heated to a considerably higher temperature than lard without smoking or burning. The high temperature to which my product can be raised without smoking or burning makes the product ideal for frying, inasmuch as a crust forms almost instantly on the food fried, which prevents any absorption of the shortening. A lard-like product thus prepared from cottonseed oil has a saponification value of about 195 and an iodine value ranging from about 55 to about 80. The product having an iodine value of 55 has a titer of about 42° and a melting point of about 40° C., that having an iodine value of 80 has a titer of about 35° and a melting point of about 33° C. While but partially hydrogenized, containing from about 1.5 per cent to 2.5 per cent of additional hydrogen more than in the non-hydrogenized material, it shows no free cottonseed oil when subjected to the Halphen test, thereby differing from all commercial lard substitutes containing this oil. It contains from twenty to twenty-five per cent of fully saturated glycerids, from five to ten per cent linolin, and from sixty-five to seventy-five per cent olein; and an average of a number of samples gives twenty-three per cent of saturated fats, seven and five-tenths per cent linolin and sixty-nine and five-tenths per cent olein, while the cottonseed oil before treatment contained seventeen per cent saturated fats, thirty-seven per cent linolin and forty-six per cent olein. It will thus be seen that I have produced an ideal food

product which is high in olein, low in linolin and lesser saturated fats and with only enough stearin to make the product congeal at ordinary temperatures.

The complainant urges that Burchenal first taught the art that a partially hydrogenated vegetable oil, preferably cottonseed oil, was edible and was a useful lard substitute. It contends that prior to Burchenal's conception it was not known that hydrogenated cottonseed oil was edible and that the only processes then in use aimed at complete saturation and produced a hard non-edible product. Before discussing the prior art, I would say in general that Normann, whose patent will later be referred to, had already disclosed a method of hydrogenating oils, and had set forth in his specification that the process was progressive and involved "no secondary reaction." The method of adding cottonseed oil to beef stearin for use as a lard compound was well known and much used, as it still is. The hydrogenation of cottonseed oil resulted in a reduction of the fluid and substitution of the solid fats. Normann's patent, as well as various experiments of scientists, indicated that the addition of hydrogen to cottonseed oil would result in the reduction or elimination of the fluid and substitution of solid or partially solid fats. No one has shown that the product resulting from such hydrogenation was ever non-edible or unsanitary in any respect.

The British patent No. 0,783 (1887), to Joseph Sears, was for a lard substitute composed of refined unbleached cottonseed oil and a fat adapted to give a stiffness to the compound corresponding substantially to that of refined lard. The specification provided that the temperature should be raised sufficiently to melt the fat or stearin, the heated ingredients mixed and then chilled rapidly so as to prevent crystallization and separation. This general process was well known in the art before the date claimed for the invention of Burchenal and indeed is referred to in the patent in suit. A very large market for such lard-like compounds exists at the present time and has existed many years past.

The British patent No. 1515 of 1903, to Normann, discloses a process for the reduction of glycerines resembling that of the patent to Burchenal. Normann's patent says that:

The property of finely divided platinum to exercise a catalytic action with hydrogen * * * is already known. * * * Recently Sabatier and Senderens of Paris have discovered that other finely divided metals will also exercise a catalytic effect on hydrogen; viz., iron, cobalt, copper and especially nickel.

By causing acetylene, ethylene or benzene vapor in mixture with hydrogen gas to pass over one of the said metals (which had just been reduced in a current of hydrogen) the said investigators obtained from the unsaturated hydrocarbons, saturated hydrocarbons, partly with simultaneous condensation.

I have found that by this catalytic method it is easy to convert unsaturated fatty acids into saturated acids.

This may be effected by causing fatty acid vapors, together with hydrogen, to pass over the catalytic metal, which is preferably distributed over a suitable support such as pumice stone. It is sufficient, however, to expose the fat or the fatty acid in a liquid condition to the action of hydrogen and the catalytic substance.

For instance, if fine nickel powder, obtained by reduction in a hydrogen current, is added to chemically pure oleic acid, the latter heated over an oil bath and a strong current of hydrogen is caused to pass through it for a considerable time, the oleic acid may be completely converted into stearic acid.

The quantity of the nickel thus added and the temperature are immaterial and will only affect the duration of the process. Apart from the formation of small quantities of nickel soap, which may be easily decomposed by dilute mineral acids, the reaction passes off without any secondary reaction. The same nickel may be used repeatedly. Instead of pure oleic acid, commercial fatty acids may be treated in the same manner. The fatty acid of tallow which melts between 44 and 48° C. has an iodine number 35.1 and a yellow color will after hydrogenation melt between 56.5 and 59°, while its iodine number is 98 and its color slightly lighter than before, and it will be very hard.

The same method is applicable not only to free fatty acids, but also to the glycerines occurring in nature, that is to say, the fats and oils. Olive oil will yield a hard tallow-like mass; linseed oil and fish oil will give similar results.

By the new method all kinds of unsaturated fatty acids and their glycerides may be easily hydrogenized.

The Normann patent clearly discloses that oils may be completely hydrogenized, that the process is progressive and that it

involves "no secondary reaction," in other words, that cottonseed oil which starts edible remains so. The experiments and articles of Paul and Roth, which were alluded to at the trial, show that hydrogenization of oils including cottonseed oil was understood in the prior art.

Such being the state of the art, Edwin Cuno Kayser wrote Procter & Gamble from England that he had a process of considerable value and would like to talk to them about it; thereafter he came to America, about November, 1907, bringing samples of hydrogenized cottonseed oil. He showed these to Burchenal, the superintendent of Procter & Gamble. As a result of his visit, he made an arrangement under a preliminary contract of January, 1908, to experiment upon the hydrogenized cottonseed oil as a substitute for lard. The first project was apparently to use hydrogenated cottonseed oil as a compound to be added to a percentage of beef stearin and cottonseed oil. Burchenal says he had done no work in connection with hydrogenizing cottonseed oil before he saw Kayser. He testified that:

"Mr. Kayser went out to our factory and made sketches as to the apparatus that would be necessary to carry on this work, and the apparatus was ordered at once; a little plant was installed for experimental purposes and I think it was ready to operate sometime in January or February, 1908" (Deposition of Burchenal, page 11).

The defendant succeeded in obtaining contemporaneous memoranda as to some of Kayser's experiments from the records of Procter & Gamble. The first experiment was as follows:

FAT HARDENING PROCESS BY E. C. KAYSER

First experimental lot was completed January 17, 1908. Fat treated—Summer Yellow Cottonseed Oil. Used Nickel Sulfate and Kieselguhr as described. Experiment was conducted by Mr. Kayser alone. He claims to have used about 1 per cent Nickel Metal and 2 per cent Kieselguhr.

M. p. of fat after 3 hrs., 55½° C.

M. p. of fat after 6½ hrs., 60.3° C.

Dr. Bender reports as follows:

Melting point of fat, 60.3° C.

Hydrocarbons, 0.33 per cent.

Iodine value of fat, 7.14 per cent.

The fat does not contain free fatty acids. This material is much superior to the samples from J. Crossfield & Sons, which showed an iodine value of 52.26 and a melting point of 39.3° C. (The laboratory sample melted at 49.9° C.). Their samples contained 5.12 per cent free fatty acids and 2 per cent hydrocarbons.

Mr. Kayser reports as follows: "The melting point of fatty acid, prepared from first lot hardened cottonseed oil, is 62° C. This is several points higher than I ever got before. Presumably the composition of your oil differs somewhat from that of the oil I handled formerly."

Another experiment by Kayser of the date of March 5, 1908, was also obtained from the Procter & Gamble records, in which the following melting points appeared:

5 hrs. at ordinary pressure, 42° C.

1½ hrs. at 60 lb. pressure, 43° C.

Von Phul testified that Kayser told him in 1907 that he was getting up a patent for a food product and even Burchenal's own testimony shows that Kayser supposed that the product he was making was edible. If Kayser at first told him it was not edible, he did so when they were negotiating and he wished to keep his process in the dark until he had arranged his terms. That Kayser's statement that it was not edible was not taken seriously by either party is shown by the following testimony:

Q. 887. But you did not know as a matter of fact whether it would be edible or not? A. I did not. Mr. Kayser stated that it would not be, but that was his method of talking.

Both of these men were proceeding soon after Kayser's arrival in this country to develop hydrogenated cottonseed oil as a food product. Even if the thought first occurred to Burchenal I cannot see that he did anything to carry it out in practice. Kayser's patent No. 1,004,035, application for which was filed March 20, 1908, disclosed the process which was employed to make the product covered by the patent in suit, and the specification for this Kayser patent contains the statement that, "The time of treatment will vary with the progress realized and with the degree of saturation aimed at." It is to be remembered that Burchenal distinctly declined in his testimony that he had anything to do with the presentation of the process covered by the Kayser patent and so that here a situation where Kayser invented the process and developed the product to the point where it was applicable to use as a food product. He came to America with a sample which, as appears from the written record taken from the files of the complainant, had a melting point of

only 39° and developed other samples with melting points of but 42° and 43° in his March 5, 1908, experiments.

Moreover, it is to be remembered that Crossfield had employed Kayser to experiment in hydrogenating oil, that the former had been in close communication with Normann, who had patented only four years before the process I have mentioned and that Crossfield had so strenuously objected to the use by Procter & Gamble of the processes of Kayser that they were obliged to purchase their rights to them. It is also noteworthy that Kayser refused to testify in this case and that the witnesses as to the work of Kayser in America are officers or employees of the complainant. Under such circumstances the meagerness of the evidence which has been adduced to show that Burchenal had anything to do with the development of the lard-like food product which is the subject of the patent in suit, coupled with his admission that the entire process under which it was made was the work of Kayser, is most significant and makes it impossible to find that Burchenal invented anything. The defendant has been embarrassed in its defense by many difficulties and has been obliged to go into the enemy's camp to secure almost all its ammunition. In spite of this, it has been established that Kayser at the very beginning had developed not only a process but a product little differing from Crisco. Kayser remained with Procter & Gamble until well into 1910, and did not leave America until about July of that year. While there is some general evidence of what Burchenal and others did, or directed, I can find no real proof that anyone but Kayser did anything of substantial moment. No step was taken by Burchenal that could possibly amount to invention.

Complainant urges that the experiments of Kayser and the patents of Normann and Kayser aimed at complete saturation and that neither realized the importance of a partially hydrogenized product. But the process under which their products were made involved in its progress partial hydrogenation, and Kayser's patent, No. 1,004,035, distinctly stated that "The time of treatment will vary with the progress realized and with the degree of saturation aimed at." Kayser, as far as I can see, did everything that was done to develop Crisco, and if his work fell short of this, he achieved enough so that the final step was inevitable to one skilled in the art. Kayser's process was the complainant's process and his product involved a progressive reaction fitted for any purpose. The broad discovery as between him and Burchenal certainly belongs to him.

Furthermore, under any fair interpretation of the patent, there is no infringement. The file wrapper indicates that the examiner rejected the claims as originally filed, saying:

* * * If the problem of simulating lard from cottonseed oil were presented to an oil chemist, an incomplete hydrogenization of the cottonseed oil would at once suggest itself to him as a solution of the problem. All the claims are accordingly rejected on the * * * ground of lack of invention.

Thereafter new claims were rejected upon the Kayser patents for the reason that his process could be carried at any time to produce an *incompletely hydrogenated product*. Then, and for the first time, Burchenal filed an amendment setting forth certain percentages of linolin, olein and stearin which his product should contain. It seems quite evident, therefore, that Claims 1 and 2 of his patent would under such circumstances, if valid at all, be limited to substantially the chemical composition described in the amended specification. Indeed, the specification closes with the statement that the inventor has produced a product which "is high in olein, low in linolin and lesser saturated fats and with only enough stearin to make the product congeal at ordinary temperatures."

Under such circumstances it is impossible to treat the melting point as practically the determining factor, and if this is not done the defendant's product *Crisco* keeps clear of infringement. After the examiner had held that an *incomplete hydrogenation* would suggest itself to any chemist desiring to simulate lard and rejected the claims on *lack of invention*, as I have shown amended by Burchenal, a particular process and discovery upon the advancement of which percentages of linolin to avoid similarity. It therefore the process suggested everything to do with it was this special process of Burchenal which his patent discloses. Claims 1 and 2 of his patent could only be construed in the light of the process of Burchenal and Kayser's Patent 1,004,035 and not as a process which would suggest itself to any chemist. Normann, Kayser and others had been too bad persons.

Crisco keeps its chemical composition extremely regular from that contained in the composition of Burchenal. The following are the relative percentages:

PER CENT	BURCHENAL	KREAM KRISP
Saturated fats.	20 to 25	28.0
Olein	65 to 75	34.3
Linolin	5 to 10	37.7

Thus it appears that Kream Krisp, instead of being low in linolin, is extremely high, and that instead of being high in olein as specified in the Burchenal patent, it has a percentage of olein which differs but little from that existing in refined cottonseed oil unhydrogenated. In fact, Kream Krisp seems to present many of the objections referred to in Burchenal's specification and to lack the very things upon which the latter based his right to receive a patent. Indeed, the composition is much closer to the lard compound Jewel made out of stearin and cottonseed oil than to Crisco.

The bill should be dismissed with costs because the patent is void for lack of invention and for the further reason that Claims 1 and 2, if properly construed, are not infringed by the defendant.

THE AMERICAN COAL-TAR PRODUCTS INDUSTRY PRODUCTION TO BE ASCERTAINED BY THE UNITED STATES TARIFF COMMISSION

The United States Tariff Commission is planning to ascertain the production within the United States during 1917 of all substances treated in Title V of the Special Tariff Act of September 8, 1916. The substances there enumerated may be classed under the general name Coal-Tar Products and are divided into three groups.

Group I includes "all products that are found naturally in coal tar, whether produced or obtained from coal tar or other source" except phenol. These substances are admitted free of duty.

Group II includes the so-called intermediates and are made dutiable at 15 per cent plus 2½ cents per pound.

Group III includes "all colors, dyes, or stains, whether soluble or not in water, color acids, color bases, color lakes, photographic chemicals, medicinals, flavors, synthetic phenolic resins or explosives, not otherwise specially provided for in this title, when obtained, derived or manufactured, in whole or in part from any of the products provided for in Groups I and II." These articles are dutiable at 30 per cent plus 5 cents per pound with certain exceptions which are dutiable at 30 per cent.

Under the law the duties are made dependent on the growth of the industry within the United States. It is therefore the intention of the Commission to follow this growth from year to year in order to report the facts to Congress.

The Tariff Commission is planning to send to each manufacturer a questionnaire calling for information in regard to his production during 1917 of each separate commodity, as well as for certain other data. This information will be published in such a form that the operations of individual firms will not be disclosed. A preliminary questionnaire has recently been sent out, designed to aid in perfecting the mailing list. Any individual or firm engaged in the manufacture of any of these articles which did not receive a copy of the preliminary questionnaire is requested to write to the United States Tariff Commission, Washington, D. C., to insure being placed on the mailing list.

U. S. TARIFF COMMISSION
WASHINGTON, November 5, 1917
F. W. TAUSSIG, *Chairman*

SAMPLING FATS AND OILS—CORRECTION

In the "Tentative Standard Methods for the Sampling and Analysis of Commercial Fats and Oils other than those of the Coconut, Butter and Linsed Groups" as published in THIS JOURNAL, 9 (1917), 1066, the strength acid for acidifying under determination of TITER, page 1068 (1st column, 4th line above foot-notes), should read "30 per cent" instead of "50 per cent."

November 17, 1917

W. D. RICHARDSON

CONCERNING THE MANUFACTURE OF PHTHALIC ACID AND PHTHALIC ANHYDRIDE

The Department of Agriculture announced on June 16, 1917, that the Color Investigation Laboratory of the Bureau of Chemistry of this Department had perfected on a laboratory scale a new process for the manufacture of phthalic acid and phthalic anhydride, and invited coöperation with the manufacturers for the purpose of testing this laboratory process upon a commercial scale. It was also stated in the announcement that the offer of assistance would not be held open by the Department for an indefinite period.

Arrangements have been made with several concerns to test this process on a commercial scale and the Color Investigation Laboratory is not in a position to receive or handle any additional offers of coöperation. The offer made on June 16, 1917, therefore, is withdrawn and no additional offers of coöperation can be considered.

DEPARTMENT OF AGRICULTURE
WASHINGTON, November 1, 1917
D. F. HOUSTON, *Secretary*

CHICAGO CHEMICAL EXPOSITION PLANS ABANDONED

After serious consideration and correspondence with all exhibitors, the managers of the Chemical Exposition have decided to abandon plans to hold a Chemical Exposition in Chicago in the Spring. This action was taken because of insufficient support secured to make a large and representative exposition, all the exhibitors wishing to confine their efforts toward making the Fourth National Exposition of Chemical Industries in New York, week of September 23, 1918, the greatest event in the history of American Chemical Industry, it being their intention to show there the many advances they are making as a result of their researches.

NITRIC ACID SOPHISTICATION—CORRECTION

The following corrections should be made in my article printed in THIS JOURNAL, 9 (1917), 771:

Page 775, 2nd col., line 44,
"at 7¼/c. 7.28" should read "at 7¾/c. 7.25"
P. 776, 1st col., line 18,
"127 lbs. . . . \$10.16" should read "127.77 lbs. . . . \$10.22"
line 19, "1.82" should read "\$1.88"
line 21, "1.51" should read "\$1.54"
line 23, "0.51" should read "\$0.53"

October 29, 1917

JAMES R. WITHROW

THE DETERMINATION OF SULFUR DIOXIDE— CORRECTION

The following corrections should be made in my article printed in THIS JOURNAL, 9 (1917), 949:

Page 949, 2nd col., line 34, omit "Both Dymond and Hughes and the Selby Smelter Commission used sodium sulfite for their standard."

Page 950, 1st col., first line under heading APPARATUS should read "One extra heavy 24-liter, or larger, bottle such as a carboy, carefully housed to avoid serious trouble from collapse and, etc."

Page 950, first line under heading METHOD OF PROCEDURE should read "Large sample bottle is evacuated to about 380 mm. and the pressure, etc."

November 8, 1917

JAMES R. WITHROW

WASHINGTON LETTER

By PAUL WOOTON, Metropolitan Bank Building, Washington, D. C.

DEMAND FOR CHEMICALS NOW GREATER THAN SUPPLY

Despite the concerted action of many of the nation's most capable chemists the demand for many essential articles is outstripping the supply. Most of the men in Washington who are working on chemical problems are willing to admit that the shortage of many chemicals threatens to become exceedingly serious. Much has been accomplished in speeding up the production of chemicals, but the point is being reached where the spur is less effective. Many plants are reaching the maximum of their production while requirements are exceeding even the highest estimates.

NEW WAR POLICY NECESSARY TOWARD CHEMISTS OF MILITARY AGE

The situation has reached a degree of seriousness which at last is arousing the military authorities to the need of a more practicable policy with regard to the disposition of chemists of military age. Plans are now practically ready for announcement of a new policy with regard to chemists. A sweeping order such as that which gave a blanket exemption to all men engaged in the shipbuilding industry hardly is expected at this time, but it is believed that certain classes of chemists will be hurried back from military camps and again placed at their regular work.

Requirements of sulfuric acid for 1918 bid fair to exceed those of the current year by 1,500,000 tons. Unmistakable signs have come from Chile that that country intends to take advantage of the world situation to squeeze the greatest possible profit from her nitrates. Apparently importers of manganese and those who are pinning more faith on increasing the domestic production are in deadlock. After much pulling and hauling on the part of each faction in an effort to influence the Shipping Board, Chairman Hurley apparently has shunted the responsibility to the War Industries Board. The result is an uncertainty which is retarding domestic production and is causing much concern to the steel makers. The iron pyrite situation is substantially in the same position. Visible supplies of platinum, so imperatively needed as a catalyzer, are entirely inadequate for war uses. The situation has become more complicated by the attitude of Colombian producers whose tendency to hold back shipments to this country is believed to be meeting with official favor in that country. Regardless of the seriousness of this situation, heavy articles of jewelry made of this metal continue to appear for sale. Those who are charged with responsibilities in connection with the ammonia situation are working day and night in their efforts to keep the supply in advance of the demand. Arsenic is becoming harder and harder to obtain, while the Explosives Act has added to the difficulties of those handling its ingredients. These are just a few of the problems which are confronting the government's chemical specialists and those who have come here to aid in coordinating the country's industries looking to the most effective conduct of the war.

Some one high in authority seems to have fallen under the spell of the Alabama Senators and there no longer is a question that the most ambitious plans of the Muscle Shoals promoters have begun to be carried out. Members of the Senate and of the House of Representatives who favor the manufacture of nitrates, in accordance with the recommendations of the nitrate board, are marshalling their facts and a battle royal between the two camps is certain to be staged at the approaching session of Congress. In the meantime, the uncertainty is pushing further into the future the day when the United States will be able to contribute to the amount of nitrates it is consuming, and plans for the Chilean monopoly are reported to be progressing rapidly toward consummation.

COMMITTEE ON CHEMICALS DISBANDED

Further impediment of the efforts being made to secure the maximum production of chemicals and in the general work being done in the handling of the chemical problems which the war has thrust to the fore has come with the reorganization of the Council of National Defense. The Committee on Chemicals, of which Dr. W. H. Nichols is the head, has been instructed to terminate its work as an official division of the Council of National Defense. No conclusions as to the future plans of the committee have been announced. It is very evident, however, that the War Industries Board expects to take a leading part in the handling of the entire chemical situation. The naming of a director of chemicals by this body is expected to be one of the developments of the near future. The director of chemicals will be incorporated in the raw materials division of the War Industries Board. L. L. Summers and M. F. Chase already have the chemical work of the War Industries Board well started. The Board, however, is not yet prepared to outline officially the plans of its chemical division. Mr. Summers, who demonstrated unusual ability in the handling of munitions purchases for J. P. Morgan and Co., when that concern was doing the purchasing for the Allies, has been connected with Bernard Baruch's committee on raw materials since the formation of the Council of National Defense. Mr. Chase comes from the staff of the Commercial Acid Company, of St. Louis. He is well known among eastern chemists, due to his long connection with the New Jersey Zinc Company.

ADVISORY BOARD FOR BUREAU OF MINES

Because of the great amount of war work being done by the Bureau of Mines, Secretary of the Interior Lane has asked six of the prominent chemists of the country to act as an advisory board to the bureau.

The members of this board are: Dr. Wm. H. Nichols, General Chemical Company, New York, *Chairman* of the board; Prof. H. P. Talbot, head of the chemical department of Massachusetts Institute of Technology, Boston, Mass.; William Hoskins, consulting chemist, Chicago, Ill.; Prof. F. P. Venable, head of the chemistry department, North Carolina University, Chapel Hill, N. C.; E. C. Franklin, professor of chemistry, Leland Stanford University, Stanford, Cal.; and Dr. Charles L. Parsons, chief chemist of the Bureau of Mines.

The board will discuss and advise upon gas warfare research, the minerals especially needed for munitions, and the recently enacted law for the regulation of explosives.

An important expansion in the exports of chemicals was registered in September, as compared with September of 1916. The increases, however, were confined to shipments to the countries associated with the United States in the war. As the export licensing plan was in effect throughout the month of September, shipments to neutral countries were curtailed. To France, however, shipments of chemicals increased from \$12,076 worth to \$25,050 worth. To the United Kingdom, the increase was from \$11,434 worth to \$23,026 worth. Exports to Italy increased from \$6,794 to \$8,816. The exports of acids did not greatly increase, as 4,061,925 lbs. were forwarded in September of this year, while the shipments of the corresponding month of last year were 4,434,105 lbs. Notable increases were made in the exports of calcium carbide. In September of 1916, exports were 2,269,646 lbs. In September of this year they were 3,128,168 lbs. Exports of copper sulfate increased from 96,862 lbs. to 226,491 lbs. Exports of sulfur showed a falling off, as 10,002 tons were shipped abroad this year in September,

whereas the record for last year shows forwardings of 19,424 tons. The first exports of chemical glassware in years are now being made. In September, the value of such ware exported was \$5,650.

That full advantage may be taken of America's petroleum in war operations, steps are being considered by the government which will place more tank ships in the transatlantic service. It is regarded as probable that the vessels now engaged in transporting crude oil from Tampico will be drawn upon. An effort now is being made to ascertain just how many of these ships can be diverted to transatlantic service without crippling any essential domestic petroleum activity. One of the suggestions made in this connection is that imports of Mexican oil all be made through Galveston for delivery in tank cars, instead of using ships to carry crude oil from Tampico to practically every important port as far north as Portland, Maine. It is believed that sufficient tank cars can be secured to take care of the distribution within the United States, thereby releasing a number of ships. As the situation stands at present, it is tank ship space, rather than production, which is limiting the forwardings of petroleum products destined for use in Europe. It is probable that the use of ships

to bring asphalt to the United States from Trinidad and Venezuela will be curtailed entirely, as it is believed that domestically produced asphaltic materials, while inferior to the imported article, can be made to suffice very well.

SHORTAGE OF CYANIDE IN MEXICO

A serious situation has been precipitated in Mexico by the curtailment of exports of cyanide. Numerous large plants have been forced to suspend operation, on account of its shortage. The trouble has been remedied in part by the War Trade Board, which is allowing some cyanide to go to Mexico. Until this step was taken, serious disorders were threatened by the large numbers of workmen whose enforced idleness was caused by the lack of cyanide. It is probable that the policy of the War Trade Board in regard to the amount of cyanide exports will not be defined formally until more definite information is available as to the possibility of meeting all domestic requirements. It is probable that one of the conditions under which exports of cyanide will be permitted will be the formation of an association of all consumers which will guarantee complete equity in its distribution.

PERSONAL NOTES

The United States Department of Labor recently created, as a part of its employment service, a Division whose function it is to aid the employer in obtaining suitable help, and professional persons in securing suitable employment. This is known as the Teachers and Professional Service Division. While intended to embrace all professions, attention has thus far been confined to the teaching and engineering professions. The services of the Division are absolutely free to both employer and employee, all expenses being borne by the United States Government. Its methods are quite thorough, and no service is rendered the applicant until the Division has learned, from persons familiar with the applicant, that he is qualified as to training, experience, and personal qualities for the position he seeks. When an applicant is recommended for a reported vacancy, the employer is given an opportunity to examine the data gathered in the course of this investigation, thus effectually preparing for the final and most important step, the personal interview, and for this ample facilities are provided in the offices of the Division where employers may meet with prospects on appointment.

Employers and professional engineers everywhere are invited to avail themselves of the services of this Division which, as stated above, are entirely free. Employers in reporting positions are asked to state the nature of the position, its duties, requirements, etc., the probable salary, and probable duration of employment. Applicants for registration should indicate in the first letter the nature of the position desired so that the proper blank may be furnished. All communications should be addressed: Teachers and Professional Service Division, U. S. Employment Service, 845 South Wabash Avenue, Chicago, Illinois.

Dr. Andrew Bender, chief chemist of the Carnegie Plant of the Aetna Explosives Company, has been transferred to the Company's New York office as technical assistant to the General Manager of the Company.

Prof. E. Bartow of the University of Illinois has been commissioned as a Major in the Army Reserve Corps. He will go to France to take charge of the sanitary condition of our army camps.

Dr. W. L. Lewis, associate professor of chemistry at Northwestern University, has been commissioned a Captain in the Officers Reserve Corps. He is to be engaged in research work.

Dr. L. M. Henderson, instructor in chemistry at the University of Minnesota, is located at the American University at Washington. He is in the instruction department of the Government service.

Dr. Chas. S. Palmer, fellow in the Mellon Institute of Industrial Research, Pittsburgh, Pa., has disposed of his patent petroleum cracking process to the Standard Oil Company of Indiana, which also owns the Burton process.

Mr. Oscar Charles Sumner Carter, for 37 years professor of chemistry, geology and mineralogy at Central High School, Philadelphia, died November 8th, at his home.

Dr. Charles L. Reese, chemical director of the du Pont Powder Company, has been elected a member of the board of directors of that company.

Miss Leola E. Marrs, for the past six years Assistant Editor of THIS JOURNAL, has accepted the position of Managing Editor of the *Color Trade Journal*. Miss Marrs takes up her new duties on December 3rd at 200 Fifth Avenue, New York City.

Professor H. Lewis Jackson, state chemist of Idaho for four and a half years, has accepted the position of professor of industrial chemistry at North Dakota Agricultural College, Fargo, N. D. He will also be in charge of the paint and oil laboratory and paint investigational work.

The chemists of Duluth, Minn., Superior, Wis., and the range towns have organized a 'Chemists' Club, for the purpose of promoting the interests of chemistry, and stimulating friendship and sociability among its members. The organization has been perfected, and meetings will be held monthly at the Duluth Commercial Club or at various plants in the city. The officers for the ensuing year are: *President*, Walter H. Benson, *Vice-President*, A. D. Wheelodon; *Secretary-Treasurer*, Max Latshaw.

Mr. Lawrence Addicks, consulting, metallurgical engineer of New York City, has sailed for Burma to make a metallurgical investigation of the ores of the Baldwin Mines.

Dr. James J. Johnson, Newark, N. J., formerly connected with the Maas and Waldstein Company in the capacity of chief chemist, has been commissioned a Captain in the Ordnance Department, to serve in the gun division. Dr. Johnson is an expert on high explosives, having been formerly associated with the du Pont plants and also at the Picatinny Arsenal.

Messrs. Philip A. Singer and Harris Perlstein, formerly of the Industrial Chemical Institute of Milwaukee, have associated as Singer-Perlstein Company, chemical and industrial engineers, with offices in the Railway Exchange, Milwaukee. Mr. Singer was for many years with the Corn Products Refining Company as member of the Manufacturing Committee and superintendent of various departments of that corporation's plants. He has also made contribution to the technique of the ethyl alcohol from wood waste and other chemical industries. Mr. Perlstein has been connected with Mr. Singer in a number of recent enterprises.

The Pfaunder Co. announces the establishment of a branch sales office at 440 Pierce Building, St. Louis, Mo., with Mr. George E. Gray, formerly of their Chicago offices, in charge. The Atlanta agency has been granted to C. M. Jackson Co. of that city.

Mr. W. G. Gaessler has been appointed acting chief of the Chemical Section of the Iowa State College Agricultural Experiment Station, filling the position left vacant by Dr. A. W. Dox, who has been appointed Captain of the Sanitary Corps.

Mr. G. P. Plaisance, formerly of the Iowa State College Agricultural Experiment Station, has been appointed chief chemist of the Oklahoma Experiment Station at Stillwater, Okla.

Dr. J. M. Crafts, formerly president of the Massachusetts Institute of Technology, was elected honorary member of La Société Chimique de France on July 13, 1917.

Dr. John Charles Hessler, professor of chemistry in the James Millikin University at Decatur, Illinois, has been elected to the presidency of the Illinois State Academy of Science.

Mr. Victor K. LaMer, formerly chemist at the Carnegie Institution, Cold Spring Harbor, Long Island, has received a commission of First Lieutenant in the Sanitary Corps.

Professor Clarence A. Morrow, formerly professor of chemistry in the Nebraska Wesleyan University, has been elected assistant professor of agricultural biochemistry in the University of Minnesota.

Mr. E. J. Barth, formerly with the Texas Company, has accepted the position of chief chemist with the Freeport Mexican Fuel Oil Corporation at Meraux, La.

Mr. O. W. Palmenberg, 50 Church St., New York City, reports the following platinum ware to have been stolen from his laboratory: 4 crucibles (marked E. & A.) weighing about 22 g. each; 3 covers weighing about 7 g. each; lipped dish (marked E. & A.) weighing about 48.9 g.; gauze cylindrical anode weighing $8\frac{1}{2}$ g., for electrolytic deposits; and spiral wire weighing 7.10 g.

Mr. L. Drew Betz, formerly chemist with the Animal Oil Company, has recently been appointed chemical director of the Philadelphia Plant of E. F. Drew and Company.

The U. S. Civil Service Commission announces an open competitive examination for junior chemical engineer, for men only, on December 5, 1917. Applicants should at once apply for Form 1312, stating the title of the examination desired, to the Civil Service Commission, Washington, D. C. The salary ranges from \$1200 to \$1500 a year.

Mr. F. L. White has resigned from the laboratory staff of the National Carbon Company, Inc., to accept the position of chief chemist in the K-W Ignition Laboratory, Cleveland, Ohio.

Dr. Benjamin T. Brooks formerly with the Bayway Chemical Co. is now connected with the Commercial Research Co., Flushing, L. I.

Mr. R. P. Noble, of Indianapolis, is now with the Government and is located in Washington. H. E. Cory and J. R. Keubler, both of Indianapolis, are now in training with the National Army.

Mr. Geo. G. Schmidt, formerly engineer for the Metropolitan Street Railway Company, piping engineer for the Pennsylvania Railroad Co., Belmont Tunnels and the Ashokan Dam, is now with the Carrier Engineering Company as piping engineer. Mr. Schmidt's department has its headquarters at the main offices of the company, 39 Cortlandt Street, New York, and will have charge of all work connected with the layout and installation of piping on installations of Carrier Air Conditioning Apparatus.

Mr. Edwin G. Pierce, Youngstown, Ohio, has been named consulting chemist for the Republic Motor Truck Co. of Alma, Mich. He has equipped a laboratory at that city for general chemical work and testing materials. The laboratory is under the immediate charge of Mr. Clyde S. Morgan, a graduate of the University of Wisconsin.

Dr. R. B. Owens, secretary of the Franklin Institute, now in France on leave of absence, acting as head of the Army Intelligence Bureau, has been elevated to the rank of Major. He is serving under General Pershing.

Dr. B. A. Stagner has resigned his position as head of the chemistry department of the Fresno, California, Junior College, to accept a position in the Mellon Institute of Industrial Research.

Mr. W. R. Gildard has resigned from the research staff of the Pittsburgh Plate Glass Co. to become Director of Research for the Lancaster Lens Co.

Dr. F. B. Kingsbury, assistant professor of physiological chemistry in the University of Minnesota, has been granted leave of absence for the duration of the war. He has been commissioned First Lieutenant in the sanitary corps of the Army and will be directly under Major John R. Murlin, of the Food Division.

Mr. Richard K. Meade, Consulting Chemical and Industrial Engineer, Law Building, Baltimore, Md., announces that he has formed a partnership with Mr. Howard C. Tompkins, one of his associates, under the name of Richard K. Meade & Co.

Prof. Alexander Silverman, of the University of Pittsburgh, gave a lecture to the chemists and engineers of Delaware on Thursday evening, November 15, in Wilmington. The subject was "The Chemistry and the Manufacture of Glass."

W. H. Doran, of the Alcan Hirsch Laboratories, is leaving for Japan on December 7, to act as construction engineer of the Japan Dyestuff Manufacturing Company.

INDUSTRIAL NOTES

We learn from *Oil, Paint and Drug Reporter* that plans are under way for the establishment of a casinghead gasoline plant in the Viking field of Northern Alberta, where a considerable gas production has been developed by the Northern Alberta Natural Gas and Development Company. The casinghead proposition is backed by Montreal capitalists, who are planning to commence actual development work next spring.

Experiments have recently been conducted in Sweden in the production of potash, iodine and bromine from seaweed. It is said that the experiments have been attended by good results, and that two factories are to be erected for the purpose of extracting the materials mentioned.

Work has been started on the new potash recovery plant of the Clinchfield Portland Cement Corporation at Kingsport, Tenn. This plant will employ the Cottrell or electrical precipitation system in its latest form and will include a wet treater by means of which potash salts will be obtained.

Under the provisions of a new federal law which became effective November 14th, all persons manufacturing, distributing or using explosives must be licensed.

The largest plant in the world for the manufacture of nitrous oxide is to be established in France under the direction of chemists from Cleveland, O. The Ohio Chemical and Manufacturing Company had a \$5000 contract from the Red Cross for this gas, which Dr. George W. Crile, of Cleveland, has taught French physicians to use as an anesthetic.

The British Chemical Gas Association has been carefully investigating the question of driving motor vehicles with coal gas as a substitute for gasoline, and in its report declares that coal gas in the present emergency may be advantageously used as a gasoline substitute by providing a large flexible holder in which the gas is stored approximately under atmospheric pressure. Experiments led to the conclusion that the equivalent of one gallon of gasoline is about 300 cu. ft. of gas, but other experiments have given only 250 cu. ft. or less, depending on the quality of the gas. In practice it seems that coal gas will show appreciable economy compared with gasoline, as at normal prices gas worth 10 cents would do the work of a gallon of gasoline. The one ground for complaint with reference to the new fuel is that it is inconvenient because of the large amount of space required for the bulky containers.

The Pure Academy of Sciences is to establish a national physical and mechanical laboratory for extensive industrial research.

The Canadian Advisory Council for Scientific and Industrial Research has appointed a committee of twenty members to assist the development of the Canadian chemical industry and a committee of the same number to promote the metallurgical and mining industries. The Council has also taken over the exploit of natural resources started by the Arthur D. Little Company of Montreal.

A process of electrode plating on both sides of paper by means of electrode plates has been patented in Germany.

It is reported that the United States Government has struck a deposit of potash in the exploration well which it has been boring near Cliffside, Texas, during the past two years. The exploration work will be extended to the territory lying 85 to 100 miles south of the present well and bordering New Mexico, where brackish water is found in many wells, and there are salt lakes which show strong indications of the near presence of potash.

The entire stock of dyestuffs, colors and chemicals of the Badische Company of New York has been taken over by a recently organized company known as Kuttroff, Pickhardt & Co., Inc., which will continue the business of the Badische Company, with offices at 128 Duane Street, New York City. The new concern was recently incorporated under the laws of the State of New York and has taken over the staff of employees and the laboratories of the old concern.

As soap is not obtainable in Germany there are many substitutes consisting of earths, chalk, alkali carbonates, sodium sulfate, sodium silicate, etc., bound together with some binding material such as gelatine. Salicylic acid or some other preservative is required also. In some of the washing powders sodium peroxide and sodium perborate are used and as accidents have resulted from their use a warning has been issued to the public.

The National Oil Products Company of Chicago has been incorporated under the laws of Illinois with a capital stock of \$100,000.

The United States Potash Products Company has been incorporated under the laws of Delaware, with a capital stock of \$5,500,000. Incorporators, D. T. Connet, White Plains, N. Y.; J. F. Roach and E. C. Bahn, of New York.

The Standard Asphalt and Refining Company of Chicago has purchased the plants and trade marks of the Sarco Petroleum Products Company. The Cities Service Co., of New York City, is the new interest back of the company, although the management will remain practically the same as in the old company.

The Aircraft Fireproofing Corporation has been incorporated at Portland, Me., to manufacture chemicals and paints. Capital \$600,000.

A coke plant that will cost \$10,000,000 will be erected in East St. Louis by the American Coke and Chemical Company of Chicago. The secretary of the company says his company will undertake an innovation in the way of coking Illinois coal. The erection of the plant will require a year under favorable circumstances.

Virginia sulfides will be mined by the American Sulfides Corporation, Charlottesville, Va., incorporated with \$400,000 capital.

A Norwegian electrical company has, after successful experiments, erected a plant for preparing aluminum sulfate from labradorite, a mineral which occurs in Western Norway. The plant is expected to supply the entire Norwegian demand for alum for the paper industry, which has hitherto been obtained from other countries.

Statistics compiled under the supervision of the U. S. Geological Survey, Department of the Interior, show that the volume of natural gas commercially utilized in the United States in 1916 was greater than that so utilized in any other year in the history of the natural-gas industry. The general increase in the production of natural gas in the United States is attributed principally to an enormous expansion of the casinghead gasoline industry in all natural gas producing States and to a greatly augmented demand for natural gas as fuel by industries engaged in the manufacture of the munitions of war.

The Lenz Apparatus Co., Inc., of New York City, announces that their capital stock has been increased to \$50,000, of which increased capital stock \$35,000 have been subscribed and actually paid for in cash, thus giving the company ample working capital to conduct its business profitably.

It is reported that Swift and Company of Chicago are to erect a sulfuric acid plant at New Orleans costing \$250,000 and having a daily capacity of 60 tons.

Vice-Consul Arthur E. J. Reilly reports from Stockholm that a company has been formed to finance a Swedish dyestuff establishment to compete with the German manufacture at home and abroad. The founding of the Company follows about two years of experimenting and the movement is supported by the country's scientific and technical experts.

The fuel oil stringency on the West Coast has pressed the Southern Pacific Railroad into a driving campaign for the development of its California producing properties with the hope of covering its needs.

The Fuelite Corporation of Manhattan, to handle compounds and chemicals for the treatment of coke, has been incorporated under the laws of New York by A. R. Bremer and E. A. and C. Alexander of Yonkers.

Mr. W. H. Thurston, connected with Clarence Whitman & Co., of New York, has answered a call from the Government to go to Washington to serve under Major Tilt in the Department of Aircraft development. Mr. Thurston is to take charge of balloon and airplane fabrics.

The E. Virgil Neal Chemical Works, 110 West 40th Street, New York, has plans prepared for the construction of a new addition to their chemical manufacturing plant at Var Dam Street and Borden Avenue, Long Island City.

Imports of colors and dyes for the eight months ending August 31 aggregate in value \$1,825,434, as against \$3,071,213 during the same period last year. Included in these imports were 2240 pounds of alizarines, valued at \$10,545.

The United States Industrial Chemical Company has been incorporated under the laws of Maryland with a capitalization of \$24,000,000. It will manufacture fertilizers and chemicals at Curtis Bay, a suburb of Baltimore.

A new fertilizer plant at Greenville, Mich., owned by the Michigan Fertilizer Company, was destroyed last Wednesday by fire.

The Color Service Corporation, Inc., has been incorporated with a capital of \$50,000, to manufacture chemicals, dyes and kindred products. The incorporators are M. M. Clancy, Wilmington, and C. M. Egner, Elkton, Md.

The manufacture of soap from sewer fat in Sweden has been taken up by the Hapbach Soap Company of Stockholm, which has worked out a new method for the purpose. There are also plans for using native vegetable fats, such as beechmast, horse chestnuts, etc. All this is due to the shortage in raw materials for the soap and soft soap industry.

Negotiations have been completed through the Tulsa, Okla., office of the Tidal Oil Company, whereby the Company is to purchase the Maple Oil Company in the Irvine Field of Kentucky.

One of the most prominent of the Japanese industries that have developed since the outbreak of the war is the manufacture of chlorate of potash. The *Japan Chronicle* refers to the fact that in the early stages of the war the suspension of imports sent prices up greatly, and states that established manufacturers of chlorate of potash extended their equipment, while numerous new manufacturing plants came into existence. The output was so great that prices fell considerably. Efforts were then made to ship the product abroad, and it is said that the quantity shipped to this country since the beginning of the war exceeds 10,000 barrels.

Manganese properties in Virginia will be developed by the Virginia Manganese Mining Corporation of Attaway, Va. This company has been chartered with a capitalization of \$50,000,000 and the following officers: *President*, J. W. Ruff, of Bluefield, W. Va.; *Secretary*, J. L. Phillips, of Attaway.

A fire of mysterious origin destroyed the large potash plant of the Mineral Products Corporation at Alunite, Utah, on Thursday night, causing \$250,000 loss. The fire originated in the coal dryer and was preceded by an explosion.

The Superior Oil Corporation has been incorporated under the laws of Delaware, capital \$10,000,000, by Arthur W. Britten, S. B. Howard and G. C. Reilly, all of New York.

Lyster Bros., Inc., dealing in drugs, chemicals, etc., has been incorporated under the laws of New York with a capital stock of \$50,000. Incorporators, H. W., M. J. and B. R. Lyster, New Rochelle.

The Compound Specialty Co., of Queens, makers of chemical compounds, has been incorporated with a capital stock of \$50,000 by S. Baer, M. L. Schalleck, J. R. Roth, 104 St. Nicholas Avenue.

The Illinois Platinum Corporation, of Eddyville, has been incorporated under the laws of New York; 3,500 shares common stock, no par value, active capital \$17,500.

GOVERNMENT PUBLICATIONS

By R. S. McBRIDE, Bureau of Standards, Washington

NOTICE—Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate. Commerce Reports are received by all large libraries and may be consulted there, or single numbers can be secured by application to the Bureau of Foreign and Domestic Commerce, Department of Commerce, Washington. The regular subscription rate for these Commerce Reports mailed daily is \$2.50 per year, payable in advance, to the Superintendent of Documents.

GEOLOGICAL SURVEY

Geology of Massachusetts and Rhode Island. B. K. EMERSON. Bulletin 597, 289 pp. This report includes a general discussion of the geologic conditions, and is accompanied by a large map giving full information.

The Enrichment of Ore Deposits. W. H. EMMONS. Bulletin 625, 530 pp. This report is an amplification of an earlier Survey Bulletin on the enrichment of sulfide ores (Bulletin 529). Fifteen elements and their compounds not considered in the earlier report are discussed with reference to their reactions in the zone of oxidation. All recent important advances in the subject have been incorporated and the general treatment has been considerably broadened.

The geologic conditions favorable and unfavorable to the formation of enriched mineral deposits are described and the criteria by which such deposits may be recognized are outlined. The natural chemical processes by which enrichment is produced are fully discussed and the behavior of each metal is considered separately and is illustrated by descriptions of many of its known valuable enriched ore bodies.

The Bull Mountain Coal Field, Musselshell and Yellowstone Counties, Montana. L. H. WOOLSEY, R. W. RICHARDS AND C. T. LUTPON. Bulletin 647, 218 pp. Paper, 50 cents.

Notes on the Greensand Deposits of the Eastern United States. G. H. ASHLEY. Bulletin 660-B, from Contributions to Economic Geology, 1917, Part I. 30 pp. Issued August 28. No attempt was made at a detailed survey of the greensands but samples were collected from the most accessible of the deposits and analyzed to determine their percentage of potash. The results of the study show that the richest and largest deposits of greensand occur in New Jersey, extending down into Delaware. Lower grade greensands occur abundantly in Maryland and less abundantly in Virginia, North Carolina, Arkansas, Texas, and doubtless the other Southern States.

The richest deposits show a potash content around 7 per cent, which is close to the percentage of potash in glauconite, of which the best greensands are almost entirely made up. These greensands occur in the basal part of the Cretaceous formation of New Jersey and Delaware and in the upper part of the Eocene. Those of New Jersey are entirely in the Cretaceous, while those of Maryland are in both Cretaceous and Eocene.

The paper also contains a contribution on "Methods of Analysis of Greensands" by WILLIAM B. HICKS AND R. K. BAILEY, discussing the methods used in making these analyses, which differ somewhat from methods previously used.

Manganese Deposits of the Caddo Gap and De Queen Quadrangles, Arkansas. H. D. MISER. Bulletin 660-C, 63 pp. From Contributions to Economic Geology, 1917, Part I. Published September 12, 1917.

The Irvine Oil Field, Estill County, Kentucky. E. W. SHAW. Bulletin 661-D, from Contributions to Economic Geology, 1917, Part II. 50 pp. Published September 5, 1917. The

Irvine oil field is by far the most productive yet developed in Kentucky. In fact, its output in 1917 will be more than twice as great as that of the dozens of other oil fields in the State, some of them long productive; and it will probably produce much more in 1918. The field is in a region where oil showings have long been known and oil has long been sought, and yet somehow this great pool 10 miles long and 2 miles wide was missed. The west side of the Irvine field is within a mile of outcrops of the oil-bearing bed, which may be seen at several places in and around Irvine. Some of the wells are less than 100 ft. deep and yet furnish good yields, even the oldest showing a relatively low rate of decline.

The Corsicana Oil and Gas Field, Texas. G. C. MATSON AND O. B. HOPKINS. Bulletin 661-F, from Contributions to Economic Geology, 1917, Part II. 41 pp. Published August 30, 1917.

The Bowdoin Dome, Montana. A Possible Reservoir of Oil or Gas. A. J. COLLIER. Bulletin 661-E, from Contributions to Economic Geology, 1917, Part II. 16 pp. Published July 27. The dome is a broadly arched portion of the earth's crust from which the strata dip away on all sides, its structure being a type known to be favorable for the accumulation of oil or gas in many fields. A well drilled here for water several years ago has been yielding a small flow of gas, sufficient probably for domestic use in one family, ever since, and it is thought that the region offers a chance of success to the driller of deeper wells. In 1915 a large gas well was drilled at Havre.

Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico, and Utah. H. E. GREGORY. Professional Paper 93. 161 pp. Paper, 40 cents.

The Geology and Ore Deposits of Ely, Nevada. A. C. SPENCER. Professional Paper 96. 189 pp. Paper, 40 cents.

Shorter Contributions to General Geology, 1916. D. WHITE. Professional Paper 98. 395 pp. This includes about twenty short papers which have been issued separately in advance.

Hydraulic-Mining Debris in the Sierra Nevada. G. K. GILBERT. Professional Paper 105. 142 pp.

Mineral Resources of the Kantishna Region, Alaska. S. R. CAPPS. Bulletin 662-E, from Contributions to Mineral Resources of Alaska, 1916-E. 53 pp.

Secondary Metals in 1916. J. P. DUNLOP. Pages 39 to 52 of Mineral Resources of the United States, 1916, Part II. Published October 6. The much higher prices for all metal products and for manufactured articles made wholly or in part from waste material has made a deep impression as to the importance of the waste-trade industry. The collection of old metals, paper bags, foil, rags, felt, and other things has been stimulated by appeals from many sources. Collections of metal have been so large that it has been difficult to obtain labor properly to break, segregate, and ship the varied classes of material. In fact, the public has been educated sufficiently to appreciate the importance of waste, even the farmmen in remote regions are being asked to collect and ship scrap iron, steel, and other metals. Efforts are now being made to have the housekeepers and small dealers properly segregate the different wastes, for by so doing better prices can be obtained and an immense amount of labor can be saved. The large manufacturing plants, foundries and smelters have increased their facilities for saving and segregating scrap metals and have also adopted methods for decreasing melting losses. They have realized that more scrap metals can be used if greater care is taken in removing deleterious substances and in better smelting practice.

Dealers in and refiners and smelters of waste metals did a large and profitable business in 1916. Stocks of many new metals were small, and spot shipments frequently were not available. The scarcity and the high prices demanded for new pig metals stimulated the sale of scrap metal. Frequently higher prices were paid for prompt shipments of scrap metals than were obtained for new metals sold under contract. There was also a large increase in the sale of guaranteed composition ingots made from scrap.

The value of the secondary metals, exclusive of gold, silver, platinum, iron, steel, and ferro-alloys, recovered in the United States, increased from \$114,304,930 in 1915 to \$265,377,856 in 1916. The increase was partly due to larger use and partly to much higher average prices.

The value of the secondary platinum, iridium, and palladium recovered in 1916 amounted to about \$4,000,000, and the value of old jewelry, dental waste, silver spoons, ornaments, and other material containing gold or silver, remelted and refined, was probably more than \$20,000,000. It is difficult to estimate the value of ferrous scrap remelted in 1916. Some of the scrap ferrous metal contained nickel, tungsten, manganese, or other alloys, which made it many times more valuable than the more ordinary commercial products. Old rails, car wheels, pipe, and other iron and steel shapes, were often sold at prices in excess of the original cost. Iron and steel scrap is used by all foundries and rolling mills, and hundreds of thousands of tons are collected, sorted, and shipped. Prices of iron and steel scrap have increased to record figures. The value of all other waste materials has increased so greatly that the total value of waste metals and other junk was 100 per cent more in 1916 than in 1915.

SECONDARY METALS RECOVERED IN THE UNITED STATES IN 1915 AND 1916

	1915		1916	
	Quantity (Short tons)	Value	Quantity (Short tons)	Value
Secondary copper, including that in alloys other than brass.....	99,937	\$33,498,882	140,000	\$68,880,000
Remelted brass.....	137,500	40,788,000	300,000	127,440,000
Secondary lead.....	36,400		56,700	
Recovered lead in alloys	42,500	7,416,600	39,600	13,289,400
Secondary spelter.....	52,900		50,700	
Recovered zinc in alloys other than brass.....	5,300	14,433,600	2,600	14,284,400
Secondary tin.....	5,250		7,600	
Recovered tin in alloys.....	8,400	10,534,180	9,800	15,131,040
Secondary antimony.....	2		80	
Recovered antimony in alloys.....	3,100	1,811,568	4,400	2,270,016
Secondary aluminum.....	5,700		12,900	
Recovered aluminum in alloys.....	2,800	5,802,100	6,400	23,430,200
Secondary nickel (1).....			16	
Recovered nickel in alloys (1).....			800	652,800
		\$114,304,930		\$265,377,856

(1) Recoveries made by International Nickel Company from scrap nickel or alloys and from nickel in scrap ferrous alloys from any source are not included.

A reprint of the classification standards for old metal as adopted by the National Association of Waste Material Dealers for the year beginning July 1, 1917, is included; and there are detailed statistics for each of the several classes of metals summarized in the preceding table.

BUREAU OF FISHERIES

Fish Isinglass and Glue. G. F. WHITE. Document 852. 15 pp. Paper, 5 cents.

BUREAU OF MINES

Bibliography of Recent Literature on Flotation of Ores. July to December, 1916. D. A. LYON, O. C. RALSTON, F. B. LANEY AND R. S. LEWIS. Technical Paper 176. 27 pp. Paper, 5 cents. This bibliography is a continuation of that given in Technical Paper 135 of the Bureau of Mines, which covered the first half of 1916. The present paper includes references to articles that appeared from July 1 to December 31, 1916.

Abstracts of Current Decisions on Mines and Mining. Reported from January to April, 1917. J. W. THOMPSON. Bulletin 152. 77 pp. Paper, 10 cents.

Coking of Illinois Coals. F. K. OVITZ. Bulletin 138. 71 pp. Paper, 20 cents. In its endeavor to promote a more efficient use of coal the Bureau of Mines, in cooperation with the Illinois State Geological Survey and the University of Illinois, has undertaken an investigation of the coking of Illinois coals. The investigation was started by collecting from various sources the data regarding experiments already made by others; these data have been compiled and are presented herein.

The first part of this report outlines the present factors in the problem of coking Illinois coals and points out the future prospects. The quality of coke from Illinois coals alone, and from mixtures of Illinois coals with low-volatile coals is described, and the uses for which the coke is suitable are discussed. The gas-making properties and the value of the coals for making by-products are noted. Desirable methods of preparation of the coals, the impurities in them, and the effect of the impurities on the value of the coals for coke and gas making are considered.

The second part of the report deals with the character of Illinois coals, their nature, physical properties, and chemical composition. The nonhomogenous structure of the coal, the variation in composition of different beds, and even of the same bed in different localities are pointed out. Those districts in which the coals contain the smaller amounts of impurities and are more favorable for coking are grouped together.

The last part describes the tests made and gives detailed results. The tests are considered under three classes—those with beehive ovens, those with by-product ovens, and those with gas retorts. The details are as complete as the material available permits. The results of a few tests of the coke for furnace or other use are given.

Extraction of Gasoline from Natural Gas by Absorption

Methods. G. A. BURRELL, P. M. BIDDISON AND G. G. OBERFELL. Bulletin 120. 71 pp. 10 cents. The Bureau of Mines is conducting a series of investigations, with a view to ascertaining the most efficient methods of obtaining gasoline from petroleum and natural gas. This report deals with a method of extracting gasoline from natural gas by absorbing the gasoline in oil and subsequently separating it from the oil by distillation. The process is quite different from those of compression and condensation which have been used for a number of years for extracting gasoline from casing-head natural gas, and has not heretofore been described in the literature.

A description of the methods employed in the manufacture of casing-head gasoline and a discussion of tests to determine whether a natural gas contains enough gasoline to warrant the installation of an extracting plant is contained in Bulletin 88 and Technical Paper 87.

Deterioration in the Heating Value of Coal during Storage. H. C. PORTER AND F. K. OVITZ. Bulletin 136. 28 pp. Paper, 10 cents.

Absorption of Methane and Other Gases by Coal. S. H. KATZ. Technical Paper 147. 16 pp. Paper, 5 cents.

Laboratory Determination of the Explosibility of Coal Dust and Air Mixtures. J. K. CLEMENT AND J. N. LAWRENCE. Technical Paper 141. 27 pp. Paper, 10 cents. "The laboratory method described in this paper is capable of measuring the inflammability of the least inflammable dusts that will propagate an explosion in the mine. A relation has been established between the results of tests on a large scale at the experimental mine and the results of laboratory tests, so that it is now possible to determine from laboratory tests alone whether or not a given dust may give rise to or propagate explosions."

BUREAU OF STANDARDS

Rules and Regulations Promulgated under Authority of the Federal Standard-Barrel Law. Circular 71. Issued September 18, 1917. 7 pp.

Some Unusual Features in the Microstructure of Wrought Iron. H. S. RAWDON. Technologic Paper 97. 25 pp. Paper, 5 cents. Issued September 20, 1917.

An Aneroid Calorimeter for Specific and Latent Heats. N. S. OSBORNE. Scientific Paper 301. 24 pp. Issued September 13, 1917. Paper, 10 cents. The calorimeter here described has been designed primarily for the measurement of the specific heats and latent heats of a certain class of materials adapted for use in the production of artificial refrigeration. These materials include ammonia, carbon dioxide, sulfur dioxide, methyl chloride, and ethyl chloride. At temperatures where the thermal properties are of importance to the engineer the vapor pressures of these materials range from less than 1 atmosphere to over 70 atmospheres.

Effects of Heat on Celluloid and Similar Materials. H. N. STOKES AND H. C. P. WEBER. Technologic Paper 98. 37 pp. "In 1907, at the request of the Steamboat-Inspection Service, the Bureau of Standards made a careful study of the literature of celluloid and other pyroxylin plastics and afterwards carried out an investigation of their properties with special reference to the hazard connected with their use and transportation. The results of the work are given in detail in this paper. In view of the present widespread interest in nitrocellulose products it seemed desirable to publish this paper, even though no account is taken in it of any advances that may have been made since 1908."

DEPARTMENT OF AGRICULTURE

The Presence of Arsenic in Hops. W. W. STOCKBERGER AND W. D. COLLINS. Department Bulletin 568. 7 pp. Issued August 8, 1917. Paper, 5 cents.

The By-Products of Rice Milling. J. B. REED AND F. W. LIEFSNER. Department Bulletin 570. 16 pp. Issued August 11, 1917. Paper, 5 cents.

Articles from the Journal of Agricultural Research

Effect of Three Annual Applications of Boron on Wheat. F. C. COOK AND J. B. WILSON. 10, 591-597 (September 17).

Energy Values of Hominy Feed and Maize Meal for Cattle. H. P. ARMSBY AND J. A. FRIES. 10, 599-613 (September 17).

Study of the Proteins of Certain Insects with Reference to Their Value as Food for Poultry. J. S. McHARGUE. 10, 633-637 (September 17).

Formation of "Black Alkali" (Sodium Carbonate) in Calcareous oils. J. F. BREAZEALE. 10, 541-590 (September 10).

Quassia Extract as a Contact Insecticide. N. E. McINDOO AND A. F. SIEVERS. 10, 497-531 (September 3).

Some Factors Affecting Nitrate-Nitrogen Accumulation in Soil. P. L. GAINES AND L. F. METZLER. 11, 43-63 (October 8).

Occurrence of Manganese in Insect Flowers and Insect Flower Stems. C. C. McDONNELL AND R. C. ROARK. 11, 77-81 (October 15).

Effect of Sulfur on Different Crops and Soils. O. M. SHEDD. 11, 91-103 (October 22).

Some Notes on the Direct Determination of the Hygroscopic Coefficient. F. J. ALWAY, M. A. KLINE AND G. R. McDOLLE. 11, 147-165 (October 22).

BUREAU OF FOREIGN AND DOMESTIC COMMERCE

Report on Cost of Production of Glass in United States. Miscellaneous Series Publication No. 60. 430 pp. Paper, 35 cents. A report on conditions in glass industry and cost of production in its various branches. Ninth of series of reports issued by Bureau regarding cost of production in different industries. Contains principal cost of production data. In addition, information is given concerning labor and industrial conditions, factory equipment, selling methods, and suggestions regarding better general accounting and more accurate cost-finding methods. A comprehensive bibliography, prepared in the Library of Congress, is appended.

BOOK REVIEWS

Elements of Mineralogy, Crystallography and Blowpipe Analysis.

By ALFRED J. MOSES AND CHARLES LATHROP PARSONS. D. Van Nostrand Co., New York. Price, \$3.00.

This fifth edition is considerably enlarged, and contains several new changes from the preceding editions, which make the volume more valuable to the student and mineralogist. The general arrangement of the volume from a determinative mineralogical standpoint is excellent, and the illustrations, which are most satisfactory, show in nearly all instances very strikingly the points that the authors have wished to emphasize. The volume is not only an excellent textbook for use in colleges and universities, but it makes a very good general book on determinative mineralogy that can be used to advantage in the laboratory and in the field.

While more particular attention is given in this volume to the physical properties of minerals, yet that part of the volume relating to the chemical properties of minerals has been very carefully worked out.

In considering this volume in more detail, Part I, relating to Crystallography, gives a very comprehensive idea of crystallography, and is arranged in such a way that the student should readily obtain a knowledge of this subject that will enable him to use the crystallographic properties of minerals to a considerable extent in their identification. The method of presenting this subject, which is always a rather difficult one, has been done in such an understandable and simple manner that it can be comprehended even without an instructor. A very valuable addi-

tion to the part on crystallography is the chapter relating to crystallo-optics; this is a very much needed side of determinative mineralogy that has too often been eliminated in textbooks on this subject. This chapter shows very careful thought and discrimination in bringing together such material as is necessary to give the student a sufficient knowledge of this subject to aid him in determining minerals, without at the same time burdening him with the more complex phases of optical mineralogy.

Part II on Blowpipe Analysis has also been developed in such a manner that the student can readily get a very clear idea of the various reactions and tests that can be made with the blowpipe in testing the various elements and compounds of which minerals are composed. The use of the spectroscope is not described in any great detail, but sufficient information is given regarding its use to enable the student to identify by a flame test many of the simpler elements that occur in minerals. This method of identification is coming more and more in use, and in the future our determinative mineralogies will include this subject to a still greater extent. Chapters 13 and 14 of Part II are in their arrangement of very great assistance in familiarizing the student with the various reactions that may be expected when certain elements are present in a mineral.

Part III on Mineralogy has been arranged in as comprehensive, complete and instructive manner as one could conceive possible in presenting the subject. The discussions of formations and occurrences add a great deal to the value of this part, and will make the student realize how closely geology and

mineralogy are connected with each other. The grouping of the minerals from an economic standpoint brings out more clearly than any other grouping the relation of mineralogy to our industrial development.

Part IV, on Determinative Mineralogy, gives tables for the determination of the common minerals, which are efficient for the identification of minerals, but are rather complicated in use.

Taking the volume as a whole it is in its present form one that should find very wide use by all who are interested in determinative mineralogy.

JOSEPH HYDE PRATT

Portland Cement Industry. By WILLIAM ALDEN BROWN, Works Manager, Aberthaw and Bristol Channel Portland Cement Co., South Wales. Pp. 153. New York: D. Van Nostrand Co., 1917. Price, \$3.00.

Probably no other industry has had so little written about its practices, in book form, as the Portland cement industry. Numerous articles appear from time to time in the various trade journals upon its many phases, but those who have the knowledge to write a general treatise have either not had the inclination nor the time to write on the subject as a whole.

Ranking with the first eight extractive industries and during the past twenty-five years showing a development quite as spectacular as that of iron and steel, it is peculiar that more books have not been written; the few that have appeared may be counted upon one's fingers.

As a textbook on Portland cement, Meade's "Portland Cement" has been the only one available, although students of the industry were able to find additional data in several other less known treatises. There now appears a book which gives a most comprehensive review of the entire process of cement manufacture and its contents indicate that its author has a thorough knowledge whereof he writes.

It is unfortunate that, in a book of this kind, the author confines himself so strictly to the English view-point and practices, as his former experience in an American plant would permit his making it more general. As his purpose seems to be to spur on his home industry to the adoption and adaptation of more modern practices, this omission may be excused.

In the different chapters the author has brought together many data which have been published in various media from time to time but never before collected. His chapter on "Power Plants" is most thorough and comprehensive.

One feature which should be of interest to American manufacturers is that all operation data are figured on a 5½-day week excepting, of course, that pertaining to the burning department. This is a goal towards which our manufacturers have been striving for several years.

In his chapter on the design and construction of plants, the author utters these words of wisdom, to the truth of which many American investors will subscribe from unpleasant past experiences: "Business men building a cement plant should see that the engineers engaged to design, construct and equip a plant are those who have gained their knowledge after years of practical experience in cement making, and not those who have visited a few cement plants, gleaming information from owners and managers that often proves very expensive to those who have speculated in cement, causing them disappointment and regret at having interested themselves in the industry. Many estimates of engineers have come very wide of the mark, and plants have been turned over to the owners by engineers erecting them, only for the former to find £10,000 to £50,000 must be spent in order to make the changes necessary to a successful, economical operation of the plant."

The book is a welcome addition to the bibliography of the Portland cement industry.

C. N. WILEY

Fats and Fatty Degeneration. By MARTIN H. FISCHER AND MARIAN O. HOOKER. 23 x 16 cm. ix + 155 pp. New York: John Wiley and Sons, 1917. Price, \$2.00.

The chapters are entitled: the argument; on the making of emulsions; on the breaking of emulsions; on the normal fat content of cells; on fatty change (fatty infiltration and fatty degeneration); the adhesive tissues and the fatty secretions; on the natural and artificial production of milk; on the mimicry of mucoid secretion; on the mimicry of some anatomical structures; concluding paragraphs.

From the text the unsophisticated reader will get the impression that the senior author has made valuable contributions to the theory of emulsions. As a matter of fact he has made one contribution which is not sound and he has put forward again a statement which everybody should know is wrong. When oil is emulsified in water by means of a third substance, one has drops of oil each coated by a gelatinous film and, outside of that, water containing some of the emulsifying agent. If we cut down the water sufficiently we shall get a limiting case where we have merely drops of oil surrounded by gelatinous films which then coalesce more or less completely. The authors consider that the emulsifying agent, gum acacia, soap, or something like that, forms a compound with water and that the oil is emulsified in hydrated acacia, hydrated soap, etc. (pp. 21, 29, 38). In so far as an emulsion of oil in water is stabilized by a hydrophilic colloid, there is nothing new about this. The author's contribution is that we are dealing with colloid hydrates and he considers that the colloid must bind all the water. The author offers no evidence for the existence of these alleged compounds for the very simple reason that there are no criteria which these alleged compounds could satisfy.

The author also puts forward the statement that a change in the relative amounts of the water and oil causes an emulsion to change from the oil-in-water to the water-in-oil type (pp. 12, 41, 80, 94). Pickering showed a number of years ago that with kerosene, water, and soap, only one type of emulsion can be obtained, that of oil in water, no matter what the relative amounts of kerosene and water. Pickering's results have been confirmed and generalized since then. It is also interesting to note that the author does not cite Pickering's first paper though he must be familiar with it. It is a little difficult to characterize the author's methods and yet keep within parliamentary limits. It is certainly being over-charitable to say that the author has the unhappy gift of remembering what he has read but of forgetting that he has read it.

The second part of the book on the biological emulsification of fats is interesting but suffers from the double defect that the underlying conception is wrong and that it is impossible to tell from the text just what the author has worked out for himself and what he has appropriated in an absent-minded fashion. The author's books are all interesting reading and this one is no exception; but they should be considered as advertising matter in the guise of scientific fiction.

WILDER D. BANCROFT

Annual Chemical Directory of the United States. By B. F. LOVELACE, Editor. Williams & Wilkins Company, Publishers. Price, \$5.00.

There is a very big need for a book of the kind this title indicates, and the one before us is a start in the right direction.

The essential part of the book consists of two complete lists, one being a list of American manufacturers of chemicals and dealers in chemicals, and the second a list of American manufacturers of and dealers in apparatus and equipment for laboratories and industrial plants. Following this there are: (1) a list of professional chemical firms; (2) a list of Federal, State, Municipal, industrial and professional laboratories; (3) a list of colleges, American and Foreign, offering courses in chemistry; (4)

a list of Experiment Stations; and other lists that might be interesting to the man interested in chemicals, chemistry, or chemical equipment.

This book will no doubt be of great value to anyone who is interested in having these various classified lists, and as the publishers have determined to make the Directory an annual affair, and invite criticism, there is no doubt it will improve greatly from year to year. It is a good start.

The two chief criticisms at present would probably be its lack of completeness, and, to a certain extent, a lack of proportion. It is questionable whether such headings as "Acids, all kinds," "Chemicals, all kinds," "Chemicals, technical," "Chemicals, industrial," have sufficient value to warrant the amount of space devoted to them, particularly as these lists are very far from complete. In the matter of proportion and need of technical supervision, two or three instances will indicate what is meant. If one wants, for example, methylanthranilate, there is a list of five names from which to choose, but if he wants acetate of lime he finds only two names out of the scores making and marketing this product, listed under "Calcium Acetate," and one of these is repeated under "Lime Acetate." Nitre cake is another product that is certainly very generally and widely manufactured in this country, but one finds only one name listed under that heading, and four more under the heading "Cake, Nitre" out of the scores of manufacturers and dealers. On the other hand, if one is interested in chlorine he finds four under that heading, one under the heading "Chlorine, Electrolytic" and twelve under the heading "Chlorine, Liquid," to represent the three or four manufacturers in the United States. It is not quite obvious why these three headings are needed for the one material, "Chlorine," or two headings for "Nitre Cake," or why the headings "Chlorobenzene" and "Monochlorobenzol" are both necessary to indicate one product, all without any cross-references.

It is also interesting to see that there are only five Consulting Chemists listed in New York City. One sometimes gathers the impression that the town is full of them, and it is difficult to see just what basis of selection has been used.

These few samples indicate the direction of criticism that should be carefully considered in preparing succeeding issues. It would be well, also, to have the lists distinguish clearly between manufacturers and dealers.

The book is valuable as it exists, and no doubt will improve yearly.

J. E. TEMPLE

Technical Chemists' Handbook. By GEORGE LUNGE, Ph.D. 2nd Ed. Published by D. Van Nostrand Co., New York City. Price, \$3.50 net.

This second edition of the Technical Chemists' Handbook follows the fifth German edition which appeared in 1914, under the title "Taschenbuch fuer die anorganisch-chemischen Gross-industrie." Originally known as the "Taschenbuch fuer die Sodaindustrie," the subsequent German editions, as in the fourth and fifth, were revised and extended to a wider range of subject.

As set forth in the prefaces, the German work and the English edition, the second of which is the subject of this notice, have retained throughout, as a cardinal feature, such selection of methods of analysis for works control and the testing of market products that acceptable reliability and uniformity may be attained, particularly by the analyst in discussions between buyer and seller. To this end a single analytical process, with few exceptions, is presented. The new methods described in current literature as the result of recent investigations are permitted to replace those tried by long experience only after critical examination with evidence of advantage. This treatment of the

subject matter has developed in the minds of the older practitioners concerned, in the course of the 34 years since the first German edition, a sense of keen regard, almost of indispensability.

The new edition maintains in all respects the high standards set in the older issues and the same principle in the choice of material. Its chief purpose has been to revise the numerical data of the work on the basis of the report for 1916 of the International Committee on Atomic Weights. This has been felt a necessity by the author in view of the significance of such revision in some instances, even for practical purposes. In the matter of contents, as concerns detail and range of subject, the present is identical with the first edition. The general tables led off by the 1916 table of atomic weights contain a compilation covering mainly physico-chemical data, but include also mathematical features and abstracts from the patent laws of all nations. This collection is emphatically of value to the technical chemist and chemical engineer whatever his activities. The special part comprehends a selective analytical method digest for nearly every branch of the alkali, acid and related chemical industries.

The publishers present the work as before in distinctive manual form, in excellent typography and bound in flexible covers.

E. S. JOHNSON

Talks to Platers. By F. C. STANLEY. 16mo. 82 pp. Published by the Bridgeport Branch of the American Electroplaters' Society. Price, 50 cents.

The electroplating industry of to-day is in the midst of a transition from the stage of empiricism and secrecy, to that of scientific research and dissemination of knowledge. Foremost among the agencies in this movement is the American Electroplaters' Society, an educational society with numerous branches, many of which are conducting classes and laboratories. In the conduct of such classes, the importance of a study of the fundamental principles of chemistry cannot be too strongly emphasized.

The first portion of this booklet is therefore very properly devoted to an explanation of the principles of chemistry and the use of chemical formulae, equations, etc. This section of the book contains in clear, condensed form a large amount of useful information. It is difficult to understand, however, why the author uses (though not consistently) such archaic terms as sodic, calcic, ammonic, etc.

The major portion of the book is devoted to a description of methods for the analysis of various plating solutions, in which in general the chemical principles are so simply and clearly stated that with some practice the platers should have no difficulty in obtaining approximate results.

The unpardonable fault of the book is the heterogeneous mixture of metric and English units, *e. g.*, "Dissolve 1 oz. of cyanide in a liter of water," etc. Apparently the author has assumed that although platers are willing and able to learn the principles of chemistry, they are unable to use the metric system. Surely the advantages of the metric system warrant its use throughout, at least up to the point where the composition is determined in grams per liter. If then, as will probably be the case for a long time to come, the plater desires to convert this result to ounces per gallon, it is much easier to use the factor 0.134, than, as recommended by the author, to titrate 18 cc. of 100 gallon, and to divide the result in grams, by 0.835 to obtain ounces per gallon. Incidentally the author has no conception of significant figures, when, *e. g.*, he refers to 0.26508 g. of zinc, or 0.000002 g. nickel. There is no hope for the general adoption of the metric system when its advocates, at times, tangle with it, who should be its advocates, dodge its use on every possible occasion.

WILLIAM BLUM

Examination of Water: Chemical and Bacteriological. By WILLIAM P. MASON. Revised. 5th Ed. vi + 186 pp. 5 × 7 1/4 in. John Wiley & Sons, Inc., New York, N. Y. Cloth, \$1.25 net.

This new edition (fifth) of Professor Mason's excellent little laboratory textbook has been printed from entirely new plates with a heavier, blacker, and therefore more distinct type; this change will be welcomed by all readers since a more readable page has resulted.

In general the new edition follows closely the former editions in arrangement, matter presented and actual text. The book consists of three chapters and two appendices as follows:

CHAPTER I—Introduction, Misconception as to the Character of Water Analysis, Knowledge of the Source of the Sample Necessary (7 pp.).

CHAPTER II—Chemical Examination of Water (112 pp.). Sampling, Sanitary Surveys, Keeping Samples, Reports, Equipment of the Laboratory, Turbidity, Odor, Taste, Temperature, Reaction, Color, Solids, "Compares," Hardness, Chlorine, Nitrites, Nitrates, Free and Albuminoid Ammonia, Required Oxygen, Lead, Copper, Iron, Zinc, Arsenic, Chromium, Phosphates; Analysis Mineral Residue, Manganese, Dissolved Oxygen, Carbon Dioxide, "Putrescibility," "Relative Stability," Lime Value, Soda Value, Free Chlorine, Hypochlorite. Table Conversion parts per million into Grains per U. S. Gallon.

CHAPTER III—Bacteriological Examination of Water (33 pp.). Preparation of Media; Nutrient Broth; Nutrient Gelatine; Sugar Media; Nutrient Agar; Sampling, Sowing Media, etc., Counting Colonies. Gas Forming Bacteria. Tests for *Bacillus coli*, *Bacillus typhosus*. Diagnostic Value of the "Colon Group." Enumeration of Organisms not Bacterial.

APPENDIX A—(12 pp.). Interpretation of a Water Examination.

APPENDIX B—(2 pp.). Method of Treating Oysters for *Bacillus coli*.

INDEX.

The typography, including plates and cuts, is excellent and remarkably free from errors. The text is clearly and forcefully written and the directions easily followed and understood by students. In only one instance has the reviewer found the text confusing; on page 77 are found the directions, "Add 50 cc. of normal NaOH sodium carbonate and proceed as usual."

A full index with cross references adds greatly to the usefulness of the book.

The variations from the last edition consist in the suppression of a few unimportant paragraphs here and there and the insertion of short sentences under various methods, either making them conform more closely to the A. P. H. A. Standard Methods or rendering the methods more easily followed by the student. In the latter respect the fifth edition is a decided improvement over former editions. The methods described are, in most instances, those proposed by the Committee of the American Public Health Association (3rd Ed.). Where the author has deviated from the "Standard" most water analysts will agree that the changes are well advised.

In the chapter devoted to the bacteriological examination of water, it is a pity that Professor Mason has substituted the A. P. H. A. culture media instead of retaining those described in earlier editions of his textbook. The old media are far more reliable and have been repeatedly shown to be superior. Media made from beef extract with the addition of only 0.5 per cent peptone are unreliable for general diagnostic purposes and are not adapted to the study of many waters.

It is also to be regretted that the author, who is one of the most experienced American water experts and is thoroughly conversant with the vagaries of water bacteriology, has not given the beginner a more comprehensive discussion of the

problems confronting the analyst in the interpretation of his bacteriological findings. At the present time, when there is danger of water analysts drifting back to strictly rule-of-thumb methods, a brief outline of the broad field of bacterial water examination and the importance of a knowledge of the characteristics and habitats of the great groups of the misnamed "water bacteria" could have accomplished untold good.

The pages devoted to "hardness" have been materially changed and with the exception of the questionable expediency of determining "alkalinity" with tenth normal HCl, the methods as described are better than before. Especially to be commended is the change in the preparation of the standard calcium chloride solution without the addition of ammonium hydroxide.

Other revisions of importance are to be found under the determination of nitrates, the discussion of the interpretation of results, and in the insertion of new matter such as the estimation of "relative stability" and "putrescibility" by methylene blue, the detection of "free" chlorine by ortho-tolidine and the tabulation of the analytical results of a larger number of typical waters.

There appears in this little manual one of the oversights so frequently encountered in American texts devoted to sanitary problems—the comparison of results obtained by one method of analysis with those obtained by an entirely different one. In this new edition, for example, the author has changed from Ammonia (NH₃) as Free and as Albuminoid Ammonia to Nitrogen (N) as Free and as Albuminoid Ammonia. Yet in the tables of "Compares" the results are the same as in the fourth edition. Again, we find that the time for boiling with permanganate in "Oxygen consumed" has been raised from fifteen minutes to a full thirty minutes' boiling in a casserole. Yet here also the "compares" which are supposed to serve as guides in the interpretation of results have not been recalculated but remain the same as before. One cannot avoid asking oneself the question: "If the results obtained by ten, fifteen and thirty minutes' boiling with permanganate can all be compared, why continue the boiling for the full half hour?" It is true that the author states very definitely that the figures given under "Compares" are to serve as a guide in a very broad way only. Water experts will doubtless find no ground for criticism, for in their diagnosis they consider the analysis as a whole. It must be remembered, however, that beginners and laymen read into these discrepancies evidence of a carelessness in our work, and a laxity in our view-points always difficult to explain.

E. M. CHAMOT

The Aniline Color, Dyestuff and Chemical Conditions from 1914 to 1917. By I. F. STONE.

This volume consists of a series of addresses and articles compiled by Mr. Stone. While a large part of the book consists of Mr. Stone's own addresses on various subjects related to the dyestuff industry, the author has also included other important articles from various sources relating to the same subject. The volume, in fact, is a very welcome and successful attempt to put into permanent form the literature relating to the development of the American Dyestuff Industry, being collated from numerous journals, addresses before societies and organizations and tariff committees. Mr. Stone has done a good piece of work in collecting all this matter together in one volume for the benefit of chemists and all others interested in dyestuffs, and he deserves the thanks of his fellow chemists for his generosity in publishing this book for free distribution among those interested in the subject. This volume will prove a valuable and useful reference book for those connected with the dyestuff industry and for those interested in tariff matters related to this subject.

J. MERRITT MATTHEWS

NEW PUBLICATIONS

By IRENE DEMATTY, Librarian, Mellon Institute of Industrial Research, Pittsburgh

- Agriculture:** *Cyclopedia of Agriculture*. L. H. BAILEY. 4 Vol. New Ed. 4to. Price, \$20.00. The Macmillan Co., New York.
- Analysis:** *An Advanced Course in Quantitative Analysis*. H. FAY. 8vo. 111 pp. Price, \$1.25. John Wiley & Sons, New York.
- Anthocyanin Pigments:** M. WHELDALE. 8vo. 318 pp. Price, \$4.50. C. P. Putnam's Sons, New York.
- Brass:** *The Technical Analysis of Brass and the Non-Ferrous Alloys*. W. B. PRICE AND R. K. MEADE. 12mo. 376 pp. Price, \$3.00. John Wiley & Sons, New York.
- Business Law for Engineers.** C. F. ALLEN. 8vo. 456 pp. Price, \$3.00. McGraw-Hill Book Co., New York.
- Chemistry:** *Laboratory Exercises in Chemistry*. W. A. NOYES AND B. S. HOPKINS. 12mo 91 pp. Price, \$0.60. Henry Holt & Co., New York.
- Chemistry in the Service of Man.** ALEXANDER FINDLAY. 2nd Ed. 8vo 272 pp. Price, \$2.00. Longmans, Green & Co., New York.
- Coal:** *The Elements of Coal Mining*. DANIEL BURNS. 12mo 236 pp. Price, \$1.10. Longmans, Green & Co., New York.
- Commerce:** *History of Commerce and Industry*. C. A. HERRICK. 12mo. 562 pp. Price, \$1.60. The Macmillan Co., New York.
- Correction Tables for Thermodynamic Efficiency.** C. H. NAYLOR. 8vo. Price, 5s. Edward Arnold, London.
- Dyestuffs:** *The Chemistry of Dyestuffs*. M. FORT AND L. L. LLOYD. 8vo. 311 pp. Price, \$2.50. G. P. Putnam's Sons, New York.
- Dynamometers:** *The Management of Dynamometers*. G. W. LUMMIS-PATERSON. 8vo. 292 pp. Price, 5s. Crosby Lockwood & Son, London.
- Earthenware:** *Notes on the Manufacture of Earthenware*. E. A. SANDERMAN. 8vo. 390 pp. Price, 7s. 6d. Crosby Lockwood & Son, London.
- Feeds and Feeding Abridged.** W. A. HENRY AND F. B. MORRISON. 8vo. 440 pp. Price, \$1.75. Henry Morrison Co., Madison, Wis.
- Hydrology:** *The Elements of Hydrology*. A. F. MEYER. 8vo. 374 pp. Price, \$4.00. John Wiley & Sons, New York.
- Inorganic Chemistry.** H. G. BYERS. 8vo. 651 pp. Price, \$2.25. Charles Scribner's Sons, New York.
- Lubricating Engineer's Handbook.** J. R. BATTLE. 8vo. 333 pp. Price, 15s. Charles Griffin & Co., London.
- Machine Design:** *Elements of Machine Design*. O. A. LEUTWILER. 8vo. 607 pp. Price, \$4.00. McGraw-Hill Book Co., New York.
- Materials:** *Textbook of the Materials of Engineering*. H. F. MOORE. 8vo. 204 pp. Price, \$2.00. McGraw-Hill Book Co., New York.
- Mechanical Science Methods.** F. H. SELDEN. 16mo. 76 pp. Price, \$0.60. Maudslay Press, Valley City, N. D.
- Mineral Foote-Notes.** Vol. I, No. 11. Published by Foote Mineral Company, 107 No. 19th St., Philadelphia, Pa.
- Mineral Industry during 1916.** Ed. by G. A. ROUSH. 8vo. 937 pp. Price, \$10.00. McGraw-Hill Book Co., New York.
- Mining:** *Scientific Mining; Modern Ideas*. M. T. McDONOUGH. 8vo. 109 pp. Price, \$3.50. New Publishing Co., Wheeling, W. Va.
- Oils, Fats and Waxes:** *Technical Handbook of Oils, Fats and Waxes*. Vol. I. P. E. FRYER AND F. E. WESTON. 8vo. 279 pp. Price, 9s. Cambridge University Press.
- Organic Chemistry.** H. D. HASKINS. 12mo. 472 pp. Price, \$2.00. John Wiley & Sons, New York.
- Oxy-Acetylene Welding Practice.** R. J. Kuhl. 8vo 110 pp. Price, \$1.00. Acetylene Journal Publishing Co., Chicago.
- Paper:** *Handmade Paper and Its Watermarks*. DAVID HUNTER. 8vo. 22 pp. Technical Association of the Pulp and Paper Industry, New York.
- Smoke Abatement:** *Scientific Treatise on Smoke Abatement*. H. HAMILTON. 8vo 168 pp. Price, 5s. Sherratt & Hughes, London.
- Soils and Fertilizers.** L. J. LYTLETON. 12mo. 288 pp. Price, \$1.10. The Macmillan Co., New York.
- Trade Catalogs:** *Manual of Instructions for Trade Catalog Compilation*. O. A. MORGENTHAU. 4to. 87 pp. Price, \$5.00. Wynkoop Hallenbeck Crawford Co., New York.
- Water:** *Examination of Water; Chemical and Bacteriological*. W. P. MASON. 5th Ed. 12mo 186 pp. Price, \$1.25. John Wiley & Sons, New York.
- Watt and the Steam Age.** J. W. GREST. 8vo. 117 pp. Price, 7s. 6d. St. Bridges Press, London.
- Wood and Other Organic Structural Materials.** C. H. SNOW. 8vo. 428 pp. Price, \$5.00. McGraw-Hill Book Co., New York.

RECENT JOURNAL ARTICLES

- Antimony:** *Production of Electrolytic Antimony from Impure Ores*. W. A. BURR. *Engineering and Mining Journal*, Vol. 104 (1917), No. 18, pp. 789-790.
- Benzol:** *Laboratory Methods for Benzol-Recovery Plant Operation*. F. W. SPERR. *Metallurgical and Chemical Engineering*, Vol. 17 (1917), No. 9, pp. 548-555.
- Bleaching:** *Comparison of Lime and Electrolytic Bleaching*. ALLEN ABRAMS. *Textile World Journal*, Vol. 13 (1917), No. 17, pp. 23-25.
- By-Product Coke Oven Pressure Regulation.** C. H. SMOOT. *Blast Furnace and Steel Plant*, Vol. 5 (1917), No. 11, pp. 503-506.
- Cast Iron—Its Rust Resisting Power.** E. A. AND L. T. RICHARDSON. *The Iron Trade Review*, Vol. 61 (1917), No. 16, pp. 834-835.
- Coal-Tar Pitch.** J. M. WEISS. *The Chemical News*, Vol. 116 (1917), No. 3017, pp. 139-142.
- Color and Color Photography.** C. D. HODGMAN. *Journal of the Cleveland Engineering Society*, Vol. 10 (1917), No. 2, pp. 127-136.
- Copper:** *Development of Copper Converting*. M. W. KREJC. *Engineering and Mining Journal*, Vol. 104 (1917), No. 16, pp. 669-674.
- Corrosion in Refrigerating Plants.** M. A. SALLER. *Power*, Vol. 46 (1917), No. 17, pp. 553-554.
- Electric Melting in the Foundry.** DOUGLAS WALKER. *The Iron Trade Review*, Vol. 61 (1917), No. 19, pp. 994-995.
- Electric Pig Iron in War Times.** ROBERT TURNBULL. *The Iron Trade Review*, Vol. 61 (1917), No. 16, pp. 828-829.
- Elements:** *The Complexity of the Chemical Elements*. FREDERICK SODDY. *The Scientific Monthly*, Vol. 5 (1917), No. 4, pp. 451-462.
- Heat Calculation for Baking and Drying Ovens.** W. S. SCOTT. *The Electric Journal*, Vol. 19 (1917), No. 11, pp. 456-458.
- Hot-Water Heating under Forced Circulation.** C. D. ALLAN. *Power*, Vol. 46 (1917), No. 16, pp. 520-523.
- Iron Atom:** *The Experiences of an Iron Atom*. C. R. STURDEVANT. *Journal of the Cleveland Engineering Society*, Vol. 10 (1917), No. 2, pp. 93-112.
- Leather Belting Maker's Association.** L. W. ARNY. *The Iron Age*, Vol. 100 (1917), pp. 928-929.
- Mechanical Ventilation for Metal Mines.** GEORGE RICE. *Mining and Scientific Press*, Vol. 115 (1917), No. 16, pp. 579-581.
- Metallurgical Smoke:** *The Treatment of Metallurgical Smoke in Japan*. TETSURO KOMAKINE. *Metallurgical and Chemical Engineering*, Vol. 17 (1917), No. 8, pp. 484-486.
- Nitrogen:** *How Do the Warring Nations Obtain Their Nitrogen Supply?* S. NAUCKHOFF. *Metallurgical and Chemical Engineering*, Vol. 17 (1917), No. 9, pp. 525-536.
- Preferential Flotation.** W. SHELLSHEAR. *Mining and Scientific Press*, Vol. 115 (1917), No. 17, pp. 613-617.
- Pulp Wood Resources of Northern Manitoba.** J. A. CAMPBELL. *Pulp and Paper Magazine*, Vol. 15 (1917), No. 43, pp. 1007-1008.
- Radioactivity and Some Advances in Physical Science.** H. H. BARKER. *Metallurgical and Chemical Engineering*, Vol. 17 (1917), No. 8, pp. 486-488.
- Sodium Cyanide:** *The Synthetic Making of Sodium Cyanide*. G. H. CLEVELAND. *Mining and Scientific Press*, Vol. 115 (1917), No. 18, pp. 537-542.
- Sulfite Acid:** *Removing Sulfur Trioxide in Preparing Sulfite Acid*. R. B. WOLF. *Pulp and Paper Magazine*, Vol. 15 (1917), No. 44, pp. 1027-1028.
- Sulfur:** *The Determination of Sulfur in Paper*. E. S. WOODMAN. *Pulp and Paper Magazine*, Vol. 15 (1917), No. 44, pp. 1031-1032.
- Sulfur:** *Effect of Sulfur on Different Crops and Soils*. O. M. SHEDD. *Journal of Agricultural Research*, Vol. 11 (1917), No. 3, pp. 91-101.
- Superheated Steam and Driving Cans.** W. B. LEWIS. *Textile World Journal*, Vol. 13 (1917), No. 17, pp. 27 and 37.
- Varnish:** *The Ingredients of Top Roll Varnish*. JOHN VALENTINE. *Textile World Journal*, Vol. 13 (1917), No. 16, pp. 17-18.
- Viscosity Principle in Beating.** A. B. GREEN. *Paper*, Vol. 21 (1917), No. 1, pp. c and 84.
- Water:** *A Sanitary Interpretation of Water Analysis*. E. C. RICHARDSON. *Journal of the American Engineering Society*, Vol. 10 (1917), No. 2, pp. 13-144.
- Water Gages on Marine Boilers.** W. M. McROBERT. *Power*, Vol. 46 (1917), No. 14, pp. 677-678.
- White Pigments:** *The Future of White Pigments in Great Britain*. A. S. DENNING. *The American Paper Journal*, Vol. 1 (1917), No. 8, pp. 1 and 11.
- Zinc Ore:** *Principles Governing Zinc Ore Deposits*. F. I. NASSON. *Mining and Scientific Press*, Vol. 115 (1917), No. 18, pp. 647-651.
- Zinc Oxide Furnaces.** J. F. CROGAN. *Engineering and Mining Journal*, Vol. 104 (1917), No. 16, pp. 675-680.

NEW JOURNALS

- Journal of the Society of Glass Technology.** Edited by W. E. S. THORP. Quarterly. Price, 2s. 6d. per annum. The Society of Glass Technology, The University, Sheffield.

MARKET REPORT—NOVEMBER, 1917

WHOLESALE PRICES PREVAILING IN THE NEW YORK MARKET ON NOV. 20

INORGANIC CHEMICALS

Acetate of Lime.....	100 Lbs.	6.00	5	6.05
Alum. Ammonia, lump.....	100 Lbs.	4.75	@	5.00
Aluminum Sulfate, high-grade.....	Ton	70.00	@	75.00
Ammonium Carbonate, domestic.....	Lb.	11	@	11 1/4
Ammonium Chloride, white.....	Lb.	14 1/2	@	15
Aqua Ammonia, 26°, drums.....	Lb.	18 1/2	@	19
Arsenic, white.....	Lb.	16	@	16 1/2
Barium Chloride.....	Ton	75.00	@	85.00
Barium Nitrate.....	Lb.	8 1/2	@	11
Barytes, prime white, foreign.....	Ton	28.00	@	30.00
Bleaching Powder, 35 per cent.....	100 Lbs.	1.00	@	1.50
Blue Vitriol.....	Lb.	9 1/2	@	10
Borax, crystals, in bags.....	Lb.	7 1/4	@	8 1/2
Boric Acid, powdered crystals.....	Lb.	13 1/2	@	13 3/4
Bristolone, crude, domestic.....	Long Ton		nominal	
Bromine, technical, bulk.....	Lb.	60	@	65
Calcium Chloride, lump, 70 to 75% fused.....	Ton	30.00	@	35.00
Caustic Soda, 76 per cent.....	100 Lbs.	8.00	@	8.10
Chalk, light precipitated.....	Lb.	4 1/2	@	4 3/4
China Clay, imported.....	Ton	18.00	@	30.00
Feldspar.....	Ton	8.00	@	15.00
Fuller's Earth, foreign, powdered.....	Ton		35.00	
Fuller's Earth, domestic.....	Ton	8.50	@	15.00
Glauber's Salt, in bbls.....	100 Lbs.	1.00	@	1.05
Green Vitriol, bulk.....	100 Lbs.	1.00	@	1.05
Hydrochloric Acid, commercial, 20°.....	Lb.	2	@	2 1/2
Hydrochloric Acid, C. P. conc., 22°.....	Lb.	2 1/2	@	2 3/4
Iodine, resublimed.....	Lb.	3.50	@	3.55
Lead Acetate, white crystals.....	Lb.	17	@	19
Lead Nitrate.....	Lb.		nominal	
Litharge, American.....	Lb.	9 1/2	@	10
Lithium Carbonate.....	Lb.		1 50	
Magnesium Carbonate, U. S. P.....	Lb.	18	@	20
Magnesite, "Calcined".....	Ton	60.00	@	65.00
Nitric Acid, 40°.....	Lb.	9	@	9 1/4
Nitric Acid, 42°.....	Lb.	9 1/4	@	9 1/2
Phosphoric Acid, sp. gr. 1.710.....	Lb.	33	@	37
Phosphorus, yellow.....	Lb.	2.05	@	2.10
Plaster of Paris.....	Lb.	1.50	@	1.70
Potassium Bichromate, casks.....	Bbl.	45	@	46
Potassium Bromide, granular.....	Lb.	1.35	@	1.36
Potassium Carbonate, calcined, 80 @ 85%.....	Lb.	65	@	70
Potassium Chlorate, crystals, spot.....	Lb.	47	@	48
Potassium Cyanide, bulk, 98-99 per cent.....	Lb.		nominal	
Potassium Hydroxide, 88 @ 92%.....	Lb.	82 1/2	@	83 1/2
Potassium Iodide, bulk.....	Lb.		2.90	
Potassium Nitrate.....	Lb.	28	@	30
Potassium Permanganate, bulk.....	Lb.	3.85	@	3.90
Quicksilver, flask.....	75 Lbs.	100.00	@	—
Red Lead, American, dry.....	Lb.	10	@	10 1/2
Salt Cake, glass makers'.....	Ton	28.00	@	30.00
Silver Nitrate.....	Oz.	57	@	60
Soapstone, in bags.....	Ton	10.00	@	12.50
Soda Ash, 58%, in bags.....	100 Lbs.	3.05	@	3.10
Sodium Acetate.....	Lb.	13 1/4	@	13 1/2
Sodium Bicarbonate, domestic.....	100 Lbs.	2.50	@	2.60
Sodium Bichromate.....	Lb.	18 1/2	@	19
Sodium Chloride.....	Lb.	23 1/2	@	24 1/2
Sodium Chloride, commercial.....	Lb.	18	@	19
Sodium Hyposulfite.....	100 Lbs.	1.75	@	1.85
Sodium Nitrate, 95 per cent, spot.....	100 Lbs.	4.70	@	4.75
Sodium Silicate, liquid, 40° Bé.....	100 Lbs.	2.00	@	2.10
Sodium Sulfate, 60%, crystals, in bbls.....	Lb.	34 1/4	@	4
Sodium Bisulfite, powdered.....	Lb.	6 1/4	@	7
Strontium Nitrate.....	Lb.	28	@	30
Sulfur, flowers, sublimed.....	100 Lbs.	4.05	@	4.06
Sulfur, roll.....	100 Lbs.	3.70	@	4.15
Sulfuric Acid, chamber, 66° Bé.....	Ton	35.00	@	38.00
Sulfuric Acid, oleum (fuming).....	Ton	55.00	@	60.00
Talc, American white.....	Ton	15.00	@	18.00
Terra Alba, American, No. 1.....	100 Lbs.	85	@	90
Tin Bichloride, 50°.....	100 Lbs.	20.25	@	20.75
Tin Oxide.....	Lb.	68	@	68 1/2
White Lead, American, dry.....	Lb.	9	@	9 1/2
Zinc Carbonate.....	Lb.	35	@	36
Zinc Chloride, commercial.....	Lb.	10 1/2	@	11
Zinc Oxide, American process XX.....	Lb.	14	@	15

ORGANIC CHEMICALS

Acetanilid, C. P., in bbls.....	Lb.	70	@	75
Acetic Acid, 56 per cent, in bbls.....	Lb.	11	@	11 1/2
Acetic Acid, glacial, 99 1/2%, in carboys.....	Lb.	35	@	36
Acetone, drums.....	Lb.	35	@	36
Alcohol, denatured, 180 proof.....	Gal.	82	@	84

Alcohol, sugar cane, 188 proof.....	Gal.	5.25	@	5.40
Alcohol, wood, 95 per cent, refined.....	Gal.	1.30	@	1.35
Amyl Acetate.....	Gal.	5.25	@	5.50
Aniline Oil, drums extra.....	Lb.	26	@	27
Benzoic Acid, ex-toluol.....	Lb.	2.50	@	2.75
Benzol, Pure.....	Gal.	45	@	46
Camphor, refined in bulk, bbls.....	Lb.	74 1/2	@	75
Carbolic Acid, U. S. P., crystals, drums.....	Lb.	53	@	54
Carbon Bisulfide.....	Lb.	7 1/2	@	8
Carbon Tetrachloride, drums, 100 gals.....	Lb.	16	@	16 1/2
Chloroform.....	Lb.	63	@	65
Citric Acid, domestic, crystals.....	Lb.	72	@	73
Cresote, beechwood.....	Lb.	1.90	@	2.00
Cresol, U. S. P.....	Lb.	18	@	20
Dextrine, corn (carloads, bags).....	Lb.	7	@	7 1/2
Dextrine, imported potato.....	Lb.	18	@	20
Ether, U. S. P. 1900.....	Lb.	31	@	39
Formaldehyde, 40 per cent.....	Lb.	18 1/2	@	19
Glycerine, dynamite, drums included.....	Lb.	69	@	70
Oxalic Acid, in casks.....	Lb.	45	@	46
Pyrogallie Acid, resublimed, bulk.....	Lb.	3.25	@	3.50
Salicylic Acid.....	Lb.	1.30	@	1.35
Starch, cassava.....	Lb.	—	@	—
Starch, corn (carloads, bags) pearl.....	100 Lbs.	6.30	@	6.40
Starch, potato.....	Lb.	13	@	14
Starch, rice.....	Lb.	10	@	12
Starch, sago flour.....	Lb.	6	@	6 1/2
Starch, wheat.....	Lb.	5 1/4	@	6 1/2
Tannic Acid, commercial.....	Lb.	80	@	95
Tartaric Acid, crystals.....	Lb.	78 1/2	@	79

OILS, WAXES, ETC.

Beeswax, pure, white.....	Lb.	54	@	60
Black Mineral Oil, 29 gravity.....	Gal.	13 1/2	@	14
Castor Oil, No. 3.....	Lb.	25 1/2	@	26
Ceresein, yellow.....	Lb.	16	@	17
Corn Oil, crude.....	Lb.	—	@	—
Cottonseed Oil, crude, f. o. b. M.U.....	Gal.	1.30	@	1.35
Cottonseed Oil, p. a. y.....	Lb.	18 1/2	@	19
Menhaden Oil, crude (southern).....	Gal.	—	@	—
Neat's-foot Oil, 20°.....	Gal.	2.25	@	2.30
Paraffin, crude, 118 to 120 m. p.....	Lb.	8	@	8 1/2
Paraffin Oil, high viscosity.....	Gal.	29 1/2	@	30
Rosin, "F" Grade, 280 lbs.....	Bbl.	6.80	@	7.00
Rosin Oil, first run.....	Gal.	42	@	43
Shellac, T. N.....	Lb.	48	@	49
Spermaceti, cake.....	Lb.	25	@	—
Sperm Oil, bleached, winter, 38°.....	Gal.	1.70	@	1.72
Spindle Oil, No. 200.....	Gal.	24	@	25
Stearic Acid, double-pressed.....	Lb.	23	@	24
Tallow, acidless.....	Gal.	1.55	@	1.60
Tar Oil, distilled.....	Gal.	31	@	33
Turpentine, spirits of.....	Gal.	49 1/2	@	50

METALS

Aluminum, No. 1, ingots.....	Lb.	36	@	37
Antimony, ordinary.....	Lb.	13 1/2	@	14
Bismuth, N. Y.....	Lb.	2.85	@	2.90
Copper, electrolytic.....	Lb.	23 1/2	@	—
Copper, lake.....	Lb.	23 1/2	@	—
Lead, N. Y.....	Lb.	6 1/2	@	6 1/2
Nickel, electrolytic.....	Lb.	55	@	56
Platinum, refined, soft.....	Oz.	105.00	@	—
Silver.....	Oz.	85 1/4	@	86
Tin, Straits.....	Lb.	72	@	73
Tungsten (W.O.).....	Per Unit	24.00	@	26.00
Zinc, N. Y.....	Lb.	8	@	8 1/4

FERTILIZER MATERIALS

Ammonium Sulfate.....	100 Lbs.	7.00	@	—
Blood, dried, f. o. b. Chicago.....	Unit	6.10	@	6.15
Bone, 3 and 50, ground, raw.....	Ton	32.00	@	35.00
Calcium Cyanamid.....	Unit of Ammonia		nominal	
Calcium Nitrate, Norwegian.....	100 Lbs.		—	
Castor Meal.....	Unit	—	@	—
Fish Scrap, domestic, dried, f. o. b. works.....	Unit	6.65	@	10
Phosphate, acid, 16 per cent.....	Ton	16.00	@	18.00
Phosphate rock, f. o. b. mine:				
Florida land pebble, 68 per cent.....	Ton	3.15	@	3.25
Tennessee, 78-80 per cent.....	Ton	5.50	@	6.00
Potassium "muriate," basis 80 per cent.....	Ton	330.00	@	350.00
Pyrites, furnace size, imported.....	Unit		nominal	
Tankage, high-grade, f. o. b. Chicago.....	Unit	5.90	@	10

DAVIS, C. W. The Industrial Chemistry of Chile and Chilean Products.....	670
DAVIS, C. W. The Composition of Loganberry Juice and Pulp.....	1043
DAVIS, C. W. Studies on the Phenoldisulfonic Acid Method for Determining Nitrates in Soils.....	290
DEAN, J. D. and H. TAYLOR. Analytical Control of the American Oxidation Process.....	1106
DEAN, J. D. and H. K. BENSON. Low Temperature Fractionation of Lignite Coal.....	946
The Free Carbon Wood-Tar Pitch.....	141
DEMATTEY, I. L. F. New Publications.....	1159
115, 221, 329, 439, 541, 633, 727, 823, 919, 999, 1081.....	
DE WABLE, A. The Manufacture of Linoleum and Its Valuation, 623; Correction.....	321
DORMEUS, C. Charles Marchand. Obituary.....	370
DOVER, M. V. and J. W. MARDEN. The Thermal Values of the Fats and Oils. II—The Sulfuric Acid or Mauméné Number.....	858
DOWD, I. E. and F. E. HALE. Thermocline Studies at Kensico Reservoir.....	370
DOWNS, C. R. and J. M. WEISS. The Determination of Phenol in Crude Carboic Acid and Tar Oils.....	569
DRAKE, E. S. On Analyzing Chemicals. Note to Council of A. C. S. by California Section of A. C. S.....	109
DREYFUS, W. Alois Von Isakovics. Obituary.....	716
DUNBAR, P. B. and W. D. BIGELOW. Acid Content of Fruits.....	762
DUNSTAN, A. E. and P. B. TAYLOR. The Pyrogenesis of Hydrocarbons. Part II—General Considerations.....	888
DURAND, H. The Detection of Added Water in Milk.....	44
DUREX CHEMICAL CORPORATION. Per M. TOCH. Durex Barium Plant Burned. Note.....	414
See Plant Precautions. Editorial.....	337
EAUGH, W. C. Potash and a World Emergency.....	688
EDDY, H. P. Industrial Waste Disposal.....	696
EDWARDS, J. D. Determination of Gas Density.....	790
EDELHOFF, G. and J. E. ZANETTI. Aromatic Hydrocarbons from the Thermal Decomposition of Natural Gas Condensate.....	474
The Thermal Decomposition of Benzene.....	350
AND R. J. MOORE. The Cracking of an Aromatic Base Oil. The Temperature Factor at Constant Rate under Pressure.....	40
EISENHART, M. F. The Handling and Transportation of Babcock EKROTH, C. V. An Improved Tabular Arrangement for Chemical Factors.....	980
AND L. P. BROWN. Chemical Quality of New York City Market Milk.....	169
Relation of the Fat in Milk to the Solids-Not-Fat, 297; Note, 417. See Race.....	299
ELYOVE, E. A Method for the Colorimetric Estimation of Small Amounts of Fat in Milk.....	416
A Note on the Detection and Estimation of Small Amounts of Methyl Alcohol.....	953
EOFF, J. R., Jr. Levulose the Preponderant Sugar of Apple Juices.....	295
ERKSON, E. J. A New Method of Separating Zinc from Cadmium and the Latter's Determination Iodometrically.....	587
ESTES, C. A New Qualitative Test and Colorimetric Method for the Estimation of Vanillin.....	671
EVENSON, O. L. The Correction Required in Applying the Babcock Formula to the Estimation of Total Solids in Evaporated Milk.....	142
AND C. H. BIESTERFELD. A Study of the Estimation of Fat in Condensed Milk and Milk Powders.....	499
1111	
FAHRENWALD, F. A. New Alloys to Replace Platinum.....	590
FAHRELY, W. H., R. E. LEE and F. H. REICHEL. Phosphor-Tin. A Volumetric Method for Its Analysis.....	663
FERGUSON, J. B. The Determination of Iron in Glass Sand, 941. See Correction, P. Gelstharp.....	1074
FERGUSON, J. B. The Determination of Iron in Glass Sand. Correction, P. Gelstharp.....	957
FINE, C. G. Chemical Composition vs. Electrical Conductivity.....	34
Greeting from the Electrochemists. Address, Chemical Exposition FLANDERS, F. F. The Use of a Condenser to Prevent Arcing in Bomb Calorimeters.....	1006
FOX, C. P. Effect of Copper on Crude Rubber.....	390
FOX, P. J. Chemical Control of Ammonia Oxidation.....	1092
FRANCIS, C. K. and C. W. CRAWFORD. The Detection and Determination of Sulfur in Petroleum.....	737
AND D. G. MORGAN. The Determination of Fat in Certain Milk Products.....	479
FRAZER, J. C. W., W. W. HOLLAND and E. MILLER. A New Method for the Recovery of Salts of Potassium and Aluminum from Mineral Silicates.....	861
FRY, W. H. and E. C. SHOREY. The Influence of Calcite Inclusions on the Determination of Organic Carbon in Soils.....	935
FULLER, A. V. Technological Automatic Device for Rapidly Washing Pipettes.....	588
A Simple Improvised Apparatus for Hydrogen Sulfide Precipitation under Pressure.....	1046
792	
GARDINER, R. F. and E. C. SHOREY. The Action of Solutions of Ammonium Sulfate on Muscovite.....	589
GATES, W. D. The Manufacturers' Dependence on Ceramic Research. Dedication New Ceramic Engineering Building, University of Illinois.....	91
GELSTHARP, P. F. The Determination of Iron in Glass Sand. Correction, 1074. See Ferguson.....	941
CERICKS, W. F. Nitrate Determinations in the Presence of Chlorides.....	585
GILL, A. H. Color Tests for Oils—Palm Oil.....	136
Notes upon Oil Testing.....	136
GILBERT, H. W. Emulsions and Suspensions with Molten Metals.....	31
AND E. L. MACK. Ferro-Uranium.....	342
GOFF, B. C. Y. The Influence of Potassium Proteins and Its Relation to the Solution of Tin by Canned Foods.....	144
GOTT, E. J., P. L. BLUMENTHAL, A. M. PETER and D. J. HEALY. A Method of Ashing Organic Materials for the Determination of Potassium.....	753
GORTSCH, F., O. H. KLEIN and J. H. LINE. Determination of Mineral Fillers in Rubber. Aniline Method.....	740
GRABER, H. T. The Rennetic Properties of Pepsin.....	1125
GRAFF, J. H. Technological Photography and Its Use in Industrial and Commercial Organizations.....	1052
GREENFIELD, M. and W. N. SKOURUP. Seasonal Distribution of Soil and Fecal Strains of the Colon-Aerogenes Group in Surface Waters, 675. See Letters.....	989
GREGG, E. T. An Improved Compensator for Gas Analysis.....	528
GRIGNARD, V. A. France and a Scientific Use.....	1142
Translation from French by L. H. Bakeland.....	321
GROVER, N. C. Richard Bryant Dole. Obituary.....	776
GYZANDER, C. R. Determination of the Explosibility of Pyrites as well as Its Available Sulfur and the Sulfur Content of Its Cinders.....	
HAPP, R. C. and E. H. SCHWARTZ. A Practical Revision of the Croci-Nitrite Method for the Determination of Potash, 785; Correction.....	909
HAINES, C. J. and J. W. MARDEN. A Method for the Determination of Alcohol.....	1126
HALE, F. E. and J. E. DOWD. Thermocline Studies at Kensico Reservoir.....	370
HALL, W. T. Standard Methods of Chemical Analysis, Edited by Wilfred W. Scott. (Book Review).....	917
HAMMOND, G. T. Some Remarks on the Biochemical Treatment of Sewage with Special Reference to the Activated Sludge Method.....	399
HAND, A. N. Opinion on the Burchenal Patent No. 1,135,351, Case of Procter and Gamble Co. vs. Berlin Mills Co.....	1146
HANDS, H. E. and A. W. HIXSON. Some Relations of the Effect of Oxygenation to Certain Physical and Chemical Properties of Asphalts.....	651
HANDY, J. O. The Founder's Manual. A Presentation of Modern Foundry Operations for the Use of Foundrymen, Foremen, Sturgeons and Apprentices, by Davis W. Payne. (Book Review).....	917
HARKINS, W. D. Life and Personality of Dr. Stieglitz. Editorial.....	118
HART, R. The Analysis of Sulfated Oils.....	850
HARTMAN, B. G. and L. M. TOLMAN. Vinegar Investigation. A Study of the Changes that Occur in Vinegar during Fermentation and Prolonged Storage and Its Subsequent Conversion into Vinegar in Rotating Generators.....	759
HAWLEY, L. F. Discontinuous Extraction Processes.....	866
Statutes of the State of Kansas.....	58
HAYNES, W. G. Handling a Standard Solution of Barium Hydrate.....	705
HAYNES, W. P. The New Zinc Fields of Kansas-Oklahoma. Address HEALY, D. J., P. L. BLUMENTHAL, A. M. PETER and E. J. GOTT. A Method of Ashing Organic Materials for the Determination of Potassium.....	753
HENDRICE, E. Merchandise Control Laboratories.....	1133
The Chemical Development at Berlin, N. H.....	793
HERTY, C. H. Again I say "America for Americans." Reply to article by A. Smith.....	332
A German-English Dictionary for Chemists, by Dr. M. Patterson. (Book Review).....	422
The Battle of the American Chemical Industries. Address, Chemical Exposition.....	1005
The Opening of the National Association of Retail Druggists (Formal Opening of the New Chemical Laboratory, University of Cincinnati).....	608
UNSIGNED EDITORIALS:	
America for Americans.....	224
A Noteworthy Contribution.....	546
A Reversible Failure to Cooperate.....	336
A Timely Proposal.....	1086
An A. C. S. Pin for Every Member.....	1085
An Advance in Advertising Rates.....	445
An Appeal to the National Association of Retail Druggists.....	547
An Appeal to the Wives and Daughters of Chemists.....	122
An Embarrassment of Riches.....	4
An Institute for Analytical Research.....	448
An Open Letter to the House of Representatives.....	638
Another Phase of Cooperation.....	228
Another Possible Form of Cooperation between Universities and the Chemical Industry.....	547
Announcement Concerning Letters of Criticism.....	922
Announcement Concerning Washington Letter.....	731
Annual Meeting American Chemical Society.....	2
Aviation and the Chemist.....	228
British Control of Platinum.....	3
By Way of Introduction.....	332
Chemical Abstracts Again in the Saddle.....	224
Chemical Statistics Assured.....	637
Chemistry and the War.....	1004
Chemists and Preparedness.....	1084
Chemists and the Country's Crisis.....	828
Chemists and War Service.....	636
Concerning the Exposition of Chemical Industries.....	638
Dr. E. F. Roeber.....	676
Expanding Nitrate Plants.....	227
Explosives and Dyestuffs.....	122
Financial Support of the National Research Council.....	544
First Place to Government Needs.....	226
Friendly Confirmation of a Policy.....	446
Government Nitrogen Fixation Plans.....	730
Greeting to the House of Representatives.....	731
Hail to Branigan!.....	121
In Search of One's Own.....	228
Intellect Conquers Appetite.....	544
No Tootle Company for Chemists.....	226
Investments for Wartime Profits of the Chemical Industries.....	446
Legislation for Electrochemical Industries at Niagara.....	730
Licenses for the Preparation of Synthetic Drugs Subject to Foreign Patents.....	731
Neglected Resources.....	121
"Neither Fish, Nor Flesh, Nor Good Red Herring".....	228
No Nichols Medal This Year.....	544
No Tootle Company for Chemists.....	226
Permanent Progress.....	827
Plant Precautions.....	337
Platinum Conservation in France.....	828
Press and Publishers for Local Sections of the American Chemical Society.....	546
Prospective Enlargement of Chemists' Club Building.....	442
Spring Meeting American Chemical Society.....	731
Status of Chemists in Hospital Units.....	548
The Boston Chapter Revived.....	
The Canadian Chemical Journal.....	

HERTY, C. H. UNSIGNED EDITORIALS (concluded):	545	KELSEY, V. V. Building a Complete Cycle of Chemical Expositions on the Illinois State Fair Grounds. Extracts from Address, Chemical Exposition . . .	1023
The Chemist as a Railway Industrial Agent . . .	1084	KERK, C. Discussion. Dedication New Ceramic Engineering Building, University of Illinois . . .	96
The Chemist, the Draft and Patriotism . . .	732	KIRBY, W. S. The Development of Our Export Trade. Extracts from Address, Chemical Exposition . . .	1018
The Color Trade Journal . . .	1148	KINGSLEY, F. W. Development of Chemical Industries in Southern California since January 1, 1916 . . .	391
The Exposition and the Chemical Industry . . .	448	KLEIN, O. H. The Chemist in the Service of the City of New York. Public Service Symposium . . .	79
The Greatest Chemical Library in the World . . .	732	J. H. LANGE AND J. GOTTSCH. Determination of Mineral Fillers in Rubber, Aniline Method . . .	140
The New Advertising Manager . . .	4	KNOER, E. S. AND L. G. WESSON. Wet Combustion in the Nitrosite Combustion Method for the Direct Determination of Rubber . . .	139
The New Press and Publicity . . .	120	KOBEL, F. A. Improvements in the Copper Method for Estimating Amino Acids . . .	50
The Niagara Situation . . .	544, 1085	KOES, O., AND G. C. McNAUGHTON. Further Studies on a Numerical Expression for the Color as Given by the Ives-Tin Photometer . . .	282
The Platinum Situation . . .	1004	AND ALFRED SILVERSTEIN. Some Observations on the Influence of Humidity on the Physical Constants of Paper . . .	277
The September Meeting . . .	1004	LANGMUIR, A. C. The Twitchell Process and the Glycerine Trade. Perkin Medal Award . . .	195
The Slacker Ring Again . . .	636	LATOPPE, C. A Simple Device for the Automatic and Intermittent Washing of Precipitates . . .	527
The Tariff Commission and Schedule A . . .	447	LEE, R. E. AND M. G. MELLON. A Study of Certain Ferments with a View to Determining the Method for the Differentiation of the Various Kinds of Milk. I.—Reductases . . .	360
The Tariff Commission's Exception . . .	447	W. H. FEELY AND F. H. REICHEL. Phosphor-Tin and a Volumetric Method for Its Analysis . . .	663
The Willard Gibbs Medal Award . . .	1002	LEFMAN, H. L. Water-Metals of the Chemical and Allied Industries in LEMMAIRE, R. France during the War . . .	229
Toluol, Toluol and Then Toluol . . .	1084	LENIER, V. AND M. P. SCULTZ. The Recovery of Molybdenum Residues . . .	684
Useless Work for the Chemist to Cease . . .	1086	LEWIS, R. H. AND C. S. KEEVE. Effect of Exposure on Some Fluid Residues . . .	743
Worms Will Never Cease . . .	1128	LINDMUTH, J. R. AND W. J. O'BRIEN. The Fertilizer Value of City Waste. I.—The Composition of Carbonaceous Residues . . .	49
ISSA, B. C. "Doing Our Bit." Address at Mass. Inst. of Tech. . .	1008	LINKE, J. H. Fillers in Rubber, Aniline Method . . .	140
Introductions to National Research Council and U. S. Tariff Commission Addresses, Chemical Exposition . . .	337	LIPMAN, C. B. Some Observations on the Present Status of the Subject of the Availability of Nitrogen in the Chemistry of Wood Decay . . .	189
The American Chemical Society and the Nation. A. C. S.'s Board of Directors . . .	504	LISSE, M. W. AND R. E. ROSS. Introductory . . .	284
HINBARD, P. L. A Study of the Determination of Potash, Chiefly Concerned with the Lindo-Gladding Method . . .	716	LITTLE, A. D. The Chemist. Symposium: The Chemist and the Banker. Chemical Exposition . . .	1027
HILLBRAND, W. F. Our Analytical Chemistry and Its Future. Address, 170 F. Editorial, 122. See also Brinton . . .	449	LLOYD, J. U. Reply on Behalf of the American Chemical Society, University of Cincinnati . . .	606
HIRSCH, A. Japan Starts Its Dyeing Industry . . .	170	LODGE, F. S. Report of Committee on Sampling, Fertilizer Division, A. C. S. . .	1071
HIXSON, A. W. AND H. E. HANDS. Some Relations of the Properties of Overheating to Certain Physical and Chemical Properties of Asphalts . . .	651	LOESCH, H. G. AND S. A. TUCKER. The Influence of Superimposed Alternating Current on the Electrodeposition of Nickel . . .	841
Hochstetter, R. Presentation of the Building, at the Formal Opening of the New Chemical Laboratory, University of Cincinnati . . .	604	LOMAN, E. L. The Pyrogenesis of Hydrocarbons. Part I—Historical and Bibliographical . . .	879
HODGSON, M. B. The Photomicrography of Paper Structure . . .	782	LOWENSTEIN, A. On the Incomplete Hydrogenation of Cottonseed Oil. See Letters . . .	719
HOPKINS, W. H. The Utilization of Ammonium Chloride by Yeast . . .	148	MACK, E. L. AND H. W. GILBERT. Ferro-Uranium . . .	342
HOLLAND, W. W. J. C. W. FRAZER AND E. MILLER. A New Method for the Recovery of Salts of Potassium and Aluminum from Mineral Silicates . . .	935	MACINTYRE, W. H. AND L. G. WILLIS. A Rapid Method for the Determination of Lime as Calcium Sulfate . . .	1114
Hood, J. P. Factors Causing Variation in the Yield of Camphor in the Florida Camphor Tree . . .	552	MACLAURIN, R. C. Address of the 55th Meeting American Chemical Society, Boston, Mass. . .	922
HOOPER, C. B. Steam Inspection in Connection with the Operation of Sewage Treatment Works . . .	398	MACLEOD, G. M. A Practical Method for Determining the Viscosity of Starch for Mill Purposes . . .	597
HOSKINS, H. R. Literature of the Nitrogen Industries, 1912-1916, 424; Correction . . .	720	MAGRIDER, E. W. The Action of Calcium Carbonate on Acid Phosphate . . .	155
HOUSEMAN, P. A. Glue for Use on Aeroplanes . . .	356	MAIR, C. H. AND H. E. PATTEN. An Apparatus for the Purification of Mercury . . .	600
HOUSER, D. F. Concerning Manufacturing of Phthalic Acid and Phthalic Anhydride. Note . . .	1148	MARDEN, J. W. AND C. J. HAINES. A Method for the Determination of Alcohol . . .	787
HOWE, H. E. Chemical Industry in Canada. Address . . .	548	MARDEN, J. W. AND C. J. HAINES. The Thermal Values of the Fats and Oils . . .	858
The German Alarm Clock. Address . . .	417	MARDEN, ORTH AND HASTINGS CO., INC. per R. S. BICKNELL. An Explosion of an Aniline Stripping . . .	1141
Howe, M. AND A. SILVERMAN. The Deposition of Silver Films on Glass . . .	1032	MATTHEWSON, E. The Importance of the Plotation Process in the Metallurgy of Copper. Metallurgical Symposium . . .	1058
HUBBARD, W. S. The Identification of Emodin-Bearing Drugs . . .	518	MATTHEWSON, E. M. The Aniline Color, Dyeing and Chemical Conditions from 1914 to 1917, by L. F. Stone. (Book Review) . . .	1158
HUGHES, W. S. AND C. E. SWETT. Spontaneous Combustion of Oleic Acid. Outline of Iron. Note . . .	623	MELBRIE, R. S. Government Publications . . .	1073
HULME, G. A. AND J. H. CAPPS. Coal Distillation under Pressure . . .	927	MCCABE, C. R. The Analysis of Antimond Lead . . .	423
HUMPHREY, C. J., S. P. ACREE AND E. J. PIERCE. On the Effect of a Wood-Destroying Fungus of Maplewood Cressote and of Some of Its Constituents and Derivatives, together with a Comparison with Beechwood Cressote . . .	566	MCHARGUE, J. S. An Improved Form of Featureless Digestion Apparatus . . .	686
The Chemical Composition of the Higher Fractions of Maplewood Cressote . . .	462	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
HUMPHREY, L. W. AND B. P. BROOKS. The Oxidation of Mineral Oils by Air. I.—The Effect of Sulfur on the Oxidation of Hydrocarbons with Particular Reference to Asphalt . . .	746	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
The Preparation of Ethylene Glycol . . .	750	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
ILLINGWORTH, C. B., G. L. KELLEY AND F. B. MYERS. The Determination of Tantalum in Alloy Steels . . .	852	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
INGERSOLL, E. C. A Modification of the Price Method of Separation of the Permitted Coal-Tar Colors to Include Tartrazine . . .	953	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
ITTSKY, E. F. The Twitchell Process in the Soap and Candle Industry. Perkin Medal Award . . .	196	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JAMES, C. C. Reversion of Acid Phosphate . . .	852	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JAYNE, D. W. Coal Tar and Ammonia, by G. Lunge. (Book Review) . . .	215	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JAYSON, R. AND R. E. OESPER. The Influence of Added Substances on the End-Point in the Iodometric Titration of Hydrogen Sulfide . . .	975	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JOHNSON, E. S. Technical Chemists' Handbook, by G. Lunge. (Book Review) . . .	1157	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JOHNSON, M. G. Ganguense as a Cause of the Depression of the Assimilation of Iron by Pineapple Plants . . .	873	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JOHNSTON, J. The Vapor Pressure and Volatility of Several High-Boiling Metals—A Review . . .	1096	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JONES, M. M. AND H. C. BENSON. Tannin Content of Pacific Coast Conifers . . .	1016	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JONES, G. The Tariff Commission and Its Operation with Reference to the Chemical Schedule. Address, Chemical Exposition . . .	604	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JONES, L. W. Reply on Behalf of the Department of Chemistry at the Formal Opening of the New Chemical Laboratory, University of Cincinnati . . .	770	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE, J. S. Manual for the Essence Industry, by Erich Wal . . .	918
JORDAN, S. A Comparison of American and Oriental Storax . . .	756	MCHARGUE,	

MILNER, H. D. Recent Developments in Chemical Engineering Equipment.....	161	PRANKE, E. J. The Valuation of Water-Soluble vs. Citrate-Soluble Phosphoric Acid.....	54
MILNER, H. J. C. W. FRAZER AND W. W. HOLLAND. A New Method for the Recovery of Salts of Potassium and Aluminum from Mineral Silicates.....	935	PRATT, J. H. Elements of Mineralogy, Crystallography and Blow-pipe Analysis from a Practical Standpoint, by A. J. Moses and C. L. Parsons. (Book Review).....	1155
MOFFITT, G. W. A New, Direct-Reading Precision Refractometer, with Uniformly Divided Scale.....	305	PRICE, W. B. Analysis of Spelter. Supplementary Note from the Committee on Analysis of Non-Ferrous Alloys, Division of Industrial Chemists and Chemical Engineers.....	621
MOHLMAN, F. W. Copper in Sewage at the New Haven Sewage Effluent Station, C. and C. FRANCIS. The Determination of Fat in Solvents on Tars in the "Free Carbon" Determination.....	1093	PROBECK, E. J., M. V. SEATON AND G. B. SAWYER. Varnish Analysis and Varnish Control. II—Viscosity of Varnishes.....	35
MONROE, C. S. AND H. J. BRODERSON. Some Effects of Certain Solvents on Tars in the "Free Carbon" Determination.....	1100	QUINN, R. J. On Fuller's Earth and Its Valuation for the Oil Industry. See Letters.....	909
MOORE, H. K., G. A. RICHTER AND W. B. VAN ARSDEL. The Incomplete Hydrogenation of Cottonseed Oil, 451; Correction, 623. See Letter.....	719		
MOORE, R. J. AND C. EGLOFF. The Cracking of an Aromatic Base Oil. The Temperature Factor at Constant Rate under Pressure.....	40		
MORGAN, D. C. AND C. K. FRANCIS. The Determination of Fat in Certain Milk Products.....	861		
MORLEY, E. W. Early Researches in Hydrogen and Oxygen. Medal Address. Willard Gibbs Medal Award.....	616		
MORV, V. H. Introductory Address. Willard Gibbs Medal Award.....	616		
MUNROE, C. E. Explosives, by A. Marshall. (Book Review).....	822	RACE, J. Relation of the Fat in Milk to the Solids-Not-Fat. See Letters.....	416, 417
MYERS, F. B. AND C. B. ILLINGWORTH. The Determination of Tantalum in Alloy Steels.....	852	RALSTON, O. C. AND L. D. YUNDT. Chemicals Used in Ore Flotation. Metallurgical Symposium, Boston Meeting, A. C. S.....	1058
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	1047	READ, T. T. The Analysis of Copper and Its Ores and Alloys, by G. L. Heath. (Book Review).....	220
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	586	REDMAN, L. V., A. J. WEITH AND F. P. BROCK. Printing Plates from Phenol Resin Compounds.....	388
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	924	REEVE, C. S. AND R. H. LEWIS. Effect of Exposure on Some Fluid Bitumens.....	763
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100	REICHEL, F. H., W. H. FROELY AND K. E. LEE. Phosphor-Tin and a Volumetric Method for Its Analysis.....	643
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423	REID, E. A. Notes on the Analysis of Cast Nicrome.....	488
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814	REILLY, E. A. AND A. G. BLAKELEY. Some Data on Sperm Oils Used for Burning Purposes.....	1099
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253	RICHARDS, J. W. Recovering the Phosphoric Acid Evolved in the Metallurgical Symposium, Boston Meeting, A. C. S.....	1056
NICHOLS, J. B. An Asbestos Stopper.....	1047	RICHARDSON, W. D. Tentative Standard Methods for the Sampling and Analysis of Commercial Fats and Oils, Other than Those of the Coconut, Butter and Lined Groups.....	1148
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586	RICHERT, F. T. The Chemistry of Earth and Its Valuation for the Oil Industry, 599; Correction, 624. See Letters.....	909
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924	RICHTER, G. A., H. K. MOORE AND W. B. VAN ARSDEL. The Incomplete Hydrogenation of Cottonseed Oil, 451; Correction, 623. See Letters.....	719
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100	RITTMAN, W. F. One Billion Gallons of Synthetic Gasoline in 1918.....	528
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100	ROON, L. AND R. E. OESPER. A Contribution to the Theory of Emulsification Based on Pharmaceutical Practice—I.....	156
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423	ROSE, R. E. AND M. W. LEBER. The Chemistry of Wood Decay. Paper. I—Introductory.....	284
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814	ROSENGARTEN, C. D. Unpreparedness. Presidential Address, New York Meeting American Institute of Chemical Engineers.....	202
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253	ROSENTHAL, J. H. The Art of Coloring Glass.....	734
NICHOLS, J. B. An Asbestos Stopper.....	1047	ROSS, W. H. The Extraction of Potash from Silicate Rocks—II.....	467
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586	ROSS, W. A. R. MERZ. The Recovery of Water-Soluble Potash as a By-Product in the Cement Industry.....	1035
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924	ROSS, W. A. R. Modified Method for the Determination of Fluorine with Special Application to the Analysis of Phosphates.....	1114
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100	J. N. CAROTHERS AND A. R. MERZ. The Use of the Cottrell Precipitator in Recovering the Phosphoric Acid Evolved in the Volatilization Method of Treating Phosphate Rock.....	26
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100	RUDNICK, P. Report of Committee on Research and Methods of Analysis, Fertilizer Division, A. C. S.....	1071
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423	AND R. D. COOKE. On the Recovery of Molybdenum.....	109
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814	RYAN, J. H. Advantages of Softened Water in Laundry Work.....	397
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047		
NICHOLS, M. A. Note on the Phenolsulfonate. A Method for Nitrates in Waters High in Magnesium Salts.....	586		
NICHOLS, W. H. Address. 55th Meeting American Chemical Society, Boston.....	924		
NORTH, C. O. Address. 55th Meeting American Chemical Society, Boston.....	100		
NOYES, W. A. Coal Analysis. Final Report of the Joint Committee of the American Society for Testing Materials and the American Chemical Society.....	100		
NEISCH, A. C. Modern Chemistry and Its Wonders, by G. Martin. (Book Review).....	423		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	814		
NESTLÉ, R. C. AND J. ANDERSON. The Nature of Cement Mill Potash, 646; Correction.....	253		
NICHOLS, J. B. An Asbestos Stopper.....	1047</		

SHOUB, H. L. AND E. B. PHELPS. The Determination of Nitrate in Sewage by Means of Ortho-Tolidine.	767	VAN ARSDEL, W. B., G. A. RICHTER AND H. E. MOORE. The Incomplete Hydrogenation of Cottonseed Oil, 451; Correction, 623. See Letters.	719
SHURY, P. McG. A Study of the Volumetric or Pemberton Method for Determining Phosphoric Acid, with Some Experiments Showing the Influence of Temperature and the Sulfuric Acid Radical on Results.	367	VAWTER, W. E. A Note on Silicon-Coated Metal.	580
Some Suggestions Concerning the Preparation of Ammonium Chloride Solution and the Determination of Insoluble Phosphoric Acid.	1045	WAGNER, C. R. AND W. H. ROSS. A Modified Method for the Determination of Fluorine with Special Application to the Analysis of Phosphates.	1116
SILVERMAN, A. A New Illuminator for Microscopes.	971	WALDSTEIN, P. J. AND H. A. SCHOLZ. A Rapid Method for the Determination of Water-Soluble Arsenic in Lead Arsenate.	682
Similarity of Vitreous and Aqueous Solutions.	33	WALKER, E. C., SR. On the Substitution of Potchloric Acid for Chloro-Platinic Acid in the Determination of Potassium. Note.	810
AND E. M. HOWE. The Deposition of Silver Films on Glasses.	1032	WALKER, H. S. A Simplified Inversion Process for the Determination of Sucrose by Double Polarization.	490
SILVERSTEIN, P. AND O. KRESS. Some Observations on the Influence of Humidity on the Physical Constants of Paper.	277	WALKER, P. H. AND F. W. SMITH. Comparative Tests of Chemical Glassware.	1090
SKINNER, P. C. The Western Chemical Manufacturing Company's Chemical Course, 1913. See Editorial.	638	WALKER, W. H. Mass Inst. of Tech. School of Chemical Engineering Practice: A Year's Experience.	1087
SKINNER, W. W. AND W. F. BAUGHMAN. The Removal of Barium from Brines Used in Manufacture of Salt.	18	WEIDLEIN, E. R. Recent Developments in Connection with the Use of Sulfur Dioxide in Hydrometallurgy. Metallurgical Symposium, Boston Meeting, A. C. S.	1057
SKIRROW, F. W. The Estimation of Phenol in Crude Carbolic Acid and in Coal-Tar Oils.	1102	WEISS, J. M. AND C. R. DOWNS. The Determination of Phenol in Crude Carbolic Acid and Tar Oils.	569
SKOURUP, W. N. AND M. CRIENFIELD. Seasonal Distribution of Soil and Fecal Strains of the Colon-Aerogenes Group in Surface Waters, 675. See Letters.	989	WEITH, A. J., L. V. REDMAN AND F. P. BROCK. Printing Plates from Phenol Resin Compounds.	388
SMITH, H. K. AND S. F. ACKRE. A Study of Commercial Beechwood Creosote.	332	Synthetic Phenol Resins. See Letters.	207
SMITH, F. W. AND P. H. WALKER. Comparative Tests of Chemical Glassware, 1913. See Editorial.	275	WELLS, A. E. An Investigation of the Wet Titration Process.	872
SMITH, F. W. AND P. H. WALKER. Comparative Tests of Chemical Glassware, 1913. See Editorial.	1090	WELLS, H. L. Engineering Chemistry, T. B. Stillman. (Book Review)	422
STEARNS, O. A Useful Distilling Head.	972	WESNER, J. A. AND G. L. TELLER. The Chemical Composition of Commercial Glucose and Its Digestibility, 812. See Browne.	810
STEVENS, K. K. The Inspection and Testing of Trinitrotoluene.	801	WESSON, L. G. Carbon Dioxide Absorption Apparatus.	59
STIEGLITZ, J. Address at Opening Session, Kansas City Meeting, American Chemical Industry and the American Chemical Society. Address, Chemical Exhibition.	443	AND E. S. KNORR. Wet Combustion in the Nitrosite Combustion Method for the Direct Determination of Rubber.	139
AND C. L. PARSONS. War Service of Chemists. Announcements.	1005	WEST, F. O. The Manufacture of Picric Acid from the Medical Standpoint.	303
SUTHER, J. M. A Model of the Burtell and Oberfell Apparatus for the Analysis of Illuminating Gas.	730	WESTERN CHEMICAL MANUFACTURING COMPANY: Industrial Course, 1913. See Editorial.	638
SWEENEY, O. R. AND H. E. OUTCAULT. The Determination of Sulfur Dioxide, 949; Correction.	972	WHITTELL, J. C. The Effect of Exposure on Commercial Limes.	287
AND E. R. WILSON. Chemical Examination of Natural Brines.	1148	WHITAKER, M. C. Our Nitrogen Demand and Supply in the Event of War. Letters, 203, 204. See Childs.	322
SWETT, C. E. AND W. S. HUGHES. Spontaneous Combustion of Oleic Acid Containing Iron. Note.	671	AND W. R. CROWELL. The Effect of Temperature and Duration of Reaction on the Formation of Light Oils in Coal Carbonization at Atmospheric Pressure.	261
	623	WHITE, A. H. Fellowships in Chemical Engineering, 1917-18, Graduate School, University of Michigan. Note.	207
TAUSSIG, F. W. The American Coal-Tar Products Industry Production to be Ascertained by the U. S. Tariff Commission. Note, 148. See Editorial.	1084	WILEY, C. N. The Portland Cement Industry, by W. A. Brown. (Book Review)	1156
TAYLOR, G. B. AND J. D. DAVIS. Analytical Control of the Ammonia Oxidation Process.	1106	WILEY, H. W. The Chemist in the Public Service. Public Service Symposium.	81
TEPPE, J. E. Annual Chemical Directory of the United States, Edited by B. F. Lovelace. (Book Review).	1156	WILEY, J. A., G. L. KELLEY AND J. R. ADAMS. A Convenient Apparatus for Electrometric Titration Depending on the Change of Oxidation Potential, and Its Application to the Determination of Small Quantities of Chromium in Steel.	780
TETTER, G. L. AND J. A. WESNER. The Chemical Composition of Commercial Glucose and Its Digestibility, 812. See Browne.	810	WILL, R. T. Cooperation in Industrial Research Work. Note.	322
TING, C. W. Potash from Incinerator Ash of the Northwest.	472	WILLIS, L. G. AND W. H. MACINTYRE. A Rapid Method for the Determination of Lime as Calcium Sulfate.	1114
THOLE, F. B. AND A. E. DUNSTAN. The Pyrogenesis of Hydrocarbons. Part II—General Considerations.	888	WILSON, C. P. AND C. O. YOUNG. A Method for the Determination of the Volatile Oil Content of Citrus Fruits.	959
THOMAS, E. O. Insoluble Phosphoric Acid in Organic Base Gases.	865	WINSLOW, C. P. Kiln Drying of Wood. Letter, 1073. See Editorial.	826
THOMPSON, G. W. The Human Side of the Development of Chemical Industry. Presidential Address, New York Meeting American Institute of Chemical Engineers.	181	WITHROW, J. R. Elements of Industrial Chemistry, by A. Rogers. (Book Review)	821
The Progress of American Chemical Engineering. Address, Chemical Exposition.	1007	Nitric Acid Sophistication. A Serious Production Menace, 771; Correction	1148
TULLOTSON, E. W., JR. On the Relation between the Physical Properties and Chemical Composition of Glass. VII—Etch Figures.	937	Transactions of the American Institute of Chemical Engineers. (Book Review)	220
TOCH, M. Durex Barium Plant Burned. Note, 414. See Plant Precautions. Editorial.	337	AND H. OUTCAULT. The Determination of Sulfur Dioxide, 949; Correction	1148
TOLMAN, L. M. AND B. G. HARTMAN. Vinegar Investigation. A Study of the Changes that Cider Undergoes during Fermentation and Prolonged Storage and Its Subsequent Conversion into Vinegar in Rotating Generators.	759	AND O. R. SWEENEY. The Chemical Examination of Natural Brines.	671
TOROSSIAN, G. Iodometric Determination of Chlorine in Chlorides	751	WOLMAN, A. Seasonal Distribution of Soil and Fecal Strains of the Colon-Aerogenes Group in Surface Waters. See Letters.	989
TRUOG, E. On the Avidity of Soil Acids. See Letters.	1072	WOOTON, P. Washington Letters. 721, 815, 910, 990, 1074.	1149
TSIROPINAS, F. A Volumetric Method for the Determination of Formic Acid or Formates in the Presence of Hydroxides, Carbonates, Oxalates, Acetates.	1110	YOUNG, C. C. The Legal Status and the Character of Work Done by the Kansas State Board of Health Water and Sewage Laboratory.	708
TSUJIMOTO, M. A Highly Unsaturated Hydrocarbon in Shark Liver Oil. Correction.	109	YOUNG, C. C. AND C. P. WILSON. A Method for the Determination of the Volatile Oil Content of Citrus Fruits.	959
Saturated Hydrocarbons in Basking-Shark Liver Oil.	1098	YUNDT, I. D. AND O. C. RABENOLD. Chemicals Used in Ore Flotation. Metallurgical Symposium, Boston Meeting, A. C. S.	1088
TUCKER, S. A. AND H. G. LOEBER. The Influence of Surface-Related Alternating Current on the Electrodeposition of Nickel.	841	ZANETTI, I. E. AND G. E. BLOFF. Aromatic Hydrocarbons from the Thermal Decomposition of Natural Gas Condensates.	474
TWITCHELL, E. Address of Acceptance. Perkin Medal Award.	194	The Thermal Decomposition of Benzene.	350
The Composition of Menhaden Oil Fatty Acids.	581	ZITKOWSKI, H. F. The Recovery of Potash from Beet-Sugar House Waste Liquors.	692
UTT, C. A. A. AND L. D. BUSHNELL. The Examination of Canned Salmon for Bacteria and Tin.	678		

SUBJECT INDEX

THE JOURNAL OF INDUSTRIAL AND ENGINEERING CHEMISTRY VOLUME IX—1917

ABRASIVE Materials. P. J. Katz. Gov. Pub.	724	1078	AMERICAN CHEMICAL SOCIETY (concluded):		
Acetic Acid from Acetylene. Note		903	<i>Industrial Chemists and Chemical Engineers Division:</i>		
Acetylene Generator. Note		620	Minutes of Business Sessions of New York Meeting. S. H.		
Acetylsalicylic Acid Testing. Note		806	Salisbury, Jr.		622
ADDRESSES. 59, 170, 391, 528, 612, 688, 793, 873, 974, 1048.	1128		Note on Analysis of Spelter. W. P. Price		621
Advertising Manager, The New. Editorial		732	Tentative Standard Methods for the Sampling and Analysis of		
Advertising Rates. An Advance in. Editorial		547	Commercial Fats and Oils, other than those of the Coconut,		
Advertising Rates: Friendly Confirmation of a Policy. Editorial		638	Butter and Linsseed Groups. W. D. Richardson, 1066; Cor-		
Aeroplanes, Glue for Use on. P. A. Houseman		359	rection		1148
Aeroplanes. Note		1065	Local Sections:		
Aeroplanes, Rubber Hose for Use and. P. A. Houseman		356	California Section. Note on Analyzed Chemicals. B. S. Drake		109
Actna Explosives Company Business to be Carried on under Court			Philadelphia Section, Editorial on Growth of. "Hail to Brancgan!"		227
Orders. Note		537	Press and Publicity Committees. Editorial		228
Agricultural Chemistry, Government Publications on. Gov. Pub.		447	54th (Spring) Meeting, Kansas City, April 10 to 14, 1917:		
Agricultural Implements for Portugal. Note		806	Announcement, 208; Editorial		442
Agricultural Machinery and Implements in Use in Palestine. Note		804	Presidential Address. President Julius Stieglitz		443
Agriculture, Department of. Gov. Pub.		113, 320, 324, 420, 540, 627, 915, 997,	Program of Meeting, 413; Program of Papers		532
Air Bath, An Electrically Heated and Controlled. W. P. Schuck		973	55th (Annual) Meeting, Boston, September 10 to 13, 1917:		
Alcohol, A Method for the Determination of. C. J. Haines and J.		1126	Announcement, 807; Editorials		637, 922
W. Marden			Address of Welcome. Richard Cockburn MacLaurin		922
Alcohol, Cetyllic, Preparation of a Wool Fat (Lanolin) Substitute and.		1123	Address. William H. Nichols		924
S. Axelrad			Conference. The Industrial Chemist in War Time		987
Alcohol and Water, Determination of, in Ether for Anaesthesia. R.			Adjourned Meeting with the American Association for the Ad-		985
L. Perkins, 521; Correction		720	vancement of Science, New York City, December 27 to 28, 1916.		
Alcohol, Denatured. The Bootstrap Method Revived. Editorial		447	Program of Papers		108
Alcohol, Domestic. Regulations and Instructions Relating to the			AMERICAN CHEMICAL SOCIETY:		
Manufacture, Redistillation, and Denaturation of. Gov. Pub.		210	32nd General Meeting, Pittsburgh, October 3 to 6, 1917:		
Alcohol from Acetylene. Note		903	General Program, 808; Program of Papers		1070
Alcohol from Wood-Pulp Lyes. Note		906	AMERICAN INSTITUTE OF CHEMICAL ENGINEERS:		
Alcohol, Methyl. A Note on the Detection and Estimation of Small			19th Annual Meeting, New York City, Jan. 10 to 13, 1917:		
Amounts of. E. Elvove		295	Editorial (Intellect Conquers Appetite) on Dr. Bucher's Lecture		121
Alcohol, The Cheap Production of. A. M. Breckler		612	Presidential Address: Unpreparedness. G. D. Rosengarten		202
Aldehydes, A New Reagent for. Note		906	Secretary's Report of Meetings and Excursions. C. Olsen		201
Ales and Beers, American, A Study of. L. M. Tolman and J. G.		627	9th Semi-Annual Meeting, Buffalo, June 20 to 22, 1917:		
Riley. Gov. Pub.			Program of Excursions and Papers		622
Alfalfa Silage, Chemical Studies in Making. C. O. Swanson and E.		997	Secretary's Report of Meetings and Excursions. J. C. Olsen		808
L. Tague. Gov. Pub.		997	AMERICAN LEATHER CHEMISTS' ASSOCIATION: 14th Annual Meeting		
Alizarine Delphinol. Note		905	Atlantic City, June 19 to 21, 1917. Program of Papers		622
Alkali, Origin of. R. Stewart and W. Peterson. Gov. Pub.		907	AMERICAN SOCIETY FOR TESTING MATERIALS: Coal Analysis—		
Alloys, Brass, Cold Work on. Note		805	Report of the Joint Committee of the American Society for Testing		
Alloys: Corrosion of Ingot Iron Containing Cobalt, Nickel, or Copper.			Materials and the A. C. S. W. A. Noyes		100
H. T. Kalmus and K. B. Blake		123	Amino acids, Improvements in the Copper Method for Estimating		
Alloys, New, to Replace Platinum. F. A. Fahrenwald		590	P. A. Kober		501
Alpha-Rays, Gas Analysis by. Note		713	Ammonia and Nitrates in the Soil, Effect of Paraffin on the Accumulation		
Aluminate, Tri-Calcic, The Formation of. E. D. Campbell		943	of. F. L. Gainey. Gov. Pub.		997
Aluminum and Bauxite. J. M. Hill. Gov. Pub.		725	Ammonia Oxidation Process, Analytical control of the. G. B. Taylor		1106
Aluminum and Potassium from Mineral Silicates, A New Method for the			Ammonia Oxidation, The Chemical Control of. P. J. Fox		737
Recovery of Salts of. J. C. W. Frazer, W. W. Holland and E.		935	Ammonia, Sulfate of, in India. Note		903
Miller			Ammoniacal Liquor, Effect of, on Concrete. Note		904
Aluminum Bronze, Hardening of. Note		1144	Ammonium Citrate Solution, Some Suggestions Concerning the		
Aluminum, Effect of Acid on. Note		98	Preparation of, and the Determination of Insoluble Phosphoric		
Aluminum from Iron by Means of Ether, The Separation of. S.			Acid. P. McG. Shuey		1045
Pulkin		951	Ammonium Sulfate, The Action of Solutions of, on Muscovite. R.		589
Aluminum, Melting Scrap. Note		99	F. Gardner and E. C. Shorey		
Aluminum Prices. Note		412	Anaesthesia, The Determination of Alcohol and Water in Ether for.		
Alunite, Psilomelanite, and Titanite, Notes on. E. T. Wherry.		209	R. L. Perkins, 521; Correction		720
Gov. Pub.			Analytical Chemistry, Our, and Its Future. W. F. Hillebrand		170
Alunite Recovery of Potash from. W. H. Waggaman and J. A. Cullen		113	Analytical Chemistry, The Teaching of. P. H. M.-P. Brinton		716
Gov. Pub.			Analyzed Chemicals, Action of California Section of A. C. S. Note		109
America and France in Scientific Union. V. Grignard. Address.		1143	Analyzed Samples, Bureau of Standards' Note		720
Translation by L. H. Baekeland			Anhydride, Phosphoric and Phthalic Acids, Concerning the Manufacture		
America for Americans. Editorial, 224. See, also Again I say "America			of. D. F. Houston. Note		1148
for Americans"			Aniline, A Method for the Colorimetric Estimation of Small Amounts		
American Academy of Engineers. Gov. Pub.		932	of. E. Elvove		953
AMERICAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE:			Antimony Strippers of all. R. Bicknell		720
"Neither Fish, Nor Flesh, Nor Good Red Herring." Editorial		121	Antimonial Lead, Analysis of. C. R. McCabe		42
AMERICAN CERAMIC SOCIETY: 19th Annual Meeting, New York City,			Antimony in 1915. F. L. Hess. Gov. Pub.		628
March 5 to 8, 1917		412	APPARATUS (see separate heading below)		
AMERICAN CHEMICAL:			Argentina, Petroleum Production in. Note		621
Board of Control: The Society and the Nation. B. C. Hesse		337	Arsenates, Toxic Value and Killing Efficiency the. A. L. Lovett		
See Editorial, "A Timely Suggestion"		336	and R. H. Robinson. Gov. Pub.		997
Coal Analysis—Final Report of the Joint Committee of the Amer-			Arsenic, A Rapid Method for the Determination of Water-Soluble in		
ican Society for Testing Materials and the American Chemical			Lead Arsenate. H. A. Scholz and P. J. Waldstein		682
Society. W. A. Noyes		100	Arsenic in Hops, The Presence of. W. W. Stockinger and W. D.		
Editorials (by C. H. Herty except as noted):			Collins. Gov. Pub.		1155
An A. C. S. Pin for Every Member		1086	Arsenic in 1915. F. L. Hess. Gov. Pub.		628
Board of Control: Friendly Suggestions		332	Arsenical Injury through the Bark of Fruit Trees. D. B. Swingle		420
Chemists and Preparedness		332	Asbestos, E. M. J. D. Gov. Pub.		631, 995
Chemists and the Country's Crisis		224	Asbestos, Blue. Note		712
Chemists in Wartime (C. L. Parsons)		730, 826, 1002	Asbestos-Cement Roofing. Note		983
Description of Testing Materials and the American Chemical		2	Asbestos in Hops, The Presence of. W. W. Stockinger and W. D.		714
Election of Officers for 1917		118	Asbestos, Purification of. Note		714
Life and Personality of Dr. Stieglitz (W. D. Harkins)		118	Ash: Utilization of Wood-Ash. W. D. Sterrett. Gov. Pub.		916
New Members: An Embarrassment of Riches		547	Asphalt, Native and Artificial. Note		319
Open Letter to U. S. House of Representatives Concerning the			Asphalt, Native and Artificial. Note		319
General Revenue Bill		4	Asphalt, Native and Artificial. Note		319
Press and Publicity Committees for Local Sections		228	Asphalt, Native and Artificial. Note		319
Press and Publicity Committee of the Society		4	Asphalt, Native and Artificial. Note		319
The Chemist, The Draft, and Petroleum		1085	Asphalt, Native and Artificial. Note		319
Fertilizer Division: Chairman's Address. J. E. Breckenridge		1054	Asphalt, Native and Artificial. Note		319
Report of Committee on Research and Methods of Analysis. P.			Asphalt, Native and Artificial. Note		319
Rudnick		1071	Asphalt, Native and Artificial. Note		319
Report of Committee on Sampling. F. S. Lodge		1071	Asphalt, Native and Artificial. Note		319

[illegible]

Carbonation Studies I—A Mechanical Stirrer for Carbonation	787
Direct in the Bottle. H. E. Patten and G. H. Mains.	787
Catalogue, International, of Scientific Literature. Gov. Pub.	324
Cellulose, The Chemical Engineering.	207
Celluloid and Similar Materials, Effects of Heat on. H. N. Stokes	1155
and H. C. P. Weber. Gov. Pub.	408
Cellulose Cement, A New. Note.	408
Celluloid, Plastic.	1064
Cellulose Ester Lacquers for Leather Trade. Note.	320
Cellulose from Spinach. Note.	1064
Cement from Sugar Beet. Note.	86
Cement, Industrial, Science as an Agency in the Development	98
of. J. P. Beck.	1035
Cement Industry in Japan. Note.	390
Cement Industry, The Recovery of Water-Soluble Potash as a By-	
Product in the. W. H. Ross and R. Merz.	86
Cement, Litharge-Glycerine, The Setting of. H. E. Merwin.	253
Cement Materials, The Volatilization of Potash from. E. Anderson	814
and R. J. Nestell.	818
Cement Mill Practice, The Nature of. R. J. Nestell and E. Anderson,	91
646; Correction.	96
Cement, Normal Portland, Properties of the Calcium Silicates and	1064
Calcium Aluminate Occurring in. P. H. Bates and A. A. Klein.	1144
Gov. Pub.	1079
Cement, Portland, F. Burchard. Gov. Pub.	720
Cement, Portland, U. S. Government Specification for. Gov. Pub.	797
Cement, Prevention of Leakage through. Note.	161
Cement, The Formation of Tri-Calcium Aluminate. Campbell,	1087
Census of Chemicals Other than Dyestuffs, A Regrettable Failure	1090
to Cooperate. Editorial.	1072
Census of Manufactures. General Totals for the U. S. by Geographic	181
Divisions, States, and Industries, 1914, 1909, 1904 and 1899. Gov.	
Pub.	122
CERAMIC ENGINEERING BUILDING, UNIV. OF ILL., DEDICATION OF	1063
Science as an Agency in the Development of the Portland Cement	
Industries. J. P. Beck.	91
The Manufacture of Pottery. Dependence on Ceramic Research.	96
W. Gates.	1064
Discussion. L. E. Barringer, 94; C. H. Kerr.	1144
Ceramic Research, Manufacturers' Dependence on. W. D. Gates.	1079
Ceramics. English China Clay. Note.	720
Ceramics. Note.	797
Ceramics. Pottery in 1916. J. Middleton. Gov. Pub.	161
Cheese, Butter and Condensed Milk. Gov. Pub.	1087
Chemical Abstracts, The Saddle in. Announcement of the Arrival of	1090
Back Numbers of German Journals. Editorial.	1072
Chemical Abstracts, Decennial Index of. C. L. Parsons.	181
Chemical Development at Berlin, N. H. E. Hendrick.	122
Chemical Engineering Education, Recent Developments in. H. J.	1063
Miles.	91
Chemical Engineering Practice, School of, at Mass. Institute of	96
Technology, A Year's Experience. W. H. Walker.	1064
Chemical Glassware, Comparative Tests of. F. H. Walker and F.	1072
W. Smither.	181
Chemical Industry in France, A Society of. Note.	122
Chemical Industry, The Human Side of the Development of. G. W.	1063
Thompson.	91
Chemical Industries of the U. S. and their Relation to National Pre-	96
paredness, The First Report upon. C. A. Browne, 177. See A Note-	1064
worthy Contribution. (Editorial).	1072
Chemical Industries, Irish. Note.	181
CHEMICAL INDUSTRIES, THIRD NATIONAL EXPOSITION OF	122
New York City, September 24-29, 1917. Editorial, 637; Program	1063
and List of Exhibitors, 907. Editorial, 1004; Addresses.	91
Chemical Legislation, but Old. Editorial.	96
See Again I say America for Americans. Editorial.	1064
Chemical Letter by Dr. Andrew Ure. C. A. Browne.	1072
Chemical Manufacture in France. Note.	181
Chemical Societies in New York City. Program for 1917-1918 Season.	122
Chemical Statistics Assured. Editorial.	1063
Chemist and Aviation. Editorial, 826; Note.	91
Chemist, The, as a Railway Industrial Agent. Editorial.	96
Chemist, The Professional Status of. R. B. Borden.	1064
Chemist, The, The Draft and Patriotism. Editorial.	1072
Chemists, American, and War Service, The Present Status of.	181
Chemists and the Country's Crisis. Editorial.	122
Chemists and War Service. Editorial.	1063
Chemists in America: "Doing Our Bit." Address. B. C. Hesse.	91
Chemists in Wartime. In the Light of Experience. Editorial.	96
Chemists' Club Building, Prospective Enlargement of. Editorial.	1064
Chemists Enlisted in the Army and Navy. Editorial. C. L. Parsons.	181
Chemists in Hospital and in the Laboratory. Editorial.	122
Chemists in Wartime. In the Light of Experience. Editorial.	1063
Chemists, War Service of. J. Stieglitz and C. L. Parsons. Editorial.	91
Chemistry. Permanent Progress. Editorial.	96
Chicago Chemical Exposition, A. Spring. Editorial, 1004; Chicago	1063
Exposition Abandoned.	91
Chicle and Chewing Gum, The Industrial Chemistry of. F. Dan-	96
nerth.	1064
China, Coal in.	759
Chlorine in Chlorides, Iodometric Determination of. G. Torossian.	617
Chromite. Note, 408. J. S. Diller. Gov. Pub.	751
Chromium in Steel: A Convenient Apparatus for Electrometric	629
Titration Done on the. Chang. Oxidation Potential, and	
Its Application to the Determination of Small Quantities of Chrom-	
ium in Steel. G. L. Kelley, J. R. Adams and J. A. Wiley.	780
Cider. Vinegar Investigation. A Study of the Changes that Cider	
Undergoes during the Fermentation and Prolonged Storage, and	
Subsequent Conversion into Vinegar in Rotating Generators. B. G.	
Hartman and L. M. Tolman.	759
CINCINNATI UNIVERSITY OPENING OF NEW CHEMICAL LABORATORY.	604
Description of the New Chemical Laboratory.	611
Presentation of the Building. R. Hochstetler.	604
Reply on Behalf of the A. C. S. J. U. Lloyd.	606
Reply on Behalf of the Department of Chemistry. L. W. Jones.	604
The Swing of the Pendulum in Chemistry. H. Herty.	604
Cinnabar and Mercury from New Zealand. Note.	407
Citrus Fruits, A Method for the Determination of the Volatile Oil	
Content of. C. P. Wilson and C. O. Young.	959
Citrus Leaves, Composition of, at Various Stages of Mottling. C. A.	
Heaven. Gov. Pub.	916
Clay and Clay Products. J. Middleton. Gov. Pub.	819
Clay-Working Industries and Building Operations in the Larger	
Cities in 1915. J. Middleton. Gov. Pub.	327
Coal. C. E. Leshner. Gov. Pub.	632
Coal, Absorption of Methane and Other Gases by. S. H. Katz. Gov.	1154
Pub.	
Coal Analysis. Fifth Report of Joint Committee of American So-	
cieties for Testing Materials and A. C. S. W. A. Noyes.	100
Coal and Other Mineral Lands. Congressional Committee Report	
Gov. Pub.	324
Coal Beds, Baked, Shale and Slag Formed by the Burning of. G. S.	
Rogers. Gov. Pub.	421
Coal Carbonization at Atmospheric Pressure, The Effect of Tem-	
perature and Duration of Reaction on the Formation of Light Oils in.	
M. C. Whitaker and W. R. Crowell.	261
Coal Detectors, The Heating Value of.	617
Porter and F. K. Ovtiz. Gov. Pub.	1154
Coal Distillation under Pressure. J. H. Capps and G. A. Hulett.	927
Coal Dust and Air Mixtures, Laboratory Determination of the Ex-	
plosibility of. J. K. Clement and J. N. Lawrence. Gov. Pub.	1154
Coal, Economic Utilization of. Note.	319
Coal Field, The Bull Mountain, Musselshell and Yellowstone Coun-	
ties, Montana. L. H. Woolsey, et al. Gov. Pub.	1153
Coalfields of the United States. General Introduction. M. R.	
Campbell. Gov. Pub.	993
Coalfields, Spitzbergen. Note.	982
Coal Gas, New Method of Extracting Vaporous Constituents from.	
Note.	530
Coal: Geology of the Upper Stillwater Basin, Stillwater and Carbon	
Counties, Montana, with Special Reference to Coal and Oil. W.	
R. Calvert. Gov. Pub.	111
Coal in Canada. Note.	324
Coal Lands. Congressional Committee Report. Gov. Pub.	324
Coal, Lignite, Low Temperature Distillation of. H. K. Benson and	
L. L. Davis.	946
Coal Production, Distribution and Consumption in 1915. C. E. Leshner.	
Gov. Pub.	212
Coal: Rendering Coal Soluble by Ozone. Note.	620
Coal: Smokeless Combustion and By-Product Recovery. Note.	97
Coal-Tar Oils and Crude Carboic Acid, The Estimation of Phenol.	
F. W. Skirrow.	1102
Coal-Tar Products Industry Production, The American, to be Ascer-	
tained by the U. S. Tariff Commission. Note. F. W. Taussig.	1148
Coal-Tar Research. Note.	805
The Primary Products of the Carbonization of. G. B.	
Taylor and H. C. Porter. Gov. Pub.	996
Coals, Illinois, Coking of. F. K. Ovtiz. Gov. Pub.	1154
Coals in the Area between Bon Air and Clifty, Tennessee. C. Butts.	
Gov. Pub.	326
Coals Purchased by the Government during the Fiscal Years 1908 to	
1915, Analyses of. G. S. Pope. Gov. Pub.	628
Cobalt in 1915. F. L. Hess. Gov. Pub.	539
Cobalt, Nickel, or Cobalt, Corrosion of Ingot Iron Containing. H.	
Kalmus and K. B. Blake, 123. See Letters.	414
Cobalt-Nitrite Method for Determination of Potash, A Practical	
Revision of the. R. C. Haff and E. H. Schwartz, 785; Correction.	909
Cocaine and Cocaine, Pharmacological Studies with. A Com-	
parative Investigation of the Effects of Cocaine on Animals and	
in Isolated Organs. G. B. Roth. Gov. Pub.	627
Coconut Industry. Note.	1143
Coke-Fuel for Electric Power Stations. Note.	319
Coke Industry of New South Wales. Note.	318
Coke in 1915. C. E. Leshner. Gov. Pub.	326
Colon-Aerogenes Group in Surface Waters, Seasonal Distribution of	
Soil and Faecal Strains of. M. Greenfield and W. N. Skourup, 675.	989
See Letters.	
Color. Further Studies on a Numerical Expression for, as Given by the	
Ives Tint Photometer. O. Kress and C. C. McNaughton.	282
Color Industry, French. Note.	410
Color Trade. Editorial.	732
COMMERCIAL REPORTS: November (1916), 11; December (1916), 21;	
January (1917), 328; February, 421; March, 540; April, 632; May,	
726; June, 820; July, 916; August, 1079; September.	1080
Concrete, Effect of Atmospheric Liquor on. Note.	900
Concrete. Ferro-Ships. Note.	1144
Concrete, Reinforced, High Tensile vs. Mild Steel for. Note.	621
Condenser-Tube Repairs. Note.	408
Congressional Committee Reports. Gov. Pub.	210, 324, 914
Congressional Committees. Gov. Pub.	210
Controversies: Announcement of Editorial Policy. Editorial.	228
Copper Bullion: The Principles and Practice of Sampling Metallic	
Metallurgical Materials with Special Reference to the Sampling of	
Copper. J. K. Kelley. Editorial.	325
Copper, Effect of, on Crude Rubber. C. P. Fox.	1092
Copper in Sewage at the New Haven Sewage Experiment Station.	
O. W. Mohlman.	1093
Copper Lead, Gold and Silver, The Ores of. C. H. Fulton. Gov.	211
Pub.	996
Copper, Nickel, or Cobalt, Corrosion of Ingot Iron Containing. H. T.	
Kalmus and B. See Blake, 123.	414
Copper Ore at Santa Rita, New Mexico, Prospecting and Mining of.	
D. F. MacDonald and C. Enzian. Gov. Pub.	325
Copper Ore, Japanese. Note.	982
Copper Production (1915). Gov. Pub.	1064
Copper, The, in the States of California and Oregon, by	
Vale, 112; South Dakota, by Henderson, 112; Colorado, by	
Henderson, 112; Utah, by Heikes, 112; Colorado, by Henderson,	
211; Arizona, Montana, and Nevada, by Heikes, 211; Washington,	
by Gerry.	211
Copper. The Importance of the Flotation Process in the Metallurgy of.	
E. P. Mathewson. Gov. Pub.	1058
Cork Used as New Proofing Material. Note.	318
Corn, Improved Apparatus for Use in Making Acidity Determinations	
of. H. B. Besley and W. B. Weston. Gov. Pub.	420
Corrosion and Electrical Properties of Steels. Note.	318
Corrosion, Structure of the Coating on Tinned Sheet Copper in Re-	
sponse to a Specific Case of. P. D. Merica. Gov. Pub.	724
Cotton Production and Distribution, Season of 1915-16. Gov. Pub.	420
Cotton, Sea Island W. A. Orton. Gov. Pub.	324
Cottonseed and Cottonseed Products, Report on. Gov. Pub.	1145
Cottonseed Oil, Industry, Russian. Note.	627
Cottonseed Oil, The Incomplete Hydrogenation of. H. K. Moore,	
and C. A. Richter and W. B. Van Arsdal, 451; Correction, 623. See	
Letters.	719
Cotton Trade in Japan. Note.	1143

Cottrell Precipitator, Use of, in Recovering the Phosphoric Acid Evolved in the Volatilization Method of Treating Phosphate Rock. W. H. Ross, J. N. Carothers and A. R. Merz. Council of National Defense. Gov. Pub. 914, 993, 1077	26	Explosives, The Inflammability of Carbonaceous Dusts. H. H. Brown, 269. H. T. Brown and J. K. Clement. Explosives and Dyestuffs—A French Confirmation. Editoriale 347	347
Council of National Defense. Gov. Pub. 914, 993, 1077	914	Explosives, Industrial Poisons Used or Produced in Manufacture of. A. Hamilton. Gov. Pub. 915	915
Cresote, Commercial Beechwood, A Study of. S. F. Acree. S. F. Acree. 275	275	Explosives, in the United States during the Calendar Year 1916, Production of. A. H. Pay. Gov. Pub. 996	996
Cresote, Crude Wood, A Method of Producing from Hardwood Tar. S. F. Acree and S. F. Acree. 276	276	Explosives, Manufacture of. Gov. Pub. 993	993
Cresote, Maplewood, Chemical Composition of the Higher Fractions of. E. J. Pieper, S. F. Acree and C. J. Humphrey. 462	462	Explosives, Permissible, Tested Prior to Jan. 1, 1917. S. P. Howell. Gov. Pub. 996	996
Cresote, Maplewood, On the Toxicity to a Wood-Destroying Fungus and of Some of Its Constituents and Derivatives, together with a Comparison with Beechwood Cresote. E. J. Pieper, S. F. Acree and C. J. Humphrey. 566	566	Explosives, The Determination of Nitrogen in Substances Used in. W. C. Cope and G. B. Taylor. Gov. Pub. 996	996
Cryoscopic Method, Application of, for Determining Added Water in Milk. J. T. Keister. 862	862	Explosives, The Inspection and Testing of Trinitrotoluene. K. K. Stevens. 801	801
CURRENT INDUSTRIAL NEWS. A. McMillan. 97, 198, 318, 405, 530, 617, 712, 804, 903, 982, 1063, 1143	1143	Explosives, Toluol, Toluol Expod Trade. Toluol Editorial. 1002	1002
Cyanuric Acid, Isolation of, from Soil. L. E. Wise and E. H. Walters. Gov. Pub. 997	997	Export Prohibitions, French. Note. 407	407
DAIRY Products, Detection of Lime Used as a Neutralizer in. H. J. Wichmann. Gov. Pub. 915	915	Exports and Imports, British Engineering. Note. 407	407
Decay Problems, Timber Storage Conditions in the Eastern and Western States. Reference to. C. H. Kerr. 916	916	Exports and Imports, Japanese. Note. 805	805
DEDICATION OF CERAMIC ENGINEERING BUILDING, UNIV. OF ILL. Science as an Agency in the Development of the Portland Cement Industries. J. P. Beck. 86	86	Exports Prohibited by Great Britain—to July 14, 1917. 732	732
Department of Agriculture, Yearbook of. Gov. Pub. 916	916	EXPOSITION OF CHEMICAL INDUSTRIES, THIRD NATIONAL: New York City, September 24 to 29, 1917. Editorial. 637, 1004	637, 1004
Diet: Physiologic Effect on Growth and Reproduction of Rations Balanced from Restricted Sources. E. B. Hart, et al. Gov. Pub. 997	997	Program and List of Exhibitors. 907	907
Digitalis, Wild American, The Activity of. G. B. Roth. Gov. Pub. 628	628	Addresses, Production and Uses, Especially in Relation to the War. G. K. Burgess. 1026	1026
Dole, Richard C. Grover. Obituary. 200	200	American Chemical Industry and the American Chemical Society. J. Steglitz. 1005	1005
Dinking Fountains, Investigation of, at the University of Minnesota. H. A. Whittaker. Gov. Pub. 725	725	Article of the Chemical Industry. Editorial. 1005	1005
Drug Studies, Technical. Gov. Pub. 325	325	Building a Complete Cycle of Chemical Industries on the Cincinnati. V. V. Kelsey. 1023	1023
Drugs, Licenses for the Preparation of Synthetic, Subject to Foreign Patents. Editorial. 730	730	Development of Chemical Industries along the Norfolk and Western Railway. E. A. Schubert. 1025	1025
Drugs: The Ubiquitous Exception. Editorial. 447	447	Development of Oil Export Trade. W. S. Kies. 1018	1018
Drugs, Retail, An Appeal to the National Association of. Editorial. 1085	1085	Greeting from the Electrochemists. C. G. Fink. 1006	1006
Drying and Its Application to the New Humidity-Regulated and Recirculating Dry Kilo, The Theory of. H. D. Tiemann. Gov. Pub. 627	627	Future of Chemical Industry in the United States. L. H. Baekeland. 1020	1020
Drying, Introductory Grants of Cottonseed Flour and Flour Products, Based on the Dry-Matter Content. E. G. Boerner. Gov. Pub. 113	113	National Research Council and U. S. Tariff Commission Addresses. 1008	1008
Dusts, Carbonaceous, Inflammability of. H. H. Brown. 269	269	Introductions to. B. C. Hesse. 1008	1008
Dusts, Carbonaceous, Inflammability of, in the Spheres of Low Oxygen Content. H. H. Brown and J. K. Clement. 347	347	National Research Council, Chemistry Committee. Second Report. 1009	1009
Dye: Chinese Gambier. Note. 409	409	Natural Resources. C. H. Crawford. 1005	1005
Dye Factory, Aniline, New Japanese. Note. 200	200	Progress of American Chemical Engineering. G. W. Thompson. 1007	1007
Dye from Rice Leaves. Note. 619	619	Russia and Its Relationships to the United States. C. H. Boynton. 1022	1022
Dye Industry, British. Note. 904	904	Symposium: The Chemist and the Banker. 1027	1027
Dye, Natural, from Porto Rico. Note. 98	98	The Banker. G. A. O'Reilly. 1028	1028
Dyes: Action of Light on Bright Colors. Note. 1064	1064	Tariff Commission and Its Operation with Reference to the Chemical Schedule. G. Jones. 1016	1016
Dyes: Alizarine Delphinol. Note. 905	905	Tariff Commission and our Chemical Industries. W. S. Culbertson. 1013	1013
Dyes: Modification of the Price Method for the Separation of the Permitted Coal-Tar Colors to Include Tartrazine. E. H. Ingersoll. 955	955	Extraction Processes, Discontinuous. L. F. Hawley. 866	866
Dyes, Korean Vegetable. Note. 1063	1063	Eyes of Industrial Workers, Safeguarding the. 683	683
Dyes: French Color Industry. Note. 410	410	FABRICS, Balloon and Aeroplane, Investigations of. U. S. Rubber Co. Gov. Pub. 209	209
Dyes: Japan Industries. The House of Representatives Committee on the General Revenue Bill. Editorial. 4	4	Fabrics, Relative Worth of Improvements in. Goodyear Tire and Rubber Co. Gov. Pub. 209	209
Dyes: The American Coal-Tar Products Industry Production to be Ascertained by the U. S. Tariff Commission. Note. F. W. Taussig. 1148	1148	Factor, Chemical, An Improved Tabular Arrangement for. C. V. Ekroth. 169	169
Dyeing, The Estimation of the Price of Representatives of in Coal-Tar Oils. F. W. Skirrow. 1102	1102	Fahy Permeameter, An Experimental Study of the. C. W. Burrows and R. L. Sanford. Gov. Pub. 997	997
Dyestuff Industry: Japan Starts Its Dyestuff Industry. A. Hirsch. 449	449	Fat, Bone, Extraction in Germany. Note. 1063	1063
Dyestuffs: America for Americans. Editorial. 224	224	Fat in Certain Milk Products, The Determination of. C. K. Frazer and D. G. Morgan. 861	861
Dyestuffs: America for Americans. Editorial. 332	332	Fat in Condensed Milk and Milk Powders, A Study of the Estimation of. C. H. Biesterfeld and O. L. Eversen. 1111	1111
Dyestuffs Used in U. S., Artificial: Quantity and Value of Foreign Imports and of Domestic Production during Fiscal Year, 1913-14. H. H. Norton. Gov. Pub. 211	211	Fat, Wool (Lanolin), Substitute and Cetyllic Alcohol, Preparation of. S. Axelrad. 1123	1123
Dyestuffs \$20,000,000 Dyestuff Consolidation to Meet Foreign Competition after War. Note. 537	537	Fats, A Method for Fractionating. A. Seidenberg. 855	855
Dynamom, Copper, Aluminum, Zinc and Iron Windings for. Note. 903	903	Fats and Their Economical Use in the Home. A. D. Holmes and H. L. Lang. Gov. Pub. 324	324
EDITORIALS. 2, 118, 224, 332, 442, 544, 636, 730, 826, 922, 1002, 1004, 1084 (See HERTY, C. H. in AUTHOR'S INDEX for Complete List of Titles; Actual Subjects treated are to be found in place in this index.)	1084	Fats, Animal, Studies on the Digestibility of Some. C. F. Langworthy and A. D. Holmes. Gov. Pub. 627	627
Education of the Audubon Sugar School. C. E. Coates. 379	379	Fats, Commercial, Other than Those of the Coconut, Butter and Lined Groups, Tentative Standard Methods for the Sampling and Analysis of. W. D. Richardson, 1066, Correction. 1148	1148
Electrical Conductivity vs. Chemical Composition. C. G. Fink. 34	34	Fats, The Thermal Values of the. II. The Sulfuric Acid or Maumene Number. J. W. Marden and M. V. Dover. 858	858
Electrochemical Industries at Niagara, Legislation for. Editorial. 446	446	Fats, Vegetable, Digestibility of Some. C. F. Langworthy and A. D. Holmes. Gov. Pub. 840	840
Electrolytic Reduction of the Anode Apparatus for Deposition of the Change of Oxidation Potential, and Its Application to the Determination of Small Quantities of Chromium in Steel. G. L. Kelley, J. R. Adams and J. A. Wiley. 780	780	Federal Trade Commission. Gov. Pub. 420	420
Emulsion, Emulsion, The Emulsion of. W. S. Hubbard. 518	518	Feeds, Chemical Composition, Digestibility, and Feeding Value of Vegetable Food Materials and Lumber. Gov. Pub. 113	113
Emulsification Based on a Pharmaceutical Practice, A Contribution to the Theory of. I. L. Roan and R. E. Osper. 156	156	Feeds, Energy Values of Hominy Feed and Maize Meal for Cattle. H. P. Armistead and J. A. Fink. Gov. Pub. 1155	1155
Emulsions and Suspensions with Molten Metals. H. W. Gillett. 967	967	Feeds, Energy Values of Red Clover Hay and Maize Meal. H. P. Armistead, et al. Gov. Pub. 1113	1113
Engine for Motor Boats. Note. 804	804	Feeds, Value of Energy Values in the Computation of Rations for Farm Animals. H. P. Armistead. Gov. Pub. 1185	1185
Engine, Zeppelin. Note. 713	713	Feeds, in 1917. Gov. Pub. 995	995
Engines, Internal Combustion, for Aircraft, Thermodynamic Efficiency of Present Types of. Columbia University. Gov. Pub. 209	209	Relationships in Chemical Engineering. 191-18 Graduate School, University of Michigan. A. H. White. 207	207
Ether, for Anesthesia, The Determination of Alcohol and Water in. L. P. Perkins, S. J. Correction. 730	730	Periments: A Study of certain Periments with a View to Determining A Method for the Differentiation of Pasteurized Milk from Raw Milk. I. Reductions. R. E. Lee and M. G. Mellon. 360	360
Ethylene Glycol, The Preparation of. B. T. Brooks and I. W. Hum. 780	780	Fertilizer Industry. Gov. Pub. 420	420
Evaporation from the Surface of Water and River Bed Materials. R. B. Sleight. Gov. Pub. 997	997	Fertilizer Industry. Note. 1144	1144
Explosion of an Aniline Stripper. R. S. Ricknell. 730	730	Fertilizer Industry. Note. 1165	1165
Explosives, Initiation of. W. Arthur. 992	992	Fertilizer Industry. A. C. Boston Meeting, Sept. 10 to 13, 1917. 1084	1084

Modified Method for the Determination of Fluorine with Special Application to the Analysis of Phosphates. C. R. Wagner and W. H. Ross. Gov. Pub.	116
Fertilizers, Phosphate, for Hawaiian Soils, and Their Availability. E. W. McFarlane. Gov. Pub.	316
Fertilizers, Some Observations on the Present Status of the Subject of the Availability of Nitrogen in. C. B. Lipman. Gov. Pub.	189
Fertilizers: Some Suggestions Concerning the Preparation of Ammonium Citrate Solution and the Determination of	1045
Fluorophoric Acid. C. G. Shuey. Gov. Pub.	903
Fertilizers: Sulfate of Ammonia in India. Note.	322
Fertilizers, The Sampling of. F. S. Lodge, 167; Correction.	1043
Fertilizing Value of Some Household Wastes. P. E. Browning.	1065
Fluorides, Melting Points. Note.	97
Fire Protection on Ships. Note.	337
Fires: Plant Precautions. Editorial.	915
Fishes on West Coast of Florida, Mortality of. H. F. Taylor. Gov. Pub.	409
Flax-Growing Industry. Note.	915
Flotation of Ores, Answers to Question on the. O. C. Ralston. Gov. Pub.	1154
Flotation of Ores, Bibliography. Note.	481
Flotation, <i>et al.</i> Gov. Pub. Jan. to June, 1916, 325; July to Dec., 1916.	1058
Fluorine, Ore, Chemicals Used in. O. C. Ralston and L. D. Yundt.	481
Flotation, Ore, The Theory of. H. P. Corliss and C. L. Perkins.	1058
Flotation Process, The Importance of, in the Metallurgy of Copper. F. P. Mathewson. Gov. Pub.	915
Flour-Mill and Crist-Mill Products. Gov. Pub.	1116
Fluorine, A Modified Method for the Determination of, with Special Application to the Analysis of Phosphates. C. R. Wagner and W. H. Ross. Gov. Pub.	1077
Fluorspar. E. F. Burchard. Gov. Pub.	421
Fly-Destroying Agents, Experimental Studies with Muscicides and Other. E. E. Phelps and A. F. Stevenson. Gov. Pub.	113
Food and Drug Officials, State, Manual of Procedure for Guidance of. J. S. Abbott and H. S. Bailey. Gov. Pub.	540
Food-Coloring Substances, Separation and Identification of. W. E. Mathewson. Gov. Pub.	113
Food: Improving Methods of. Note.	210
Grain, with a Standard Method of Making the Test. E. G. Boerner. Gov. Pub.	187
Food Materials, American, Chemical Composition of. Gov. Pub.	113
Food: The Chemicals in the Canned Food Industry. W. D. Bigelow.	187
Food: The Intrinsic Values of Grain, Cottonseed, Flour and Similar Products, Based on the Dry-Matter Content. E. G. Boerner. Gov. Pub.	113
Food: Utilization of Olive Pomace. W. C. Christie and W. H. Christie. Gov. Pub.	45
Food Value of the Soya Bean. Note.	618
Foods: Experiments in Substitutes. Note.	906
Foods: Syrup, Canning and Preserving.	151
Forestry. Gov. Pub.	324
Formates or Formic Acid, A Volumetric Method for the Determination of, in the Presence of Hydroxides, Carbonates, Oxalates and Acetes. E. Tappin. Gov. Pub.	1110
Formulary, National, and the Pharmacopoeia. Changes in. M. I. Wilbert. Gov. Pub.	627
Fossils, Wasatch, in So-Called Fort Union Beds of the Powder River Basin, Wyoming, and Their Bearing on the Stratigraphy of the Region. C. H. Wegemann. Gov. Pub.	819
France and America in Scientific Union. V. Grignard. Address. Translation by L. H. Backeland.	1143
France, A Society of Chemical Industry.	1072
France Developing Water Power to Aid Industries. Note.	531
France, Report of American Industrial Commission to. A Survey of the Chemical and Allied Industries in France during the War. J. LeMaistre.	229
French Bauxite.	620
French Export Prohibitions. Note.	714
French Resinous Products. Note.	617
French Tungsten. Note.	619
French Union of Chemists. Report of the Committee on Chemistry, General Convention, New York, October 26, 1913.	178
Fruits, The Acid Content of. W. D. Bigelow and P. B. Dunbar.	762
Fruits: The Composition of Loganberry Juice and Pulp. M. R. Daughters. Gov. Pub.	1043
Fuel, Boiler, Natural Gas as a. Note.	904
Fuel Briquetting in 1916. C. E. Lesher. Gov. Pub.	724
Fuel from Peat. Note.	713
Fuel's Earth and Value for the Oil Field. T. G. Richert.	909
599; Correction, 624; Note, 909. See Letters.	996
Fuller's Earth in 1916. J. Middleton. Gov. Pub.	914
Fumigating Gases, The Use of Mechanical Fans to Increase the Efficiency of. Gov. Pub.	620
Furnace, New Electric. Note.	628
Furnaces, Hand-Fired, Combustion in the Fuel Bed of. H. Kreisinger, <i>et al.</i> Gov. Pub.	210
Fuses, Cartridge-Inclosed, Investigation of. Gov. Pub.	419
GALVANOMETERS, A Study of Electromagnet Moving Coil, for Use in Alternating Current Measurements. E. Weibel. Gov. Pub.	409
Gambier, Chinese. Note.	49
Gange. Comparative Fertilizer Value of Its Water. W. J. O'Brien and R. J. Lindemuth.	513
II—Its Composition; The Availability of Its Nitrogen, and Its Use as a Fertilizer. P. J. Schroeder.	628
Gas, A "Compensator" for the Determination of. E. T. Gregg.	713
Gas Analysis, An Improved Compensator for. E. T. Gregg.	142
Gas Analysis by Alpha-Rays. Note.	984
Gas Analysis: The Determination of Gasoline Vapor in Air. R. P. Anderson. Gov. Pub.	211
Gas-Annealing, Furnace, An Advantage for the. Note.	993
Gas: Anticlines in Central Wyoming. C. J. Hares. Gov. Pub.	99
Gas, Artificial, and By-products in 1915. C. E. Lesher. Gov. Pub.	972
Gas, Blast-Furnace, Appliance, from. F. H. Wilcox. Gov. Pub.	715
Gas, Casing-head, Produced from Oil Wells on Restricted Indian Lands, Regulations to Govern Utilization of. Gov. Pub.	949
Gas, Coal, New Method of Extracting Volatile Constituents from. Note.	993
Gas, Coloring Materials. Gov. Pub.	997
Gas Condensate, Natural, Aromatic Hydrocarbons from the Thermal Decomposition of. J. E. Zanetti and G. Egloff.	474
Gas Density, Determination of. J. D. Edwards, 790; Gov. Pub.	518
Gas, Estimation of Benzol in. Note.	984
Gas: Anticlines in the Blackfoot Indian Reservation. Mont. Stebbinger. Gov. Pub.	326
Gas Field, Cleveland, Cuyahoga County, Ohio, with Study of Rock Pressure. G. S. Rogers, 420; Application of Theory of Probability in Estimating Capacity of New Well. C. E. Van Orstrand. Gov. Pub.	629
Gas Field, The Corsicana, Texas. Matson and Hopkins. Gov. Pub.	1153
Gas Field, The De Soto-Red River, La. Matson and Hopkins.	993
Gas Furnaces, Metal-Working. Note.	99
Gas, Illuminating, A New Model of the Burrell and Oberfell Apparatus for the Analysis of. J. R. Suydam, Jr.	972
Gas Mixtures, The Determination of Sulfur Dioxide. O. R. Sweeney.	949
H. E. Outcalt and J. R. Withrow.	993
Gas, Natural, and Petroleum. Structure of the Northern Part of the Bristow Quadrangle, Creek County, Oklahoma. A. E. Fath. Gov. Pub.	993
Gas, Natural, as a Boiler Fuel. Note.	904
Gas, Natural, in 1915. J. D. Northrop. Gov. Pub.	327
Gas Producers, Operating Details of. R. H. Fernald. Gov. Pub.	210
Gases, A Specific Gravity Balance for. D. Edwards. Gov. Pub.	420
Gases, Mine and Industrial, Limits of Complete Inflammability of, Mixtures of, with Air. G. A. Burrell and A. W. Gauger. Gov. Pub.	996
Gasoline, Motor, Properties, Laboratory Methods of Testing, and Practical Specifications. E. W. Dean. Gov. Pub.	1154
Motor Gasoline. Note.	915
Gasoline, Solvent. C. O. North. Gov. Pub.	1038
Gasoline, Synthetic, One Billion Gallons of, in 1918. W. F. Rittman.	528
Gasoline Vapor in Air, The Determination of. R. P. Anderson.	142
Introductory address, W. H. Morley during the Calendar Year 1915, Physical and Chemical Properties of. W. F. Rittman, <i>et al.</i> Gov. Pub.	325
Gelatin. Note.	905
Gem and Precious Stones in 1915. W. T. Schaller. Gov. Pub.	213
Geographic Tables and Formulas. S. S. Gannett. Gov. Pub.	211
Geological Survey: Director's Annual Report.	1072
Geology and Ore Deposits of Ely Nevada. A. C. Spencer. Gov. Pub.	1153
Geology, General, 1916, Shorter Contributions to. D. White. Gov. Pub.	1153
Geology of Massachusetts and Rhode Island. B. K. Emerson. Gov. Pub.	1153
Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico and Utah. H. E. Gregory. Gov. Pub.	1153
German Agriculture, The.	405
Future of German Agriculture. Note.	417
German Alarm Clock, The. H. E. Howe, 59; Correction.	661
Germanium, The Occurrence of, in Missouri and Wisconsin Blendes. C. H. Buchner. Gov. Pub.	1143
Germany, Starch Substitutes in. Note.	618
Germany, Sulfur Supply In. Note.	544
GRASS MEDAL AWARD: 615. Editorial.	616
Introductory address, W. H. Morley during the Calendar Year 1915, Physical and Chemical Properties of. W. F. Rittman, <i>et al.</i> Gov. Pub.	325
Gelatin. Note.	905
Gem and Precious Stones in 1915. W. T. Schaller. Gov. Pub.	213
Geographic Tables and Formulas. S. S. Gannett. Gov. Pub.	211
Geological Survey: Director's Annual Report.	1072
Geology and Ore Deposits of Ely Nevada. A. C. Spencer. Gov. Pub.	1153
Geology, General, 1916, Shorter Contributions to. D. White. Gov. Pub.	1153
Geology of Massachusetts and Rhode Island. B. K. Emerson. Gov. Pub.	1153
Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico and Utah. H. E. Gregory. Gov. Pub.	1153
German Agriculture, The.	405
Future of German Agriculture. Note.	417
German Alarm Clock, The. H. E. Howe, 59; Correction.	661
Germanium, The Occurrence of, in Missouri and Wisconsin Blendes. C. H. Buchner. Gov. Pub.	1143
Germany, Starch Substitutes in. Note.	618
Germany, Sulfur Supply In. Note.	544
GRASS MEDAL AWARD: 615. Editorial.	616
Introductory address, W. H. Morley during the Calendar Year 1915, Physical and Chemical Properties of. W. F. Rittman, <i>et al.</i> Gov. Pub.	325
Gelatin. Note.	905
Gem and Precious Stones in 1915. W. T. Schaller. Gov. Pub.	213
Geographic Tables and Formulas. S. S. Gannett. Gov. Pub.	211
Geological Survey: Director's Annual Report.	1072
Geology and Ore Deposits of Ely Nevada. A. C. Spencer. Gov. Pub.	1153
Geology, General, 1916, Shorter Contributions to. D. White. Gov. Pub.	1153
Geology of Massachusetts and Rhode Island. B. K. Emerson. Gov. Pub.	1153
Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico and Utah. H. E. Gregory. Gov. Pub.	1153
German Agriculture, The.	405
Future of German Agriculture. Note.	417
German Alarm Clock, The. H. E. Howe, 59; Correction.	661
Germanium, The Occurrence of, in Missouri and Wisconsin Blendes. C. H. Buchner. Gov. Pub.	1143
Germany, Starch Substitutes in. Note.	618
Germany, Sulfur Supply In. Note.	544
GRASS MEDAL AWARD: 615. Editorial.	616
Introductory address, W. H. Morley during the Calendar Year 1915, Physical and Chemical Properties of. W. F. Rittman, <i>et al.</i> Gov. Pub.	325
Gelatin. Note.	905
Gem and Precious Stones in 1915. W. T. Schaller. Gov. Pub.	213
Geographic Tables and Formulas. S. S. Gannett. Gov. Pub.	211
Geological Survey: Director's Annual Report.	1072
Geology and Ore Deposits of Ely Nevada. A. C. Spencer. Gov. Pub.	1153
Geology, General, 1916, Shorter Contributions to. D. White. Gov. Pub.	1153
Geology of Massachusetts and Rhode Island. B. K. Emerson. Gov. Pub.	1153
Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico and Utah. H. E. Gregory. Gov. Pub.	1153
German Agriculture, The.	405
Future of German Agriculture. Note.	417
German Alarm Clock, The. H. E. Howe, 59; Correction.	661
Germanium, The Occurrence of, in Missouri and Wisconsin Blendes. C. H. Buchner. Gov. Pub.	1143
Germany, Starch Substitutes in. Note.	618
Germany, Sulfur Supply In. Note.	544
GRASS MEDAL AWARD: 615. Editorial.	616
Introductory address, W. H. Morley during the Calendar Year 1915, Physical and Chemical Properties of. W. F. Rittman, <i>et al.</i> Gov. Pub.	325
Gelatin. Note.	905
Gem and Precious Stones in 1915. W. T. Schaller. Gov. Pub.	213
Geographic Tables and Formulas. S. S. Gannett. Gov. Pub.	211
Geological Survey: Director's Annual Report.	1072
Geology and Ore Deposits of Ely Nevada. A. C. Spencer. Gov. Pub.	1153
Geology, General, 1916, Shorter Contributions to. D. White. Gov. Pub.	1153
Geology of Massachusetts and Rhode Island. B. K. Emerson. Gov. Pub.	1153
Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico and Utah. H. E. Gregory. Gov. Pub.	1153
German Agriculture, The.	405
Future of German Agriculture. Note.	417
German Alarm Clock, The. H. E. Howe, 59; Correction.	661
Germanium, The Occurrence of, in Missouri and Wisconsin Blendes. C. H. Buchner. Gov. Pub.	1143
Germany, Starch Substitutes in. Note.	618
Germany, Sulfur Supply In. Note.	544
GRASS MEDAL AWARD: 615. Editorial.	616
Introductory address, W. H. Morley during the Calendar Year 1915, Physical and Chemical Properties of. W. F. Rittman, <i>et al.</i> Gov. Pub.	325
Gelatin. Note.	905
Gem and Precious Stones in 1915. W. T. Schaller. Gov. Pub.	213
Geographic Tables and Formulas. S. S. Gannett. Gov. Pub.	211
Geological Survey: Director's Annual Report.	1072
Geology and Ore Deposits of Ely Nevada. A. C. Spencer. Gov. Pub.	1153
Geology, General, 1916, Shorter Contributions to. D. White. Gov. Pub.	1153
Geology of Massachusetts and Rhode Island. B. K. Emerson. Gov. Pub.	1153
Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico and Utah. H. E. Gregory. Gov. Pub.	1153
German Agriculture, The.	405
Future of German Agriculture. Note.	417
German Alarm Clock, The. H. E. Howe, 59; Correction.	661
Germanium, The Occurrence of, in Missouri and Wisconsin Blendes. C. H. Buchner. Gov. Pub.	1143
Germany, Starch Substitutes in. Note.	618
Germany, Sulfur Supply In. Note.	544
GRASS MEDAL AWARD: 615. Editorial.	616
Introductory address, W. H. Morley during the Calendar Year 1915, Physical and Chemical Properties of. W. F. Rittman, <i>et al.</i> Gov. Pub.	325
Gelatin. Note.	905
Gem and Precious Stones in 1915. W. T. Schaller. Gov. Pub.	213
Geographic Tables and Formulas. S. S. Gannett. Gov. Pub.	211
Geological Survey: Director's Annual Report.	1072
Geology and Ore Deposits of Ely Nevada. A. C. Spencer. Gov. Pub.	1153
Geology, General, 1916, Shorter Contributions to. D. White. Gov. Pub.	1153
Geology of Massachusetts and Rhode Island. B. K. Emerson. Gov. Pub.	1153
Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico and Utah. H. E. Gregory. Gov. Pub.	1153
German Agriculture, The.	405
Future of German Agriculture. Note.	417
German Alarm Clock, The. H. E. Howe, 59; Correction.	661
Germanium, The Occurrence of, in Missouri and Wisconsin Blendes. C. H. Buchner. Gov. Pub.	1143
Germany, Starch Substitutes in. Note.	618
Germany, Sulfur Supply In. Note.	544
GRASS MEDAL AWARD: 615. Editorial.	616
Introductory address, W. H. Morley during the Calendar Year 1915, Physical and Chemical Properties of. W. F. Rittman, <i>et al.</i> Gov. Pub.	325
Gelatin. Note.	905
Gem and Precious Stones in 1915. W. T. Schaller. Gov. Pub.	213
Geographic Tables and Formulas. S. S. Gannett. Gov. Pub.	211
Geological Survey: Director's Annual Report.	1072
Geology and Ore Deposits of Ely Nevada. A. C. Spencer. Gov. Pub.	1153
Geology, General, 1916, Shorter Contributions to. D. White. Gov. Pub.	1153
Geology of Massachusetts and Rhode Island. B. K. Emerson. Gov. Pub.	1153
Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico and Utah. H. E. Gregory. Gov. Pub.	1153
German Agriculture, The.	405
Future of German Agriculture. Note.	417
German Alarm Clock, The. H. E. Howe, 59; Correction.	661
Germanium, The Occurrence of, in Missouri and Wisconsin Blendes. C. H. Buchner. Gov. Pub.	1143
Germany, Starch Substitutes in. Note.	618
Germany, Sulfur Supply In. Note.	544
GRASS MEDAL AWARD: 615. Editorial.	616
Introductory address, W. H. Morley during the Calendar Year 1915, Physical and Chemical Properties of. W. F. Rittman, <i>et al.</i> Gov. Pub.	325
Gelatin. Note.	905
Gem and Precious Stones in 1915. W. T. Schaller. Gov. Pub.	213
Geographic Tables and Formulas. S. S. Gannett. Gov. Pub.	211
Geological Survey: Director's Annual Report.	1072
Geology and Ore Deposits of Ely Nevada. A. C. Spencer. Gov. Pub.	1153
Geology, General, 1916, Shorter Contributions to. D. White. Gov. Pub.	1153
Geology of Massachusetts and Rhode Island. B. K. Emerson. Gov. Pub.	1153
Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico and Utah. H. E. Gregory. Gov. Pub.	1153
German Agriculture, The.	405
Future of German Agriculture. Note.	417
German Alarm Clock, The. H. E. Howe, 59; Correction.	661
Germanium, The Occurrence of, in Missouri and Wisconsin Blendes. C. H. Buchner. Gov. Pub.	1143
Germany, Starch Substitutes in. Note.	618
Germany, Sulfur Supply In. Note.	544
GRASS MEDAL AWARD: 615. Editorial.	616
Introductory address, W. H. Morley during the Calendar Year 1915, Physical and Chemical Properties of. W. F. Rittman, <i>et al.</i> Gov. Pub.	325
Gelatin. Note.	905
Gem and Precious Stones in 1915. W. T. Schaller. Gov. Pub.	213
Geographic Tables and Formulas. S. S. Gannett. Gov. Pub.	211
Geological Survey: Director's Annual Report.	1072
Geology and Ore Deposits of Ely Nevada. A. C. Spencer. Gov. Pub.	1153
Geology, General, 1916, Shorter Contributions to. D. White. Gov. Pub.	1153
Geology of Massachusetts and Rhode Island. B. K. Emerson. Gov. Pub.	1153
Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico and Utah. H. E. Gregory. Gov. Pub.	1153
German Agriculture, The.	405
Future of German Agriculture. Note.	417
German Alarm Clock, The. H. E. Howe, 59; Correction.	661
Germanium, The Occurrence of, in Missouri and Wisconsin Blendes. C. H. Buchner. Gov. Pub.	1143
Germany, Starch Substitutes in. Note.	618
Germany, Sulfur Supply In. Note.	544
GRASS MEDAL AWARD: 615. Editorial.	616
Introductory address, W. H. Morley during the Calendar Year 1915, Physical and Chemical Properties of. W. F. Rittman, <i>et al.</i> Gov. Pub.	325
Gelatin. Note.	905
Gem and Precious Stones in 1915. W. T. Schaller. Gov. Pub.	213
Geographic Tables and Formulas. S. S. Gannett. Gov. Pub.	211
Geological Survey: Director's Annual Report.	1072
Geology and Ore Deposits of Ely Nevada. A. C. Spencer. Gov. Pub.	1153
Geology, General, 1916, Shorter Contributions to. D. White. Gov. Pub.	1153
Geology of Massachusetts and Rhode Island. B. K. Emerson. Gov. Pub.	1153
Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico and Utah. H. E. Gregory. Gov. Pub.	1153
German Agriculture, The.	405
Future of German Agriculture. Note.	417
German Alarm Clock, The. H. E. Howe, 59; Correction.	661
Germanium, The Occurrence of, in Missouri and Wisconsin Blendes. C. H. Buchner. Gov. Pub.	1143
Germany, Starch Substitutes in. Note.	618
Germany, Sulfur Supply In. Note.	544
GRASS MEDAL AWARD: 615. Editorial.	616
Introductory address, W. H. Morley during the Calendar Year 1915, Physical and Chemical Properties of. W. F. Rittman, <i>et al.</i> Gov. Pub.	325
Gelatin. Note.	905
Gem and Precious Stones in 1915. W. T. Schaller. Gov. Pub.	213
Geographic Tables and Formulas. S. S. Gannett. Gov. Pub.	211
Geological Survey: Director's Annual Report.	1072
Geology and Ore Deposits of Ely Nevada. A. C. Spencer. Gov. Pub.	1153
Geology, General, 1916, Shorter Contributions to. D. White. Gov. Pub.	1153
Geology of Massachusetts and Rhode Island. B. K. Emerson. Gov. Pub.	1153
Geology of the Navajo Country. A Reconnaissance of Parts of Arizona, New Mexico and Utah. H. E. Gregory. Gov. Pub.	1153
German Agriculture, The.	405
Future of German Agriculture. Note.	417
German Alarm Clock, The. H. E. Howe, 59; Correction.	661
Germanium, The Occurrence of, in Missouri and Wisconsin Blendes. C. H. Buchner. Gov. Pub.	1143
Germany, Starch Substitutes in. Note.	618
Germany, Sulfur Supply In. Note.	544
GRASS MEDAL AWARD: 615. Editorial.	616
Introductory address, W. H. Morley during the Calendar Year 1915, Physical and Chemical Properties of. W. F. Rittman, <i>et al.</i> Gov. Pub.	325
Gelatin. Note.	905
Gem and Precious Stones in 1915. W. T. Schaller. Gov. Pub.	213
Geographic Tables and Formulas. S. S. Gannett. Gov. Pub.	211

Chewing, The Industrial Chemistry of Chicle and. F. Dan-	679	Isakovics, Alois von. Obituary. W. Dreyfus.	716
Gypsum. R. W. Stone. Gov. Pub.	724	Italian Chemical Industry. Note.	620
Gypsum in Southern Part of Bighorn Mountains, Wyoming. C. T.	724	Italian Olive Oil Production. Note.	620
Lupton and D. D. Condit. Gov. Pub.	111.	325	
HARDWOODS. Yields from the Destructive Distillation of Certain.		JAPAN, New Companies in. Note.	412
R. C. Palmer. Gov. Pub.	627	Japan, Petroleum Production in. Note.	620
Hawaiian Soil Particles, Composition of. W. T. McGeorge. Gov. Pub.	420	Japan Starts Its Dyestuff Industry. A. Hirsch.	612
Hazard, Frederick Rowland. Obituary. J. D. Fennoch.	620	Japanese Chemicals, Exportation of. Note.	618
Health Officials. State. Manual of Procedure for Guidance of. J. S.	620	Japanese Export Trade. Note.	620
Abbott and H. S. Bailey. Gov. Pub.	113	Japanese Exports and Imports. Note.	619
Helium Spectrum, Wave Lengths of the Stronger Lines in the. Gov.	818	Java Citronella Oil. Note.	609
Hemp. Hurd as Paper-Making Materials. L. H. Dewey and J. L.	818		
Merrill. Gov. Pub.	213	KANSAS CITY ZONE. The Economic Resources of the. A. J. Boynton	700
Hemp, Sisal. Gov. Pub.	110	Kansas-Oklahoma. The New Zinc Fields of. W. P. Haynes.	705
Hide: The Indian Raw Hide Trade. Note.	805	Kansas State Board of Health Water and Sewage Laboratory, The	700
Hide, the Presence of Arsenic in. W. W. Stockberger and W. D. R.	213	Legal Status and the Character of the Work Done by the. C.	708
Collins. Gov. Pub.	1155	Kaolins, Georgia, Refining and Utilization of. I. E. Sproat. Gov.	4
Hospital Units, Status of Chemists in. Editorial.	731	Kenico Reservoir, Thermocline Studies at. F. E. Hale and J. E.	199
Hydraulic-Mining Debris in the Sierra Nevada. G. K. Gilbert. Gov.	613	Kerosene, Motor Spirit from. Note.	304
Hydrocarbons, Aromatic, from the Thermal Decomposition of Natural	408	Kiln, Dry-New Humidity-Regulated and Recirculating, The Theory	627
Gas Condensate. J. E. Zanetti and G. Egloff.	474	of Drying and Its Application to. H. D. Tiemann. Gov. Pub.	627
Hydrocarbons, Saturated, in Basking-Shark Liver Oil. M. Tsuji-	1098	Kilnsurfing—A Coating for Tools before Hardening. Note.	618
Hydrocarbons: The Oxidation of Mineral Oils by Air. I.—The Ef-		Kopak Fiber. Note.	618
fect of Sulfur on the Oxidation of Hydrocarbons with Particular			
Reference to Asphalt. B. T. Brooks and I. W. Humphrey.	746	LABORATORY AND PLANT:	
Hydrocarbons: The By-Products of Part I.—Historical and Bibliog-		Laboratory Solutions, Handling by Suction. C. L. Beals.	1044
raphical. E. G. Marx. 879. Part II.—General Considerations.	888	Laboratory Utensils. Note.	993
A. E. Dunstan and F. B. Thole.	628	Laboratories, Merchandise Control. E. Hendrick.	1033
Hydrocyanic Acid Gas, Detection of: Use of Small Animals for This		Laboratories, Scientific and Technical, Organic Chemical Reagent	685
Purpose. S. B. Grubbs. Gov. Pub.	628	for. R. Adams.	685
Hydrogenated Oil. Patent No. 1,135,351 in Case of Procter & Gam-	1146	Lamp: A New Pocket-Lamp. Note.	110
ble. A. Richter and W. B. Van Arsdell, 451; Correction, 623. See Let-	719	Lanolin Substitute and Preparation of Cetyl Alcohol. S. Axelrad.	1123
ters.		Laudry Work, Advantages of Softened Water In. J. H. Ryan.	397
Hydrogenation of Oil: Opinion Rendered by Judge Augustus N.	719	Lead. C. E. Siebenthal. Gov. Pub.	994
Hibbert. Patent No. 1,135,351 in Case of Procter & Gamble.	1146	Lead, Antimonial Analysis of. C. R. McComb.	994
Hydrogen Sulfide Precipitation under Pressure, Apparatus for. A.	792	Lead Arsenate, A Rapid Method for the Determination of Water-	682
Y. Fuller.		Soluble Arsenic in. H. A. Scholz and P. J. Waldstein.	617
Hydrogen Sulfide: Influence of Added Substances on the End-	975	Lead Ores, Low-Grade, Extractions of. Note.	617
Point of the Iodometric Titration of. A. R. Jayson and R. E.		Lead Production (1915). Gov. Pub.	112
Oesper.	975	112. South Dakota, Wyoming, New Mexico and Texas, Henderson,	975
Hydrometallurgy, Recent Developments in Connection with the Use		112. Utah; Heikes, 211. Colorado; Henderson, 211. Arizona,	211
of Sulfur Dioxide in. R. E. Weidlein.	1057	Montana, and Nevada; Heikes, 211. Washington; Gerry.	211
Hydroxy Acid. Gov. Pub.	627	Leather, Brown Paper for. Note.	984
Hydroscopic Coefficient, Some Notes on the Direct Determination	1155	Leather Trade, Cellulose Ester Lacquers for. Note.	1064
of the. F. J. Alway, et al. Gov. Pub.		Legislation, Chemical; not Wise but Otherwise. Editorial, 225. See	
		Criticism of Chemical Legislation which Are Not Wise but Other-	
		wise. A. Smith, 332. See also Again I say "America for Americans,"	
		Editorial.	382
ICE CREAM. The Manual of Bacteria in. S. H. Ayers and	916	Levulose the Preponderant Sugar of Apple Juices. J. R. Eoff, Jr.	587
W. T. Johnson, Jr. Gov. Pub.	627	Library Chemical, The Greatest in the World. Editorial.	1088
Ice, Manufactured. Gov. Pub.	407	Lighting Facilities, for Each One's Own. Editorial.	1064
Imports and Exports, British Engineering. Note.	1073	Light on Bright Colors, Action of. Note.	944
Industrial Course, The Western Chemical Manufacturing Compa-	1151	Lignite Coal, Low Temperature Distillation of. H. K. Benson and	946
ny. C. Skinner. Note.	626	Lignite Industrial and Domestic Use. Gov. Pub.	406
INDUSTRIAL NOVELTIES. Patent Nos. 1,139,997, 1,139,998, 1,139,999,	1151	Lime and Limestone. C. F. Loughlin. Gov. Pub.	993
1,140,000, 1,140,001, 1,140,002, 1,140,003, 1,140,004, 1,140,005, 1,140,006,	638	Lime as Calcium Sulfate, A Rapid Method for the Determination of.	1114
1,140,007, 1,140,008, 1,140,009, 1,140,010, 1,140,011, 1,140,012, 1,140,013,	993	L. G. Willis and W. H. MacIntire.	1114
1,140,014, 1,140,015, 1,140,016, 1,140,017, 1,140,018, 1,140,019, 1,140,020,	421	Lime-Barrel Act, Rules and Regulations for the Enforcement of the	724
1,140,021, 1,140,022, 1,140,023, 1,140,024, 1,140,025, 1,140,026, 1,140,027,	916	Anonymous. Gov. Pub.	1129
1,140,028, 1,140,029, 1,140,030, 1,140,031, 1,140,032, 1,140,033, 1,140,034,	1155	Limestone and Other Materials, Determination of Carbonates in.	786
1,140,035, 1,140,036, 1,140,037, 1,140,038, 1,140,039, 1,140,040, 1,140,041,	113	F. J. Barker.	786
1,140,042, 1,140,043, 1,140,044, 1,140,045, 1,140,046, 1,140,047, 1,140,048,	916	Lime Used as a Neutralizer in Dairy Products, Detection of. H. J.	324
1,140,049, 1,140,050, 1,140,051, 1,140,052, 1,140,053, 1,140,054, 1,140,055,	1155	Whickman. Gov. Pub.	285
1,140,056, 1,140,057, 1,140,058, 1,140,059, 1,140,060, 1,140,061, 1,140,062,	113	Limes, Commercial, Effect of Exposure on. J. C. Whetzel.	287
1,140,063, 1,140,064, 1,140,065, 1,140,066, 1,140,067, 1,140,068, 1,140,069,	997	Lime and Oil. Gov. Pub.	1079
1,140,070, 1,140,071, 1,140,072, 1,140,073, 1,140,074, 1,140,075, 1,140,076,	916	Limonium: Its Manufacture and Valuation. A. de Waele, 6; Correction.	
1,140,077, 1,140,078, 1,140,079, 1,140,080, 1,140,081, 1,140,082, 1,140,083,			
1,140,084, 1,140,085, 1,140,086, 1,140,087, 1,140,088, 1,140,089, 1,140,090,		LIQUIDS. THE HANDLING AND TRANSPORTATION OF, OR AS AN INDUSTRIAL	
1,140,091, 1,140,092, 1,		SALT. (Symposium at Rochester, N. Y., 1918.)	
		The Storage and Transportation of Liquids. A. C. Baxter.	978
		The Handling and Transportation of Liquids. M. H. Eisenhart.	978
		Transportation and Storage of Liquids in Small Packages. L. R.	980
		Adkins.	979
		Litharge-Glycerine. Note.	390
		Lithium and Strontium in Water, Note on the Determination of.	584
		S. D. Averitt.	584
		Lithium Minerals in 1916. W. I. Schaller. Gov. Pub.	993
		Lithus, A Substitute for, for Use in Milk Closures. W. M. Clerk	1043
		and H. A. Loh. Gov. Pub.	1043
		Loganberry Juice and Pulp. The Composition of M. R. Daughters.	997
		MAGNESIA. Restriction on Note.	411
		Magnesia. Gov. Pub.	994
		Magnesia in the U. S. E. J. H. Gillett. Gov. Pub.	713
		Magnesia. Standard Determination of the Bureau of Chemistry at	113
		Boston. R. F. Lupton. Gov. Pub.	113
		Magnesia. Analysis. Note.	589
		Magnesia. U. S. Bureau of Chemistry. Note.	630
		Magnesia. A. J. H.	

Manufacture, Census of..... Gov. Pub.....	420	Monazite Sand. Note.....	1064
Maplewood Creosote, Chemical Composition of the Higher Fractions..... E. J. Pieper, C. F. Acree, and C. J. Humphrey.....	462	Motor Engines, Starting from Cold. Note.....	407
Maplewood Creosote, On the Toxicity to a Wood-Destroying Fungus of, and of Some of Its Constituents and Derivatives, together with a Comparison with Beechwood Creosote. E. J. Pieper, S. F. Acree, and C. J. Humphrey.....	566	Motor Spirit from Kerosene. Note.....	904
Marchand, Charles. C. A. Doremus. Obituary.....	321	Motors, Crane and Hoist. Note.....	410
MARKET REPORT. 116, 222, 330, 440, 542, 634, 728, 824, 920, 1000, 1082.....	1160	Musciculus and Other Fly-Destroying Agencies, Experimental Studies with. E. B. Phelps and A. F. Stevenson. Gov. Pub.....	421
Medical Supervision: The Manufacture of Picric Acid from the Medical Standpoint. F. O. West.....	303	Muscovite, The Action of Solutions of Ammonium Sulfate on. R. F. Gardiner and E. C. Shorey.....	589
Medicines, Antiseptics, Disinfectants, etc. Gov. Pub.....	914	NATIONAL ACADEMY OF SCIENCES. Gov. Pub.....	914
Mercury, An Apparatus for the Purification of. H. E. Patten and G. H. Maiba.....	600	National Advisory Committee for Aeronautics. Annual Report.....	724
Mercury and Cinnabar. Note.....	407	National Exposition of Chemical Industries, New York, September 24-29, 1917; Editorial, 637; Program, List of Exhibitors, 907; Editorial, 1004, 1148; Addresses.....	1005
Metal Bearings, White, Lining. Note.....	1145	National Museum. Report.....	420
Metal Powders and Spangles. Note.....	409	National Research Council, Financial Support for the. Editorial.....	428
Metal, Silicon-Coated, A Note on. W. E. Wavter.....	580	Natural Gas as a Boiler Fuel. Note.....	904
Metal Trade, Russian. Note.....	712	Natural Gas, Extraction of Gasoline from, by Absorption Methods. G. A. Burrell, <i>et al.</i> Gov. Pub.....	1154
METALLURGICAL SYMPOSIUM (Boston Meeting, A. C. S.):		Navy Advisory Committee for Aeronautics. Gov. Pub.....	209
Chemicals Used in Ore Flotation. O. C. Ralston and L. D. Yundt.....	1058	NEW JOURNALS.....	439, 823, 1159
Physico-Chemical Data Needed by Metallurgists. J. W. Richards.....	1056	NEW PUBLICATIONS.....	
Physical Development of Corrosion with the Use of Sulfur Dioxide in Hydrometallurgy. E. R. Weidlein.....	1057	Niagara Situation and the Efficiency of a Democracy. Editorial.....	1159
The Importance of the Flotation Process in the Metallurgy of Copper. E. P. Mathewson.....	1058	Nichols Medal Not Awarded This Year. Note, 1081; Editorial.....	120
Metallurgy: Emulsions and Suspensions with..... Metals. H. W. Gillett.....	31	Nichrome, Cast, Notes on the Analysis of. E. W. Reid.....	488
Metallurgy: Melting Scrap Aluminum. Note.....	99	Nickel and Zirconium, Notes on the Analysis of Alloys of. G. L. Kelley and F. M. Myers.....	854
Metallurgy: Metal-Working Gas Furnaces. Note.....	99	Nickel, Cobalt, or Copper, Corrosion of Ingot Iron Containing. H. T. Kalmus and K. B. Blake, 123. See Letters.....	414
Metallurgy: The Reduction of Volatile Elements from Metal High Boiling Metals—A Review. J. Johnston. 873. Discussion. N. T. Bacon.....	878	Nickel in 1917. L. Hess. Gov. Pub.....	326
Metals and Ores in 1914 and 1915. J. P. Dunlop. Gov. Pub.....	212	Nickel Production in Canada. Note.....	97
Metals and Other Materials, Report of Tests of. Gov. Pub.....	914	Nickel, The Influence of Superimposed Alternating Current on the Electrodeposition of. S. H. Tucker and H. G. Loesch.....	841
Metals at Low Temperatures, Note on Electrical Conduction in. F. B. Silsbee. Gov. Pub.....	997	Nitrate Determinations in the Presence of Chlorides. W. F. Gericke, Nitrate in Sewage and Supply, in the Means of Orthotolene. E. B. Phelps and H. L. Shoub.....	585
Metals, Secondary, in 1916. J. R. Dunlop. Gov. Pub.....	1153	Nitrate-Nitrogen Accumulation in Soil, Some Factors Affecting. P. L. Gainey and L. F. Metzler. Gov. Pub.....	1155
Metals, The Rarer. P. H. Hess. Gov. Pub.....	820	Nitrate of Soda in Canada. Note.....	97
Meteoritic Irons, Notes on Whitfield County, Georgia, with New Analyses. C. P. Merrill. Gov. Pub.....	420	NITRATE SUPPLY COMMITTEE RECOMMENDATIONS.	829
Meteorite Stone Newly Found, from Lake Okechobee, Florida. G. P. Merrill. Gov. Pub.....	420	A Statement of the Action Taken and Contemplated Looking to the Fixation of Nitrogen.....	829
Meteorite, Recently Found on from Cookeville, Putnam Co., Tennessee. C. P. Merrill. Gov. Pub.....	420	Grainings supply Committee Report. War and Navy Departments. Preliminary Report. C. L. Parsons.....	833
Methane and Other Gases, Absorption of, by Coal. S. H. Katz. Gov. Pub.....	1154	Nitrogen Fixation for America. Statement by War Department Engineers. Report on. C. L. Parsons, 839; Correction.....	829
Methyl Alcohol, A Note on the Detection and Estimation of Small Amounts of. E. Elzer. Gov. Pub.....	295	Nitrates. H. S. Gale. Gov. Pub.....	994
Mica. W. T. Schaller. Gov. Pub.....	994	Nitrates and Ammonia in the Soil, Effect of Paraffin on the Accumulation of. P. L. Gainey. Gov. Pub.....	997
Microscopes, A New Illuminator for. A. Silverman.....	971	Nitrates in Soils, Studies of the Phenoldisulfonic Acid Method for Determining.....	290
Microscopic Qualitative Chemical Analysis, The Use of Textile Fibers in. E. H. Hamond and H. L. Colwell.....	969	Nitrates in Waters High in Magnesium Salts, A Note on the Phenoldisulfonic Acid Method for. M. S. Nichols.....	586
Milk, Application of the Cryoscopic Method for Determining Added Water in. J. T. Keister.....	862	Nitric Acid Sophistication, A Serious Production Menace. J. R. Withrow. Gov. Pub.....	1148
Milk: A Study of Certain Ferments with a View to Determining a Method for Differentiation of Volatile Acids from Milk. H. W. Gillett, R. E. Lee and M. G. Mellon.....	360	Nitrification in Semiarid Soils. W. P. Kelley. Gov. Pub.....	324
Milk: Chemical Quality of New York City Market Milk. L. P. Brown and C. V. Ekroth.....	299	Nitrifying Powers of Some Humid and Some Arid Soils, Comparison of. C. P. Lipman, <i>et al.</i> Gov. Pub.....	113
Milk Condensation, A Study of the Estimation of Fat in. C. H. Biesterfeld and O. L. Evenson.....	1111	Nitrogen Determination and Supply. Note.....	322
Milk, Condensed, Butter and Cheese. Gov. Pub.....	1079	Nitrogen Determination in Substances Used in Explosives. W. C. Cope and G. B. Taylor. Gov. Pub.....	996
Milk, Detection of Added Water in. H. Durand.....	44	Nitrogen, Fixation of. E. Bucher, <i>et al.</i> Gov. Pub.....	1074
Milk Detection in Water, by Means of a Simplified Molecular Concentration Constant. L. W. Ferris.....	957	Nitrogen Fixation Plans, Government, Editorial.....	730
Milk: Determination of Fat in Certain Milk Products. C. K. Francis and D. G. Morgan.....	861	Nitrogen, Fixed: Nitrate Supply Committee Recommendations, 829; Correction.....	990
Milk Evaporation, The Correlation Required in Applying the Babcock Formula to the Estimation of Total Solids in. O. L. Evenson.....	499	Nitrogen Industries, 1912-1916, LITERATURE OF. H. R. Hosmer, 424; Correction.....	720
Milk, Ewes', Its Fat Content and Relation to the Growth of Lambs. E. G. Ritzman. Gov. Pub.....	420	Nitrogen Industries, The Status of the Present Status of the Subject of the Availability of. C. B. Lipman.....	189
Milk, Hot-Bottled Pasteurized, Cooling by Forced Air. Ayers, <i>et al.</i> Gov. Pub.....	113	Nitrogen in Sewage Sludge, Is the Recovery of, Practicable? W. R. Copeland.....	374
Milk: Relation of the Fat in Milk to the Solids-Not-Fat. L. P. Brown and C. V. Ekroth. 297. See Letters.....	416	Nitrogen, Metabolic, A Study of Methods of Estimation of. E. B. Forbes, <i>et al.</i> Gov. Pub.....	916
Milk Standards, Commission on. H. Gov. Pub.....	417	Nitrogen, Soil, Relation of the Transformation and Distribution of, to the Nutrition of Citrus Plants. I. G. McBeth. Gov. Pub.....	916
Milk and Cream, Chemical Testing. R. H. Shaw. Gov. Pub.....	916	Norway, Water-Power In. Note.....	621
Milk and Milk Products. Gov. Pub.....	328	Norwegian Whale Oil Production. Note.....	619
Milk and Milk Products, Two Convenient Pipettes for Sampling. A. Perkins.....	58	NOTES AND CORRESPONDENCE.....	
Millet, Experimental Determination of the Digestibility of. C. F. Langworthy and A. D. Holmes. Gov. Pub.....	915	Novalocine and Cocaine, Pharmacological Studies with. A Comparative Investigation of These Substances in Poisoned Animals and Isolated Organs. G. B. Roth. Gov. Pub.....	1146
Mine Rescue Apparatus, Oxygen, and Physiological Effects on Users. Henderson and J. W. Paul. Gov. Pub.....	628	Obituary.....	321, 413, 715
Mines and Mineral Resources. Congressional Committee Report. Gov. Pub.....	324	Occupational Diseases. Safeguarding the Eyes of Industrial Workers. Oil: Anticlines in Central Wyoming. C. J. Hares. Gov. Pub.....	211
Mines and Mining, Abstracts of Current Decisions on. J. W. Thompson. Gov. Pub. May to August, 1916, 421; January to April, 1917.....	1154	Oil: Anticlines in the Blackfoot Indian Reservation, Montana. E. Stebinger. Gov. Pub.....	326
Mineral Lands. Gov. Pub.....	993	Oil: Arched Cracking in an Aromatic Base Oil—Temperature Factor at Natural Gas Condensate. J. E. Zanetti and G. Egloff.....	474
Mineral Oils, The Oxidation of, by Air. I. The Effect of Sulfur on the Oxidation of Hydrocarbons with Particular Reference to Asphalt. B. T. Brooks and I. W. Humphrey.....	746	Oil, Cedarwood. Note.....	618
Mineral Output, 1915. W. L. Hedder. Gov. Pub.....	905	Oil, Citronella, Java. Note.....	619
Mineral Production of Canada. Note.....	320	Oil, Clove. Note.....	1079
Mineral Production of the U. S. in 1915. H. D. McCaskey. Summary Gov. M. B. Glavin. Gov. Pub.....	632	Oil, Coconut, Detection of. Note.....	619
Mineral Products of the United States. Gov. Pub.....	211	Oil, Cod-Liver, Adulteration of, in Norway. Note.....	198
Mineral Resources of the Kantishna Region, Alaska. S. R. Capps. Gov. Pub.....	1153	Oil, Cottonseed, Incomplete Hydrogenation of. H. K. Moore, G. A. Rich, and H. C. Corradell, 451; Correction.....	719
Mineral Supplies. H. W. Brooks. Gov. Pub.....	923	Oil (Cottonseed) Industry, Fuller's Earth and Its Valuation for. T. G. Richert, 599; Correction 624. See Letters.....	909
Minerals of the U. S., Useful. F. C. Schrader, <i>et al.</i> Gov. Pub.....	420	Oil, Cottonseed, Russian Industry. Note.....	1145
Minerals: Yukon-Koyukuk Region, Alaska. H. M. Eakin. Gov. Pub. Mining Districts in Eastern Nevada, Notes on Some. J. M. Hill. Gov. Pub.....	111	Oil, Crude: Desulfuring Petroleum. Note.....	804
Mining Industry in the Territory of Alaska during the Calendar Year, 1915. S. S. Smith. Gov. Pub.....	915	Oil, Crude: Production in Japan in 1915. Note.....	200
Molybdenum. Note.....	530	Oil Emulsification, Resistance of an Oil to. W. H. Herschel. Gov. Pub.....	419
Molybdenum in 1915. W. L. Hedder. Gov. Pub.....	923		
Molybdenum: Its Ores and Their Concentration with a Discussion of Markets, Prices and Uses. F. W. Horton. Gov. Pub.....	324		
Molybdenum Residues, Recovery of. V. Lenher and M. P. Schultz.....	685		
Molybdic Acid, Recovery of. F. R. Knick and R. D. Cooke. Note.....	109		
Monazite. W. T. Schaller. Gov. Pub.....	994		

Starvation. The Relative Value of Infundibular Extracts Made from Different Species of Mammals and a Comparison of Their Physiological Activity with That of Certain Commercial Preparations. G. B. Roth. Gov. Pub.	627	Radium, Uranium and Vanadium. F. L. Hess. Gov. Pub.	540
Fluoride Deposits of the Manhattan District, Nevada. H. C. Ferguson. Gov. Pub.	627	Railway Industrial Agent, The Chemist as. Editorial.	545
Mant Preparations. Editorial.	627	Reagents, Organic Chemical, for Scientific and Technical Laboratories. R. Adams.	685
Plaster and Stucco Construction, Durability of. R. J. Wig, et al. Gov. Pub.	210	RECENT JOURNAL ARTICLES. I. L. F. DeMatty:	1159
Plastic Material, New. Note.	983	115, 221, 329, 439, 541, 633, 727, 823, 919, 999, 1081, 1159	
Platinum. J. M. Hill. Gov. Pub.	630	Research Index Suggestion: Cooperation in Industrial Research Work. Note.	322
Platinum and Allied Metals in 1916. J. M. Hill. Gov. Pub.	714	Research, Scientific and Industrial, British Department of. Note.	199
Platinum, A New Source of. Note.	838	Research: The Production of Scientific Knowledge. C. E. K. Mees. Gov. Pub.	1137
Platinum, British Control of. Editorial.	731	Research, Validity of the Survey Method of. W. J. Spillman. Gov. Pub.	915
Platinum Conservation in France. Editorial.	838	Reservoirs, Storage, as a Factor in the Purification of Surface Waters. S. T. Powell.	377
Platinum in Jewelry. Editorial, 445; C. L. Parsons, 622; Editorial.	410	Resin Compounds, Phenol, Printing Plates from. L. V. Redman, A. J. Webb, F. P. Br.	388
Platinum Mineral Resources. Note.	906	Resins, Synthetic Phenol. L. V. Redman, A. J. Webb and F. P. Brock. Note. 207. See Brown.	207
Platinum Production. Note.	1085	Resinous Products, French. Note.	617
Platinum Situation, The. Editorial. 344 (Correction inserted).	590	Resources, Economic, of the Kansas City Zone. A. Boynton.	700
PLATINUM SUBSTITUTES.		Resources, Neglected. Editorial. 731. See 756 and.	770
New Alloys to Replace Platinum. F. A. Fahrenwald.	810	Rice Leaves, Dye from. Note.	619
On the Substitution of Perchloric Acid for Chloro-Platinic Acid in the Determination of Potassium. E. C. Walker, 3rd.	804	Rice Milling, The By-Products of. J. B. Reed and F. W. Liepsner. Gov. Pub.	1155
Potash. Stellate as a Platinum Substitute. E. Haynes.	712	Road-Building Road in 1916, The Results of Physical Tests Including all Compression Tests. P. Hubbard and F. H. Jackson, Jr. Gov. Pub.	915
Potash and Wood.	996	Road Construction, Portland Cement, Influence of Grading on the Value of Fine Aggregate Used in. F. H. Jackson, Jr. Gov. Pub.	997
Potash, Availability of, in Certain Orthoclase-Bearing Soils as Affected by Lime or Gypsum. Gov. Pub. L. J. Briggs and J. F. Breazale.	210	Rocks, Silicate and Carbonate, Analysis of. W. F. Hillebrand. Gov. Pub.	211
Potash, Cement—The Nature of. R. J. Nestell and E. Anderson. 699 (Correction).	810	Rodent Destruction on Ships. Creel and Simpson. Gov. Pub.	1077
Potash Determination, A Practical Revision of the Cobalti-Nitrite Method for. C. R. Haff and E. H. Schwartz. 785; Correction.	424	Roeber, E. P. A. Note on Character of.	1004
Potash Determination, A Study of W. C. Byrd's Concoction with Potash-Gladiolus. J. C. Hibbard.	909	Roofings, Prepared, Analysis and Testing of. H. Abraham.	1048
Potash Extraction from Silicate Rocks—II. W. H. Ross.	504	Rosin, Pine Substitute for. Note.	1063
Potash, Importance of Developing our Natural Resources of. F. W. Brown. Gov. Pub.	467	Rubber, Aniline Method for Determination of Mineral Fillers in. H. Klein, H. Link and F. Gottsch.	140
Potash in 1916. G. C. F. Gov. Pub.	916	Rubber Chemistry, Industrial Fellowships in, Municipal University of Akron, Ohio. Note.	322
Potash: Notes on the Greensand Deposits of the Eastern United States. G. H. Ashley. Gov. Pub.	1077	Rubber, Crude, Effect of Copper on.	1072
Potash Recovery from Alumina. Waggaman and Cullen. Gov. Pub.	1153	Rubber, Crude, Determination of. P. A. Houseman.	356
Potash Recovery from Beet-Sugar House Waste Liquors. H. E. Zitkowski.	113	Rubber Industry: Solvent Gasoline for. C. O. North.	1038
Potash Recovery from Flue Dust. Note.	692	RUBBER: REPORT OF JOINT RUBBER INSULATION COMMITTEE.	310
Potash Recovery from Incinerator Ash of the Northwest. C. W. Tuing.	1144	Rubber, Synthetic. Note.	994
Potash, Recovery of Water-Soluble, as a By-Product in the Cement Industry. W. H. Ross and A. R. Merz.	472	Rubber, The Influence of Pigments on. M. Toch.	694
Potash Source: Banana Stalks. H. E. Billings and A. J. Nestell.	1035	Rubber: Vulcanization. Note.	319
Potash Volatilization from Cement Materials. E. Anderson and R. J. Nestell.	153	Rubber, Wet Combustion in the Nitrosite Combustion Method for the Direct Determination of. L. G. Wesson and E. S. Kuorikoski.	139
Potassium and Aluminum, Recovery of Salts of, from Mineral Silicates. A New Method. J. C. W. Frazer, W. W. Holland and E. Cullen.	253	Russia, To Promote Closer Trade Relations with. Note.	531
Potassium Determination, A Method of Ashing Organic Materials for. P. L. Blumenthal, A. M. Peter, D. J. Healy and E. J. Gott.	935	Russian Metal Trade. Note.	712
Potassium Determination, On the Substitution of Perchloric Acid for Chloro-Platinic Acid in. E. C. Walker, 3rd.	753	Russian Trade Diversion, War and. Note.	1065
Pottery in 1916. Middleton. Gov. Pub.	810	Russian Water Power. Note.	407
Preparedness: Chemists and Preparedness. Editorial.	1079	SAFETY CODE, National Electrical. Gov. Pub.	419
Preparedness, National, The First Report upon the Chemical Industries of the United States and Their Relations to. C. A. Browne, 77; A noteworthy Contribution. Editorial.	332	Saffron Market, French. Note.	904
Printing Machinery, Paper and Paper Products, Markets for in Cuba and Panama. R. S. Barrett. Gov. Pub.	122	Salmon, Canned, The Examination of, for Bacteria and Tin. L. D. Salmon.	678
Printing Plates from Phenol Resin Compounds. L. V. Redman, A. J. Webb, F. P. Br.	916	Salt, in 1916. R. W. Stone. Gov. Pub.	630
Proteins: Improvements in the Copper Method for Estimating Amino Acids. P. A. Kober.	388	Salt, Removal of Barium from Brines Used in the Manufacture of. W. W. Skinner and W. F. Baughman.	18
Public Health Administration in South Bend, Indiana. C. Fox. Gov. Pub.	501	Saltwater Production in India. Note.	1143
Public Health, Court Decisions Pertaining to. J. Waterman. Gov. Pub.	725	Sand and Gravel. R. W. Stone. Gov. Pub.	914
Public Health Service. Gov. Pub.	628	Sandstone Quarrying in the United States. O. Bowles. Gov. Pub.	915
Public Health Service in Annual Conference of the 43rd State and Territorial Health Authorities, Washington, April 30 and May 1, 1917. Gov. Pub.	725	Sanitary Legislation.	328
Public Health Service in Time of War. Executive Order Making the U. S. Public Health Service a Part of the Military Forces of the United States. Gov. Pub.	725	Sanitation: Artificial Alkalinity. Water for Filtration. A. W. Clark.	56
PUBLIC SERVICE SYMPOSIUM (N. Y. Section of A. C. S.):		Sanitation: Electrolytic Disinfecting Fluid. Note.	200
Public Service in the U. S. C. A. Beard.	63	Scandinavia, Dearth of Raw Materials in. Note.	715
Status and Compensation of the Chemist in Public Service. F. E. Jerebini.	64	Scientific Knowledge, The Production of. C. E. K. Mees.	1137
The Chemist in the Public Service. H. W. Wiley.	81	SCIENTIFIC SOCIETIES.	1066
The Chemist in the Service of the City of New York. O. H. Klein.	776	Searchlight Projectors. Note.	539
Pyrites, Determination of the Explosibility of, as Well as Its Available Sulfur and the Sulfur Content of Its Cinders. C. R. Gyzauder.	1073	Selenium and Tellurium. F. L. Hess. Gov. Pub.	318
Pyrolusite, The Determination of Available Oxygen in. O. L. Barney. 961; Correction.	1073	Sewage and Water Laboratory, Kansas State Board of Health, The Legal Status and the Character of the Work Done by the. C. C. Young.	708
QUASSIA Extract as a Contact Insecticide. N. E. McIndoo and A. F. Stevens. Gov. Pub.	1155	Sewage in the New Haven Sewage Experiment Station. Copper in. F. W. Mohlman.	1093
Quicksilver in 1915. H. D. McCaskey. Gov. Pub.	211	Sewage, Grease Recovery from. Note.	805
RADIATION Equation, Planck's Calculation of the Constants of: An Extension of the Theory of Least Squares. H. M. Roesser. Gov. Pub.	818	Sewage, Purification of, by Aeration in Presence of Activated Sludge—III. E. B. Phelps.	845
Radiation, Luminous, from a Black Body and the Mechanical Equivalent of Light. W. W. Coblenz and W. B. Limerson. Gov. Pub.	818	Sewage: Re-aeration as a Factor in the Self-Purification of Streams. E. B. Phelps.	403
Radio-Active Substances and Batteries, Application of. Note.	114	Sewage Sludge: Is the Recovery of Its Nitrogen Practicable? W. W. Mohlman.	374
Radium, Barium, Carbonates. Note.	530	Sewage, Some Remarks on the Biochemical Treatment of, with Special Reference to the Activated Sludge Method. G. T. Hammond.	399
		Sewage, The Determination of Nitrate in, by Means of Ortho-Toluidine. E. B. Phelps and H. L. Lang.	767
		Sewage Treatment Works, Stream Inspection in Connection with the Operation of. C. B. Hoover.	398
		Shark Liver Oil, A Highly Unsaturated Hydrocarbon in. Correction.	109
		Shark Liver Oil, Basking, Saturated Hydrocarbons in. M. Tsujimoto.	1098
		Shipbuilding Returns. Note.	98
		Siberian Metallurgy. Note.	99
		Silica in 1916. F. J. Katz. Gov. Pub.	1079
		Silico-Cooled Metal, A Note on. W. E. Vawter.	380
		Silver and Gold in 1915. H. D. McCaskey and J. P. Dunlop. Gov. Pub.	421
		Silver Cleaning, A Study of the Electrolytic Method of. H. L. Lang and C. F. Walton, Jr. Gov. Pub.	113
		Silver Films, The Deposition of, on Glass. A. Silverman and R. M. Howe.	1032
		Silver, Gold, Copper and Lead Ores. C. H. Fulton. Gov. Pub.	996
		Silver Production (1915). Gov. Pub. California and Oregon; Yale 112. South Dakota, Wyoming, New Mexico and Texas; Henderson, Utah; Heikes, 112. Colorado; Heikes, 211. Arizona; Heikes, 211. Heikes, 211. Washington; Gerry.	211
		Slate in 1916. G. F. Loughlin. Gov. Pub.	995

Smelter Smoke: An Investigation of the Wet Thiofen Process. A. E. Wells.	872	Storax, American and Oriental, A Comparison of. S. Jordan, 770.	731
Smelter Smoke Problem, Results of Recent Investigations of the. A. E. Wells.	640	See Editorial.	819
Smithsonian Institution. Gov. Pub.	324	Strontium and Barium in 1915. J. M. Hill. Gov. Pub.	111, 1078
Smokeless Combustion and By-product Recovery. Note.	804	Strontium and Lithium in Water, Note on the Determination of. S. D. Averitt.	584
Soap, Petroleum-. Determination of Methods of Testing. Gov. Pub.	210	Strontium in 1916. J. M. Hill. Gov. Pub.	1077
Soaps, Specifics for or Methods of Testing. Gov. Pub.	631, 995	Stucco and Plaster Construction, Durability of. R. J. Wig, et al. Gov. Pub.	210
Soil: Acidity and Adsorption in Soils as Measured by the Hydrogen Electrode. L. T. Sharp and D. R. Hoagland. Gov. Pub.	113	Sugar: A Simplified Inversion Process for the Determination of Sucrose by Double Polarization. H. S. Walker.	490
Soil Acidity, Note for Determination of; New Apparatus for Determination of Soil Carbonates. See Letters.	1072	Sugar Beet, Cement from. Note.	1064
Soil: Alpha Crotonic Acid as a Soil Constituent. E. H. Waters and L. E. Wise. Gov. Pub.	113	Sugar Beet Growing, Bruch. Note.	713
Soil and Fecal Strains of the Colon-Aerogenes Group in Surface Waters, Seasonal Distribution of. M. Greenfield and W. N. Skourup, 675. See Letters.	989	Sugar Beet, Industry. Note.	904
Soil Conditions, Acid and Neutral, Relation of Manganese Under. J. J. Skinner and F. R. Reid. Gov. Pub.	113	Sugar Beet, Manufacture in Japan. Note.	627
Soil, Effect of Decomposing Organic Matter on the Solubility of Certain Inorganic Constituents of the. C. A. Hensen. Gov. Pub.	916	Sugar-Cane Culture for Sirup Production in the U. S. P. A. Yoder. Gov. Pub.	916
Soil, Effect of Irrigation Water and Manure on the Solubility of Soluble Salts of. F. S. Harris and N. I. Butt. Gov. Pub.	420	Sugar Industry. Gov. Pub.	916
Soil, Effect of Season, and Water on the Bacterial Activities of the. E. Graves, et al. Gov. Pub.	916	Sugar Industry, Cane. Gov. Pub.	916
Soil, Factors Affecting the Evaporation of Moisture from the. F. S. Harris and J. S. Robinson. Gov. Pub.	324	Sugar: Levulose the Preponderant Sugar of Apple Juices. J. R. Eoff, Jr.	587
Soil, Influence of Bacterial Manure and Water upon Bacterial Activities of. J. E. Graves and E. G. Carter. Gov. Pub.	113	Sugar Production in the U. S. and Foreign Countries. P. Elliott. Gov. Pub.	540
Soil: Manganese as a Cause of the Depression of the Assimilation of Iron by Pineapple Plants. N. C. Johnson.	47	Sugar Syrups, Some Commercial Invert. Sources and Composition of, with Notes on Sorghum Syrup. S. Jordan and A. L. Chesley, 756. See Editorial.	731
Soil, Measurement of the Inactive, or Unfree, Moisture in, by Means of the Dilatometer Method. G. Bouyoucos. Gov. Pub.	420	Sugar: The Chemical Changes which are Caused by Defecation of Sorghum Juice for Syrup Manufacture. A. K. Anderson.	492
Soil, Movement and Distribution of Moisture in the. F. S. Harris and H. W. Turpin. Gov. Pub.	997	Sugar: The Twenty-fifth Anniversary of the Audubon Sugar School. E. C. Estes.	379
Soil, Nitrogen, Effect of the Transformation and Distribution of, to the Nutrition of Citrus Plants. I. G. McBeth. Gov. Pub.	916	Sulfate Pulp, Removal of Pitch from. Note.	806
Soil: Relation of Movement of Water in a Soil to Its Hygroscopicity and Initial Moistness. F. J. Alway and G. R. McDole. Gov. Pub.	997	Sulfate Pulp, Method of Staining to Distinguish between Bleached and Unbleached. J. S. Smith. Gov. Pub.	1044
Soil, Relation of the Water-Retaining Capacity of, to Its Hygroscopic Coefficient. F. J. Alway and G. R. McDole. Gov. Pub.	628	Sulfur. An Investigation of the Wet Thiofen Process. A. E. Wells. 872; Gov. Pub.	629
Soil, Some Factors Affecting Nitrate-Nitrogen Accumulation in. L. Gainey and L. F. Metzler. Gov. Pub.	1155	Sulfur: Determination of the Explosibility of Pyrites as Well as Its Available Sulfur and the Sulfur Content of Its Cinders. C. R. Gyzander.	996
Soils and Fertilizers. W. W. Allen. Gov. Pub.	324	Sulfur Dioxide Determination. O. R. Sweeney, H. E. Outcault and J. R. Withrow, 949; Continued.	776
Soils, Alkaline, Formation of "Black Alkali" (Sodium Carbonate) in. J. F. Breazeale. Gov. Pub.	420	Sulfur Dioxide Determination. O. R. Sweeney, H. E. Outcault and J. R. Withrow, 949; Continued.	1148
Soils, Calcium Compounds in. E. Shorey. Gov. Pub.	628	Sulfur, Recent Developments in Connection with the Use of in Hydrometallurgy. E. R. Weidlen.	1057
Soils, Fixation of Ammonia in. W. P. Kelley. Gov. Pub.	324	Sulfur, Effect of, on Different Crops and Soils. O. M. Shedd. Gov. Pub.	1155
Soils, Importance of the United States. Gov. Pub.	324	Sulfur in Petroleum. The Detection and Determination of. C. K. Francis and C. W. Crawford.	479
Soils, Semi-arid, Nitrification in. W. P. Kelley. Gov. Pub.	324	Sulfur Supply in Germany. Note.	618
Soils, Studies on the Phenolsulfonic Acid Method for Determining Nitrate in. R. F. Gardiner and E. C. Shorey.	290	Sulfur: The Oxidation of Mineral Oils by Air. I.—The Effect of Sulfur on the Oxidation of Hydrocarbons with Particular Reference to Asphalt. B. T. Brooks and I. W. Humphrey.	746
Soils, The Action of Solutions of Ammonium Sulfate on Muscovite. R. F. Gardiner and E. C. Shorey.	588	Sulfuric Acid, Concentration of. E. H. Armstrong.	386
Soils, The Influence of Calcite Inclusions in, on the Determination of Organic Carbon in. E. C. Shorey and W. H. Fry.	588	Sunach, Extraction of. Note.	424
Soils, Use of Indirect Methods for the Determination of the Hygroscopic Coefficient of Soils. Alway and Clark. Gov. Pub.	113	Suntan, Independent of Documents. Gov. Pub.	407
Soils, Variation in the Chemical Composition of. W. O. Robinson, et al. Gov. Pub.	916	Sweden, Industrial Combine in. Note.	1065
Sorghum Juice for Syrup Manufacture, The Chemical Changes which are Caused by Defecation of. A. K. Anderson.	492	Switchgear, Oil-break. Note.	1065
Sorghum Syrup, Sources and Composition of Some Commercial Invert Sugar Syrups with Notes on. S. Jordan and A. L. Chesley, 756. See Editorial.	731	TABULAR Arrangement for Chemical Factors, An Improved. C. V. Ekroth.	169
Sorghums and Corn, Daily Variation of Water and Dry Matter in the Leaves of. C. E. Miller. Gov. Pub.	931	Talc and Soapstone in 1916. J. S. Diller. Gov. Pub.	631, 999
Sorghums, Grain, Studies on the Digestibility of. C. F. Langworthy and A. D. Holt. Gov. Pub.	324	Tannin Content of Pacific Coast Trees. H. K. Benson and F. M. Jones.	1096
South African Mineral Production. Note.	198	Tanning Material, Burmese Myrobalams as. Note.	199
Soya-Bean Extraction by Trichlorethylene. Note.	618	Tanning Materials in Russia. Note.	410
Soya-Bean, Food Value of. Note.	731	Tanning, The Extraction of Sumach. Note.	200
Soya-Bean, with Special Reference to Its Utilization for Oil, Cake and Other Products. C. V. Piper and W. J. Morse. Gov. Pub.	324	Tanning: Tannin Extraction and Manufacture in Natal. Note.	852
Spain, Mineral Production of. Note.	1009	Tantalum in Alloy Steels, The Determination of. G. L. Kelley, F. B. Myers and C. B. Illingworth.	97
Spelter, Analysis of. W. B. Price, Chairman Committee on Analysis of Non-Ferrous Alloys. Note.	621	Tar Dehydration. Note.	569
Spices, The Analysis of. Note.	1099	Tar Oils and Resins, Sulfuric Acid. The Determination of Phenol in. J. M. Weiss and C. R. Downs.	903
Standard-Barrel Law. Federal Rules and Regulations Promulgated under Authority of the. Gov. Pub.	1155	Tar Varnish for Iron Work. Note.	1100
Standard Methods, Tentative, for the Sampling and Analysis of Commercial Fats and Oils, Other than those of the United States. Unissued Groups. W. D. Richardson, 1906. Correction.	1148	Tars, Some Effects of Certain Solvents on, in the "Free Carbon" Determination. G. S. Monroe and H. J. Broderick.	636
Standard Samples for Thermometric Fixed Points. Gov. Pub.	997	Tar: Commission and schedule A. Editorial.	1184
Standard Samples, General Information. Gov. Pub.	1072	Tar: Commission, Chemistry and the. Editorial.	1184
Starch and Chinese Industry. Gov. Pub.	597	Tar: Commission, Use of Work for the. Editorial.	1184
Starch for Mill Purposes, A Practical Method for Determining the Viscosity of. G. M. Noller.	1143	Tar: No Tar. Commissioner for Chemistry. Editorial.	651
Starch Substitutes in Germany. Note.	636	Tar: and Bituminous Substances and Hydrocarbon Oils, Observations on the Action of Sulfur Monochloride on. I. M. Allen.	955
Steel: A Convenient Apparatus for the Potentiometric Titration Depending on the Change of Carbon Potential, and Its Application to the Determination of Small Quantities of Chromium in Steel. G. L. Kelley, J. R. Adams and J. A. Wiley.	780	Tartrazine, A Modification of the Free Alkaloid for the Separation of the Tartrazine and Tartaric Acids to Include. F. H. Inessall.	983
Steel, Ferro-Chromium. H. W. Gillett and E. L. Mack.	542	Tellurium and Selenium. F. I. Hess. Gov. Pub.	419
Steel, High Tensile, Mild, for Reinforced Concrete. Note.	621	Testing Fees Electric, Magnetic and Photochemical. Gov. Pub.	419
Steel, Manganese. Note.	1143	Testing Miscellaneous Supplies some Technical Methods of. F. H. Walker.	419
Steel Production, Norway's. Note.	1112	Textile Conference, Second Annual Technical Textile Conference. Washington, D. C. May 21-19.	534
Steel Production (1915). Gov. Pub. E. F. Burchard.	713	Textiles: The Use of Textile Fibers in Microscopic Qualitative Chemical Analysis. G. S. Monroe and H. J. Cole.	967
Steel, Qualities of. Note.	1143	Textiles: Chemical Analysis of. Gov. Pub.	996
Steel Temperature Measurements in Bessemer and Open Hearth Practice. G. K. Burgess. Gov. Pub.	818	Thiofen Process, Wet, An Investigation of. A. E. Wells, 872; Gov. Pub.	996
Stella, Alloys, The Determination of Tantalum in. G. L. Kelley.	882	Thiofen Process, Wet, An Investigation of. A. E. Wells, 872; Gov. Pub.	996
Stella, Corrosion and Electrical Properties of. Note.	318	Thiofen Process, Wet, An Investigation of. A. E. Wells, 872; Gov. Pub.	996
Stella and Tungsten, Reflecting Power of. W. W. Coblenz and W. B. Emerson. Gov. Pub.	987	Thiofen Process, Wet, An Investigation of. A. E. Wells, 872; Gov. Pub.	996
Stella as a Substitute for Platinum. I. HANSEN.	974	Thiofen Process, Wet, An Investigation of. A. E. Wells, 872; Gov. Pub.	996
Stone in 1915. C. F. Loughlin. Gov. Pub.	213	Thiofen Process, Wet, An Investigation of. A. E. Wells, 872; Gov. Pub.	996

Tracing Cloth and Paper, Specification of the Transparency of. Gov. Pub.	618	Water-Power in Norway. Note.	621
Trade between Japan and South Africa. Note.	621	Water-Power, Niagara River. Gov. Pub.	914
Trade, British Board of. Notes.	1144	Water: Re-Aeration as a Factor in the Self-Purification of Streams. E. B. Phelps.	403
Trinitrotoluene, The Inspection and Testing of.	801	Water Resources and Geology of Big Smoky, Clayton, and Alkali Springs Valleys, Nevada. O. E. Meinzer. Gov. Pub.	819
Tungsten and Stellite, Collecting Power of. W. W. Coblenz and W. B. Emerson. Gov. Pub.	997	Water Sample Shipping Case, A New. R. R. Spencer and H. P. Letton. Gov. Pub.	1077
Tungsten: Australian Wolfram. Note.	1063	Water, Softened, Advantages of, in Laundry Work. J. H. Ryan.	397
Tungsten Deposits of Northwestern Inyo County, California. A. Knopf. Gov. Pub.	420	Water: Thermocline Stagnation at Kanisco Reservoir. F. E. Hale and J. E. Dowd.	370
Tungsten, Emissivity of Straight and Helical Filaments of. W. W. Coblenz. Gov. Pub.	818	Watertown Arsenal. Gov. Pub.	914
Tungsten Filaments. Note.	805	Waters High in Magnesium Salts, A Note on the Phenolsulfonic Acid Method for Nitrate in. M. E. Nichols.	586
Tungsten, French. Note.	619	Waters, Mineral, in 1915. E. B. Dole. Gov. Pub.	112
Tungsten in 1915. F. L. Hess. Gov. Pub.	539	Waters, Surface, Seasonal Distribution of Soil and Fecal Strains of the Colon-Aerogenes Group in. M. Greenfield and W. N. Skourup. 675.	989
Tungsten Minerals and Deposits. F. L. Hess. Gov. Pub.	914	Waters, Surface, Storage Reservoirs as a Factor in the Purification of. S. T. Powell.	377
Tungsten Ores in Rhodesia. Note.	983	Weights and Measures and Weighing and Measuring Devices, Specifications and Tolerances for. Gov. Pub.	114
Turbo-Electric Propulsion. Note.	200	Western Chemical Manufacturing Company's Industrial Coors. Tar. C Skinner. Note.	1073
UNIVERSITY Assistantships and Fellowships in Chemistry. Princeton University. Note.	322	Whaling Industry, Japanese. Note.	983
University Fellowships: Industrial Fellowships in Rubber Chemistry. Municipal University of Akron, Ohio. Note.	322	Wheat, Damp and Carlicky, The Dry of, for Milling Purposes. J. H. Gov. Pub.	384
University of Illinois: Organic Chemical Reagents for Scientific and Technical Laboratories. R. Adams.	685	Wheat, Effect of Three Annual Applications of Boron on. F. C. Cook and J. B. Wilson. Gov. Pub.	1155
Universities and the Chemical Industries, Another Possible Form of Cooperation between. Editorial, 638. Note.	1073	Wheats, American, A Comparison of the Chemical and Physical Qualities of, and a Comparison of Some Factors Influencing the Quality. L. M. Thomas. Gov. Pub.	916
Unpreparedness. G. D. Rosengarten. Editorial.	202	Windings (Copper, Aluminum, Zinc and Iron) for Dynamos. Note.	903
Uranium, Ferro. H. W. Gillett and E. L. Mack. Gov. Pub.	996	Wines, Liqueurs, Cordials and Similar Products, Regulations Relating to Imported.	209
Uranium, Preparation of Black Oxide of. C. L. Parsons.	466	Wire, Fencing, for South America. 1.	1065
Uranium, Radium and Vanadium. F. L. Hess. Gov. Pub.	510	Wolfram, Australian. Note.	1063
Ure, Dr. Andrew, A Chemical Letter by. C. A. Browne.	748	Wood, Artificial. Note.	1145
VACCINE Virus, Anonymous. Gov. Pub.	725	Wood, Cross-cut, A Method of.	276
Vaccines, Radium and Uranium. F. L. Hess. Gov. Pub.	540	Wood, F. C. Judd and S. F. Acree.	1145
Vanillin, A New Qualitative Test and Colorimetric Method for the Estimation of. C. Ristes.	142	Wood: Cross-ties Purchased and Used in 1915. A. M. McCreight. Gov. Pub.	916
Vapor Pressures of Various Compounds at Low Temperatures. A. Burrell and I. W. Robertson. Gov. Pub.	210	Wood-Decay, Chemistry of. Paper and Pulp. R. E. Rose and M. W. Lisse.	284
Varnish Analysis and Control. II—Viscosity of Varnishes. M. Y. Seaton, E. J. Probeck and G. B. Sawyer.	35	Wood-Destroying Fungus, on Its Toxin and of Some of Its Constituents: A Comparison with Beechwood Creosote and C. J. Humphrey.	566
Varnishes and Paints for Siam. Note.	1145	Wood in Gas-Making. Note.	715
Vinegar Investigation. A Study of the Changes that Cider Undergoes during Fermentation and Prolonged Storage and Its Subsequent Conversion into Vinegar in Rotating Generators. B. G. Hartman and L. M. Tolman.	759	Wood, Kiln Drying of. C. P. Winslow.	826
Viscometers, Standard Substances for the Calibration of. E. C. Bingham and R. F. Jackson. Gov. Pub.	538	Wood: Potash from Incinerator Ash.	472
Viscosity of Starch for Mill Purposes, A Practical Method for Determining the. G. M. MacNider.	597	Wood Preservatives, Tests of. Gov. Pub.	210
Viscosity: The Measurement of the Absolute Viscosity of Very Viscous Media. S. E. Sheppard.	523	Wood-Pulp Lyes, Alcohol from. Note.	906
Volcanic Heat Harnessed. Note.	198	Wood Seasoning. H. S. Betts. Gov. Pub.	997
Vulcanization. Note.	319	Wood, Silified, Remarkable Occurrence of. E. T. Wherry.	914
WAR MATERIALS: Maintenance of Health in Industries. Its Relation to the Adequate Production of War Materials. J. W. Schereschewsky. Gov. Pub.	726	Wood-Tar Pitches, The Free Carbon of. H. K. Benson and L. L. Davis.	141
War Service of Chemists. J. Stieglitz and C. L. Parsons.	1002	WOOD, THE CHEMISTRY OF. A. W. SCHORGER.	556
War Service: The Chemist, the Draft and Patriotism. Editorial.	108	I—Methods and Results of Analysis of Some American Species.	624
War Service: The Present Status of American Chemists and.	639	II—Discussion of Methods and Results, 561; Correction.	748
War, The Public Health Service in Time of. Executive Order Making the U. S. Public Health Service a Part of the Military Forces of the United States. Gov. Pub.	725	Wood: Timber Storage Conditions in the Eastern and Southern States with Reference to Decay Problems. C. J. Humphrey. Gov. Pub.	916
Wartime, Chemistry in. R. B. Pilcher. Note.	411	Wood: Utilization of Ash. W. D. Sterrett. Gov. Pub.	916
Wartime, Chemists in. In the Light of Experience. Editorial.	544	Workers, Industrial, Safeguarding the Eyes of.	683
Washington Letter for Nomenclature. Editorial.	547	X-RAY Apparatus and Supplies. Gov. Pub.	1077
WASHINGTON LETTER. P. Wootton.	721, 815, 910, 990, 1074, 1149	YEAST, the Utilization of Ammonium Chloride by. C. H. Hoffman.	148
Waste Disposal, Industrial. H. P. Eddy.	696	ZEPPELIN Engine. Note.	1043
Waste Liquors: The Recovery of Potash from Beet-Sugar House Waste Liquors. H. E. Zikowski.	1092	Zinc: C. E. Siebenthal. Gov. Pub.	914
Wastes, Household, Fertilizing Value of Some. P. E. Browning.	643	Zinc: A New Method of Separating from Cadmium, and the Latter's Determination Iodometrically. E. J. Ericson.	671
Water and Sewage Laboratory, Kansas State Board of Health, The Legal Status and the Character of Work Done by the. C. C. Young.	1002	Zinc, Electro-Metallurgy of. Note.	319
Water, Artesian for Irrigation in Little Bitter-Root Valley, Montana. O. E. Meinzer. Gov. Pub.	111	Zinc Fields of Kansas-Oklahoma, The New. W. P. Hayes. Gov. Pub.	724
Water for Filtration, Artificial Alkalinity in. A. W. Clark.	86	Zinc Production (1915). Gov. Pub. California and Oregon, Yale, 112. New Mexico and Texas; Henderson, 112. Utah; Heikes, 112. Colorado; Henderson, 211. Arizona, Montana and Nevada; Heikes, 112. Washington; Germany.	211
Water, Ground, in San Simon Valley, Arizona, and New Mexico. A. T. Schwannsen. Gov. Pub.	519	Zinc, The Electrometric Titration of. F. R. v. Bichowsky.	668
Water-Meters in Their Sanitary Relations. H. Leffmann.	395	Zirconium and Nickel, Notes on the Analysis of Alloys of. G. L. Kelley and F. B. Myers.	407
Water: Nitrate Determinations in the Presence of Chlorides. W. F. Gercke.	585	Zirkite. Note.	407
Water, Note on the Determination of Strontium and Lithium in. S. D. Averitt.	584		
Water Power: France Developing Water Power to Aid Industries. Note.	531		

Go
us, Format
size





2-10-1937

TP
1
113
v.9

I&EC. Industrial and
engineering chemistry

Engin.

ENGINE STORAGE

PLEASE DO NOT REMOVE
CARDS OR SLIPS FROM THIS POCKET

UNIVERSITY OF TORONTO LIBRARY
